Russian Chemical Reviews, Volume 61 (1992)

Contents of Volume

Number 1

Current questions concerning the theory of highly excited vibrational states 1
V B Pavlov-Verevkin

The dynamic effects of the solvent in electron transfer reactions 15
L D Zusman

The photochemistry of phenyl azide 25
M F Budyka, M M Kantor, M V Alfimov

Iodoperfluoroalkanes 40
L E Deev, T I Nazarenko, K I Pashkevich, V G Ponomarev

Organic dyes for constant memory optical discs 55
T N Gerasimova, V V Shelkovnikov

Tin—antimony oxide catalysts: preparation conditions and properties 67
R A Lemberanskii, I B Annenkova, Z A Bakhshieva

Recent trends in research into ionic polymerisation 75
B L Erusalimskii

Heterocyclic bifunctional monomers in the synthesis of polymers 87
R D Katsarava, D P Kharadze

Quinone methides in the chemistry of wood 105
S M Shevchenko, A G Apushkinskii

Number 2

Specific characteristics of catalysis by polymer-immobilised complexes 133
A D Pomogailo

Photocatalysis by transition metal complexes 154
O V Gerasimov, V N Parmon

Modern approaches to the preparation of "palladium on charcoal" catalysts 168
V A Semikolenov

Mechanism of the hydrogenolysis of thiophene on bimetallic sulfide catalysts 175
A N Startsev

X-Ray diffraction study of carriers and deposited metallic catalysts 188
E M Moroz

The theory of the equilibrium isotope effects of hydrogen 204
D A Knyazev, N F Myasoedov, A V Bochkarev

Cyclopendant ligands 221
F I Bel'skii, Yu M Polikarpov, M I Kabachnik

Heteroprostanoids: synthesis and biological activity 243
F A Lakhvich, F S Pashkovsky, E V Koroleva

Number 3

Supercritical fluid chromatography 267
M S Vigdergauz, A L Lobachev, I V Lobacheva, I A Platonov

Vinyl cations 283
V D Nefedov, E N Sinotova, V P Lebedev

***N*-Functionalised carbodiimides** 297
M V Vovk, L I Samarai

Reactions of phosphorus-containing compounds with diazo-compounds and carbenes 306
B A Khaskin, O D Molodova, N A Torgasheva

Compounds containing phosphorus and boron 335
G N Nikonov, A S Balueva

Effect of carborane groups and the structure of their surrounding organic residues on the reactivity of monomers and properties of polymers 352
N I Bekasova, N G Komarova

Retro-aldol processes in steroid chemistry 363
M Kh Dzhafarov

Number 4

Physicochemical application of capillary chromatography 373
A V Vasil'ev, E N Aleksandrov

Present state of research on the sorption of inorganic compounds by oxide hydroxides from aqueous solutions 385
S I Pechenyuk

Electrochemistry of transition metal single crystals with well defined surfaces 399
G V Khaldeev, T A Syur

Mechanism of the interaction between Group VIII metals and oxides of transition elements 417
O S Alekseev, Yu A Ryndin

Inhibition—initiation in the pyrolysis of hydrocarbon mixtures 433
L V Shevel'kova, L E Gusel'nikov, G Bach, G Zimmermann

New bis(naphthalic anhydrides) and polyheteroarylenes based on them with improved processability 446
A L Rusanov

Number 5

Stereoelectronic effects in silicon, phosphorus, and sulfur molecules. Quantum-chemical calculations and qualitative orbital models 473
A A Korkin

Radiation chemistry of crown-compounds 484
V V Makhlyarchuk, S V Zatonskii

The mechanism of photolysis of aromatic azides 500
N P Gritsan, E A Pritchina

Polyfluoroalkanesulfenyl chlorides 517
A Yu Sizov, A F Kolomiets, A V Fokin

Organic derivatives of manganese(II) in organic synthesis 537
A N Kasatkin, O Yu Tsypyshev, T Yu Romanova, G A Tolstikov

The synthesis, properties, and applications of hydrophilic polymers and copolymers of hydroxyalkyl esters of acrylic and methacrylic acids 550
Z G Asadov, V S Aliev

Number 6

Induced optical activity in cyclodextrin complexes 563
Yu A Zhdanov, Yu E Alekseev, E V Kompantseva, E N Vergeichik

Crystal phosphors for storage luminescent screens 576
A M Gurvich, V V Mikhailin

Current approach to the problem of nitrenium ions 584
T P Simonova, V D Nefedov, M A Toropova, N F Kirillov

Conjunction in organic compounds of silicon-subgroup elements 600
A N Egorochkin

Aggregation of dye molecules and its influence on the spectral luminescent properties of solutions 613
V I Yuzhakov

Silylation in polymer chemistry 629
R D Katsarava, Ya S Vygodskii

Number 7

Modern theories of chemical reactions in condensed phases 651
M V Bazilevskii, V I Faustov

Solvent effect on the kinetics of crystal growth 673
E B Treivus

The photochemistry of coumarins 683
N A Kuznetsova, O L Kaliya

The electronic structure and reactivity of alkenes 697
V G Barabanov, A V Golovin, A A Rodin, A A Ustenko

Ozonolytic transformations of labdane diterpenoids 716
P F Vlad, A N Aryku

The synthesis of insect juvenile hormones and their analogues 731
V N Odinokov, O S Kukovinets, R A Zainullin, G A Tolstikov

Number 8

Aleksandr Vasil'evich Fokin 765
P M Valetskii

The chemistry of perfluoroalkyl-substituted dicyanoethylenes 766
A V Fokin, V Yu Tyutin, N D Chkanikov

Reactions of polyfluoroketones with unsaturated compounds 779
A S Golubev, A F Kolomiets, A V Fokin

Fluorine-containing ketimines 798
S N Osipov, A F Kolomiets, A V Fokin

Chemically modified electrodes as amperometric sensors in electroanalysis 816
G K Budnikov, J Labuda

The dynamic separation of substances by liquid–liquid extraction 830
N F Kizim

Methods for increasing the efficiency of catalysts for the oxidative condensation of methane 851
O V Krylov

Progress in the field of physiologically active lanosterol compounds 859
I G Reshetova, R K Tkhaper, A V Kamernitskii

Number 9

Structural features and spectroscopic and energy characteristics of alkali metal molybdates and tungstates 877
V V Fomichev, M E Poloznikova, O I Kondratov

Cooperative models of dissolution of metal crystals 889
G V Khaldeev, V V Kamelin

The influence of relativistic effects and the crystal field on the properties of actinyl ions 907
G V Ionova, G A Gerasimova

Solid state reactions as a method of introducing transition metal cations into high-silica zeolites 925
A V Kucherov, A A Slinkin

Thermodynamics of formation reaction and hydrometallurgical application of metal–ammonia complexes in aqueous solutions 944
V E Mironov, G L Pashkov, T V Stupko

Conductometry of electrolyte solutions 959
L P Safonova, A M Kolker

Number 10

Line tension in the thermodynamics of thin liquid films 975
V G Babak

The anomalous stabilisation of the oxidation state 2+ of lanthanides and actinides 990
N B Mikheev, L N Auerman, I A Rumer, A N Kamenskaya, M Z Kazakevich

Kinetic isotope effects in the enzymic reactions of tritium- and deuterium-containing substrates 999
G P Akulov

Phosphorus derivatives of salicylic acid 1009
L V Chvertkina, P S Khoklov, V F Mironov

The formation of linear and three-dimensional polymers by polycyclisation 1022
Ya S Vygodskii, V A Pankratov

Microbiological hydroxylation of 5α-*H*-steroids 1033
A M Turuta, N E Voishvillo, A V Kamernitskii

Pesticides in the environment 1058
N N Mel'nikov

Number 11

Investigation of molecular carbonium ion rearrangements by the molecular mechanics method 1077
Yu V Gatilov, V A Barkhash

High-temperature X-ray diffraction: experience in the use of samples on a backing plate for studying crystalline phases mixed with the liquid 1085
S K Filatov

Silicon-containing 1,3-alkenynes and more unsaturated compounds 1091
M D Stadnichuk, T I Voropaeva

The partial catalytic oxidation of methane to give oxygen-containing compounds 1118
O V Krylov

Hydroxylation of aromatic compounds with nitrous oxide. New possibilities of oxidative catalysis on zeolites 1130
A S Kharitonov, V I Sobolev, G I Panov

The kinetics of gas-phase processes in systems containing carbon and sulphur 1140
V S Arutyunov

The influence of metal coordination compounds on the ionic conductivity of bilayer lipid membranes 1156
B A Bovykin, A M Omel'chenko, T V Sytnik

Number 12

Some problems in the stereochemistry of nitrogen compounds in the gas phase 1169
N I Sadova, L S Khaikin, L V Vilkov

The effect of alternation in chromatographic retention relationships 1194
M S Vigdergauz, E I Petrova

Characteristic features of the chemical kinetics of the formation of interpenetrating polymer networks 1203
Yu S Lipatov, T T Alekseeva

Aliphatic organophosphorus nitro-compounds 1220
G M Baranov, V V Perekalin

© 2008, No Rights Reserved.

Translated from *Uspekhi Khimii* **61** 3–28 (1992) U.D.C. 539.19

Current questions concerning the theory of highly excited vibrational states

V B Pavlov-Verevkin
Lomonosov State University, Moscow

ABSTRACT. Certain current questions concerning the theory of highly excited vibrational states have been examined. The change in the form and the objectives of the theory as a function of increased energy of the system has been analysed. Much attention has focused on the role of classical concepts in regard to both the definition of the objectives and the formation of concepts and models used to interpret experimental data in the field of high-energy states. The concept of localised quantum states has been introduced. This concept plays a key role in the interpretation of many processes in which highly excited vibrational states are involved. The experimental consequences of the formation of localised quantum states in different physical situations are discussed. Examples examined include rearrangements of vibrational polyads, the appearance of periodic orbits in wave functions and in low resolution spectra, and bound states in continua.

The bibliography contains 208 references.

Contents

I. Characteristics of the theory of highly excited vibrational states in different regions of the spectrum 1
II. Localised vibrational states 3
III. Localisation in the vicinity of stable equilibrium positions: a qualitative theory of vibrational polyads and their rearrangements 5
IV. Localisation in the vicinity of isolated periodic orbits: "Scars" of the periodic orbits in the wavefunctions and low resolution spectra 8
V. Spatial localisation of the basis functions: bound states in a continuous spectrum 9
VI. Conclusion 11

There has been much interest in the properties of polyatomic molecules in highly excited vibrational states as a result of the progress made in fields such as high-resolution spectroscopy, multiquantum processes, intramolecular dynamics, and laser chemistry. The appearance of new experimental data has provided a great impetus for the development of new strategies and methods associated with the highly excited vibrational states theory, and the appearance of new theoretical concepts and ideas.

The vibrational spectra of polyatomic molecules rapidly become complex with increase in energy. This leads to a change in the method used to interpret the experimental material. Certain traditional questions lose their significance and are replaced by new questions which are of a qualitatively different type. In the present review some of these new questions will be examined, and most attention will be paid to the role of classical ideas and concepts of the local quantum states.

I. Characteristics of the theory of highly excited vibrational states in different regions of the spectrum

1. The low energy range. The vibrational spectra in this energy range consist of separate clearly resolved lines. They are individual for each molecule and are used often to identify molecules or functional groups. The objectives of the theory for this energy range are traditional and involve a study of the individual states and the transitions between them. The construction of appropriate dynamic models is the main strategy for their resolution. There is currently a large selection of such models. Models of normal[1] and local[2,3] vibrations are most popular for the description of vibrational states at lower energy. In addition to the traditional models there are so-called algebraic models in which a Hamiltonian is constructed directly from generators of a dynamic group of the symmetry postulated for the system studied. In recent years such models have been widely used in the study of vibrational spectra and intramolecular dynamics of small polyatomic molecules (see Refs. 4–14, and the references cited in these reports).

Using several different models an equally satisfactory quantitative description of a limited section of the spectrum may be obtained. The simultaneous use of these models is of profound physical significance, since each model generates its own specific language, its set of quantum numbers by means of which lines in the experimental spectra may be assigned and the selection rules for different transitions may be determined, etc. In this case the states which do not have good quantum numbers in one particular model may have them in another model. Thus by using different models a more profound understanding of the quantum states may be acquired.

2. The transitional range. With increase in energy the system enters the transitional range, which separates the low-energy state range from the quasicontinuum. In this range models designed to describe low-lying states begin to lose their efficiency which is reflected as a sharp increase in computing difficulties when they are used and by the appearance of states which do not have good quantum numbers in any of the integrated models. The latter problem is of fundamental importance and is associated with the characteristics of the vibrational dynamics of polyatomic molecules in the classical limit.[15–17]

A description of the vibrational spectra of polyatomic molecules is based on the model of coupled anharmonic oscillators. At low

energies the classical dynamics of such a system is for the most part regular. This implies that under virtually all initial conditions the phase trajectories of the system lie on the surfaces of the N-dimensional tori and in the $2N$-dimensional phase space. During motion along such trajectories the meaning of the N integrals of the motion calculated along specially selected close curves on the torus are preserved. Such regular trajectories may be quantised by one of the variants of the quasiclassical method. In this case states with particular quantum numbers N will correspond to them.

Apart from regular trajectories the system contains chaotic trajectories, which fill a certain $2N$-dimensional region of the phase space. With increase in the energy in the system the relative volume of the phase space filled by chaotic trajectories usually increases. There is currently no sequential method available to quantise such trajectories, while the states corresponding to the trajectories do not have motion integrals distinct from the energy.

The rapid increase in the density of the vibrational states with increase in energy is another difficulty encountered with the theory in the transitional energy range. However in this case the characteristic groups of levels such as the vibrational and rotational polyads are preserved. This leads to the possibility of defining new objectives associated with the investigation of the properties of the separate groups of levels and the change in these properties with change in the different motion integrals.

Initially such objectives were defined in the theory of rotational spectra of highly symmetrical molecules.[18–27] In the theory of vibrational spectra the definition of analogous objectives began with the discovery of local modes, special vibrational states which arise with increase in energy within molecules containing equivalent A–H(D) bonds, where A is a heavy atom (usually O, C or N) characterised by an extremely asymmetrical distribution of vibrational energy between the bonds (see Ref. 2 and 3 and the literature cited in these papers). A distinctive feature of the vibrational spectra of such molecules is the existence of vibrational polyads, independent characteristic groups of levels corresponding to the excitation of the A–H bonds. In this case the states with $\sum n_k = N$ enter the Nth vibrational polyad, where n_K is the number of vibrational quanta in the k-th mode, whereas the number of the vibrational polyad N is expressed as the total number of vibrational quanta and is an approximated motion integral.

The appearance of local modes from normal vibrations on excitation of the molecules is a typical phenomenon caused by the significant linearity of the molecular vibrations.[28–36] It is reflected as a qualitative change in the structure (rearrangement) of vibrational polyads with increase in N and is an example of a broad class of vibrational localisation processes with increase in energy.

The rearrangements of the vibrational polyads do not exhaust all qualitative changes in the relative position of the levels with increase in energy. More complex phenomena are also known in vibrational-rotational spectra such as the redistribution of levels between different groups of states (see Refs. 37, 38 and 39, and the references cited in these papers).

3. The quasicontinuum. A further increase in energy in the system leads to a transition to the quasicontinuum, a region with a discrete spectrum with a very large density of states in which, in contrast to the transitional range, certain isolated groups of states are absent. It has also been relatively recently suggested that quasicontinua are structureless and homogeneous and that the density of the states in the quasicontinua grows systematically with increase in energy, whereas the wavefunctions of the states in the quasicontinuum are delocalised throughout the entire configuration space of the molecule. In such a study the quasicontinua of different molecules are found to be essentially constructed in an identical manner and their only important characteristic is the density of the states and the rate at which this density increases with increase in energy, i.e. in the quasicontinuum range the states of the molecules lose their individuality to a significant extent. Such a concept of the quasicontinuum is consistent with the postulates of the statistical theory of chemical kinetics of the Rice–Ramsperger–Kassel–Marcus theory.[40]

The above model was found to be too simple for many objectives. Thus, it does not explain the presence of regular periodic structures in the low resolution spectra and does not take into consideration the existence of a large number of vibrational states with localised wavefunctions.

Experimental investigations into the quasicontinuum range may be conveniently divided into two major groups, i.e. experiments with high and low spectral resolution. The first group of experiments is characterised by very high resolution and provides information on the individual states. They may be carried out only for relatively simple systems. The spectra obtained in this case have an extremely complex and irregular profile. There is a very large amount of information in these spectra, and a significant change in the method used to interprete the spectra is required. With such a large amount of information it is difficult to study the properties of all states and from a certain standpoint the study would be meaningless. The most important task was to describe and study the properties of the entire combination of states in a complete selected range of energies.

The natural approach to resolve this objective is to study the statistical properties of the selected combination of energy levels and to construct models the statistical properties of which coincide with those of the group of levels studied. A change in the properties of the combination of states with increase in energy usually has regular and irregular components. Thus for example with increase in energy the density of the states in the spectrum increases which leads to a systematic decrease in the distances $\delta_i(E) = E_i - E_{i-1}$ between adjacent levels (the regular component). We are not interested in the $\delta_i(E)$ values themselves but their fluctuations relative to the curve describing the average behaviour of these values with increase in energy (irregular component). A study of the statistical properties of these types of fluctuation in the relative position of the energy levels and in the matrix elements of certain operators (for example transition probabilities) represents the content of the statistical theory of spectra initially developed to describe the spectra of complex nuclei and recently used to analyse spectra of atoms and molecules (see Refs. 41–45 and the literature cited in these reports).

However, when this theory is used, the question arises, with which physical properties of the system are given statistical characteristics of its spectrum associated? The answer to this question proved to be quite unexpected. A profound and nontrivial relationship was found to exist between the statistical properties of the spectrum and the nature of its dynamics in the classical limit. It was thus possible to introduce the concept of regular and chaotic spectra, which differ markedly with respect to their statistical properties, and then with increase in energy a smooth transition for the first to the second is observed. In this case the statistical properties of the chaotic spectrum are described by a Gaussian orthogonal ensemble model consisting of an ensemble of symmetrical actual matrices, the elements of the latter being Gaussian random values.

A lucid and exhaustive account of the statistical theory of spectra and its application to specific physical systems may be found in

review articles.[43,45–50] The review concerning the molecular application should be noted in particular.[45]

The rapid increase in the density of the states with increase in energy of the system leads to the appearance of a new item for study, low resolution spectra obtained either directly as a result of experiments with an insufficiently high resolution or by a corresponding coarsening of high resolution spectra. By studying such spectra it was found that they often possess a structure which cannot be explained by the statistical theory. Clear examples of such a structure are the systematic oscillations of the density of the states and the regular oscillations of intensity associated with them found in the corresponding broadening in the spectra of systems such as the H atom in a magnetic field,[51–54] the molecular ion H_3^+,[55] acetylene molecules,[56] Na_3,[57] O_3,[58] and HCN.[59]

The properties of the separate states are also of interest in studies of the quasicontinuum range. However in this case the theory focuses on the search for and study of a relatively small number of special states which in certain ways are differentiated from the homogeneous background which surrounds them. The most useful and general criterion for the separation of the states from the quasicontinuum is the extent of the localisation of their wavefunctions which could be explained in different ways. It was found that the possible existence of vibrational states with localised wavefunctions and their properties is to a significant extent determined by the structure of the phase space of the system under investigation. This interrelationship is most lucidly expressed by the existence of "scars" of periodic orbits, the localisation of wavefunctions of highly excited states in the vicinity of unstable periodic orbits in configurational or phase spaces.

One more new feature of the theory in the quasicontinuum range is the interest shown towards dynamic objectives arising here quite naturally. In fact as a consequence of the high density of the states in the quasicontinuum, a coherent excitation of a large number of states occurs simultaneously on excitation of the molecule, which leads to the formation of a nonstationary wavepacket. Such wavepackets are usually spread very rapidly. In this case initially the vibrational energy, which is localised in one or in a small number of modes, is redistributed rapidly between all accessible modes. However this situation may alter abruptly, if states with localised wavefunctions which partially stabilise the wavepacket form part of the wavepacket. Thus the localised vibrational states may serve as a basis for special, relatively stable dynamic modes during the intramolecular redistribution of energy.

4. The continuous spectrum. The continuous spectrum range is situated at an even higher energy. In this range the theory ultimately focuses on the study of the dynamics and special states, the resonances of which are typical representatives of localised quantum states. As an example we shall examine below the effect of excitation capture in the continuous spectrum during the decay of a coherently excited group of (quasi)degenerate states.

II. Localised vibrational states

In the high-energy range of the system the special states which in some way can be differentiated from the homogeneous background surrounding them are of greatest interest. In order to understand the nature of such states it is necessary first of all to understand which properties of the vibrational states are typical at high energies. With this objective it was useful to analyse the dynamics of the system studied in the classical limit. In systems of coupled anharmonic oscillators, which are normally used to model the dynamics of nuclei in molecules, a transition from regular to chaotic dynamics with increase in energy is typical. In this regard Percival proposed that such a position is preserved also in the quantum limit in a quasiclassical approximation,[60] i.e. regular and chaotic quantum states with markedly different properties should exist. In this case the chaotic states will be typical by virtue of the principle of congruence.

Three different strategies are currently used to determine the randomness of separate quantum states. These strategies are based on the study of the nature of wavefunction localisation in the phase space, in the configurational space, and in the basis function space. A detailed discussion of these three kinds of localisation in relation to their use to distinguish chaotic and regular quantum states has been published.[49,50,61–65]

1. Localisation in the phase space. The dynamics of an arbitrary quantum system may be described not only in the Hilbert space of quantum mechanics but also in the normal phase space. Let $\mathbf{q}$ and $\mathbf{p}$ be a combination of generalised coordinates and momenta of the system studied respectively. Then the arbitrary wavefunction $\psi(\mathbf{q})$ determined in configuration space can be compared with a certain function $\rho(\mathbf{q}, \mathbf{p})$ determined in phase space and termed the quantum function of the distribution. This may be achieved by different methods.[66–68] The most well known of these methods was proposed by Wigner and leads to the quantum function of the distribution in the form:

$$\rho_W(\mathbf{q}, \mathbf{p}) = h^{-N} \int \ldots \int dx_1 \ldots dx_N \, \Psi^*(\mathbf{q}+\mathbf{x}/2)\, \Psi(\mathbf{q}-\mathbf{x}/2)\, e^{-i\mathbf{p}\mathbf{x}/\hbar}. \quad (1)$$

The description of the quantum states using the Wigner distribution function (1) facilitates significantly a comparison of the properties and dynamics of classical and quantum systems. However, in this case one should bear in mind that the equation of motion for the Wigner function transforms into the equation of motion for the classical distribution function (the Liouville equation) only in the limit $\hbar \to 0$. This permits the isolation of purely quantum effects in the dynamic behaviour of the system.[69]

Moreover the Wigner function does not have definite values at all points of the phase space, i.e. it possesses none of the most important properties of the classical distribution function. This property was found to be quite common for the quantum distribution functions and is associated with the need to satisfy the quantum-mechanical Heisenberg uncertainty principle according to which it is not possible to define simultaneously accurate values of the coordinates and the momenta of particles. Therefore in quantum mechanics the concept of a point in the phase space has no special physical significance and in addition the requirement for a definite value of the distribution function at each point also becomes physically meaningless. The requirement for a definite value of the coarse-grained distribution function obtained on coarsening of the distribution function with respect to the small region of the phase space is more acceptable from the point of view of the physical meaning.

One of the best known examples of such an approximated coarse-grained distribution function is the Husimi distribution function $\rho_H(\mathbf{q}, \mathbf{p})$, [70] which may be calculated as the square of the modulus of the overlap integral of function $\psi(\mathbf{q})$ with the wavefunction of the

specific state $|\alpha(\mathbf{q}, \mathbf{p})>$ parametrised by the coordinates of the phase space. Gaussian functions centred at point $(\mathbf{q}, \mathbf{p})$ are normally used as functions $|\alpha(\mathbf{q}, \mathbf{p})>$. The distribution functions thus formed are apparently positive and finite in the entire phase space.

What is the appearance of the distribution functions of chaotic and regular quantum states? In order to answer this question it would be useful to study the properties of the quantum distribution functions in the classical limit. The classical limit for the Wigner distribution function has been best studied (see discussion and literature cited in Ref. 50). When $\hbar \to 0$ the Wigner coarse-grained function is localised in the regions which fill its corresponding trajectories when $t \to \infty$. This implies that, when $\hbar \to 0$ the Wigner coarse-grained function of the regular state is localised on the surface of the N-dimension torus, whereas the chaotic state tends towards a microcanonical distribution. A similar result is also valid for the Husimi distribution function.[71,72] It would be logical to suggest that such a position is also preserved at small but finite values of $\hbar$.

Thus one might expect that at high energies the typical wavefunctions will be those, which correspond to strongly delocalised and isotropic coarse-grained higher functions more or less constant over the entire accessible volume of the phase space. In this case special states will be characterised by nonisotropic coarse-grained Wigner functions localised in only a small part of the isoenergetic hypersurface, i.e. they will be localised quantum states.

2. Localisation in the configurational space. A second possible approach to the study of the localisation of quantum states would be an investigation into their wavefunctions in the configuration space. The first attempts to use this approach were based on a study of the main surfaces of the wavefunctions. However it was found that in the transition from inseparable integrated systems to nonintegrated systems the topology of the unit surfaces does not undergo a qualitative change and therefore cannot be used to differentiate reliably these two types of states (see discussion in Refs, 49 and 50).

The methods used to isolate the regular quantum states based on the analysis of different statistical properties of their wavefunctions were found to be more valuable. The concept of the wavefunctions of chaotic states and of the random functions of coordinates in which there is no correlation between the values at adjacent points forms the basis of all of these strategies. In this case adjacent points not too close to each other should be selected with the objective of levelling the effects caused by the continuity and normalisation of the wavefunctions.

One should note the following methods, which have been used most widely to study the statistical properties of wavefunctions.[49,50,73–76]

1. Calculation of the normal autocorrelation function

$$F_\delta(\Psi) = \int \ldots \int \Psi^*(\mathbf{q}) \Psi(\mathbf{q}+\delta) \mathrm{d}q_1 \ldots \mathrm{d}q_N, \qquad (2)$$

or its discrete variant

$$F_m(\Psi) = (1/M) \sum_{i=1}^{M} \Psi^*(\mathbf{q}_i) \Psi(\mathbf{q}_{i+m}), \quad m \leqslant M. \qquad (3)$$

In formula (3) the points $\mathbf{q}_i$ are taken as lying on the closed curve in the configuration space and satisfying the condition $\mathbf{q}_{i+M} = \mathbf{q}_i$. In this case the chaotic wavefunctions differ from the regular functions with values close to zero $F_\delta(\psi)$ and $F_m(\psi)$ for all $m \leqslant M$.

2. Calculation of the moments $I_m = \int \ldots \int |\psi(\mathbf{q})|^{2m} \mathrm{d}q_1 \ldots \mathrm{d}q_N$. In the quasiclassical limit $I_m \to \infty$ for regular states and they remain finite for chaotic states.

3. Calculation of informational entropy

$$S = -\int \ldots \int |\Psi(\mathbf{q})|^2 \ln(|\Psi(\mathbf{q})|^2/\rho_{\mathrm{ref}}) \mathrm{d}q_1 \ldots \mathrm{d}q_N, \qquad (4)$$

where ρ_{ref} is the reference density of the probability corresponding completely to an ergodic situation. In this case the value of S for delocalised wavefunctions should be markedly greater than that for the localised wavefunctions.

4. Calculation of the distribution function of the wavefunction values at randomly selected points. In this case the chaotic states should be characterised by a Gaussian distribution.

5. Calculation of the fractal dimensionality D of the density of the probability $|\psi(\mathbf{q})|^2$ determined by the relationship

$$\int \ldots \int |\Psi(\mathbf{q})|^2 |\Psi(\mathbf{q}+\mathbf{q}')|^2 \theta(Y) \mathrm{d}q_1 \ldots \mathrm{d}q_N \sim L^D, \qquad (5)$$

where $Y = L - |\mathbf{q} - \mathbf{q}'|$, and $\theta(Y)$ is the Heavyside function equal to unity when $Y < 0$ or to zero when $Y > 0$.

6. A method based on the study of the surfaces of the level of density probability $[\psi(\mathbf{q})]^2$ has been widely used recently to study wavefunctions in systems with two degrees of freedom. With this method it is possible to determine directly the nature of wavefunction localisation in the configuration space. However one should note that this method becomes significantly less representative in studies of systems where the number of degrees of freedom is greater than two.

When all above analytical methods are used, the concept of random and typical states at high energies is associated with the delocalised state, and with the irregularity and isotropicity of their wavefunctions in the configuration space. It can also be seen that in such an approach the states with localised wavefunctions are separate.

3. Spatial localisation of base functions. The idea of the extent of delocalisation of wavefunctions in space of the decomposition coefficients with respect to eigenfunctions of the integrated models as a criterion of the randomness of quantum states was proposed for the first time by Nordholm and Rice.[77] The main idea of the strategy of these authors is easy to understand, if one remembers that the chaotic trajectory in general has no good integrals of motion apart from energy. One might naturally suggest that this assertion remains true also for chaotic quantum states. However this implies that the wavefunctions of such states cannot have compact decompositions with respect to the eigenfunctions of any integrated model. Let H_0 be the Hamiltonian of one such model. Then it would be natural to associate the degree of randomness of the quantum state with the width of distribution of the decomposition coefficients $\{a_k\}$ of its wavefunction with respect to the eigenfunctions of the operator H_0. In this case the greater the number of coefficients $\{a_k\}$ which are markedly different from zero the more chaotic is the state examined.

The selection of parameters for the quantitative evaluation of the degree of randomness of the quantum state with respect to the set of coefficients $\{a_k\}$ by certain authors remained an open question.[77] It has been suggested that the ratio of the share $p = \sum p_n^2$ or entropy $S = -\sum p_n \ln p_n$, where $p_n = [a_n]^2$ should be used for such an evaluation.[49] In this regard one should note that the values p and S

have been used for a long time to determine the degree of randomness of intramolecular dynamics (see Refs. 78–82 and the references cited in these reports).

A simpler criterion has been studied according to which the quantum state is regular, if an integrated model exists which is such that among the decomposition coefficients of its wavefunction with respect to the basis functions of this model there is a coefficient greater than 0.5.[83–85] By satisfying this criterion it is possible to characterise unambiguously the studied state by a complete set of good quantum numbers and provides convergence of the Brillouin–Wigner theory of perturbations for its wavefunction and energy.[83–85]

The absence of a systematic method for the reassembly of all possible integrated models is a major limitation of the approach examined for the determination of chaotic quantum states. In this regard the earlier suggestion to use a basis of natural orbits for this purpose is of interest.[86] With this approach it should be possible to systemise the search for regular states using a fixed selection of variables. However this possibility has not been exploited on account of the variation in the variables themselves.

In this approach the states localised in the space of the basis functions of a certain integrated model are specific. Although such a determination of localised quantum states is also somewhat arbitrary, since it is dependent on the selection of the basis model, it is found to be very useful when the basis functions have clear physical meaning.

III. Localisation in the vicinity of stable equilibrium positions: a qualitative theory of vibrational polyads and their rearrangements

We shall examine the molecule having M (quasi)degenerate vibrations, the frequencies of which differ markedly from the frequencies of the remaining vibrations. The local vibrations of CH bonds in organic compounds, symmetrical and antisymmetrical normal vibrations in type ABA nonlinear molecules with a heavy central atom, and many others are typical examples. The existence of vibrational polyads is a characteristic feature of the vibrational spectra of such molecules. For simplification we shall discuss the main ideas as an example the vibrational polyads formed by two vibrations. The three types of currently known polyads are illustrated in Fig. 1.

The type *a* so-called normal vibrational polyads correspond to the model of uncoupled harmonic oscillators with slightly different frequencies. The type *c* so-called local vibrational polyads are very satisfactorily described by the model of two identical uncoupled anharmonic oscillators. The type *b* vibrational polyads are mixed, their upper and lower parts corresponding to the model of normal and local vibrations respectively. In certain cases with increase in energy there is a rearrangement of the vibrational polyad-transition from polyad type *a* to polyads types *b* and *c*.

There are at present several approaches for explaining this qualitative phenomenon. One should note the strategies based on the analysis of classical trajectories,[28,29] and also later and accurate methods based on the construction and study of effective algebraic Hamiltonians for separate vibrational polyads.[30–36] We shall use as a basis a strategy developed in previous studies.[30–36] This approach not only provides a simple graphic relationship between the rearrangements of the vibrational polyads and the characteristics of the dynamics of the system under investigation in the classical limit but also permits the description of all possible simplest types of polyad and their rearrangements.

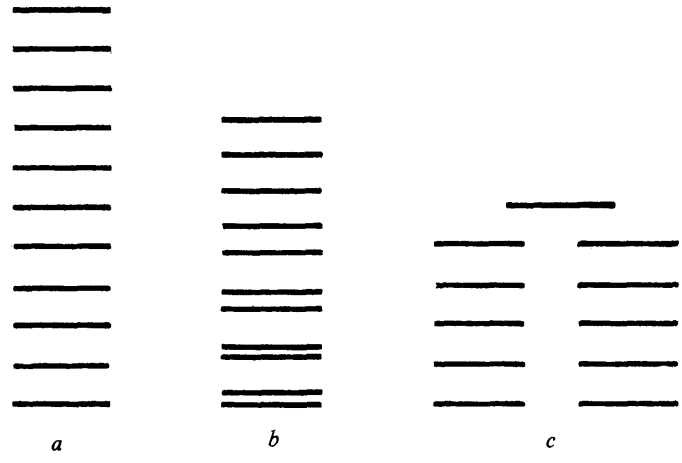


Figure 1. Types of vibrational polyads formed by two vibrations: *a*, normal; *b*, mixed; *c*, local.

We shall assume that the different vibrational polyads interact weakly with each other (N is an approximate integral of motion) and that the structure of the vibrational polyads is not perturbed by the resonance interaction with other molecular vibrations. With these assumptions the relative position of the energy levels in the N-th vibrational polyad may be described by an effective vibrational Hamiltonian $H_{\text{eff}}(N)$ parametrically dependent on N. Further analysis rests on the close relationship between the properties of the quantum system and its behaviour in the classical limit. We shall use this relationship to find a classical analogue of the quantum phenomenon studied here. This may be obtained schematically as a result of the following sequence of steps:

1) construction of the algebraic effective vibrational Hamiltonian $H_{\text{eff}}(N)$ describing the relative position of the energy levels in the N-th vibrational polyad,

2) transition to the classical limit; construction of the corresponding phase space and the Hamiltonian function H_{kl},

3) a study of the system of stationary points of the H_{kl} function and its rearrangements with increase in N.

As a simple example we shall examine the spectrum of stretching vibrations of the ABA molecule which in the formalism of the local vibrations is described approximately by the Hamiltonian

$$H/\hbar\omega = 0.5(P_1^2+Q_1^2+P_2^2+Q_2^2)+AP_1P_2+BQ_1Q_2+C(Q_1^3+Q_2^3)+ +DQ_1Q_2(Q_1+Q_2)+E(Q_1^4+Q_2^4)+FQ_1Q_2(Q_1^2+Q_2^2)+CQ_1^2Q_2^2, \quad (6)$$

where Q_k and P_k are normal dimensionless coordinates and momenta and the constants $A-G$ are dimensionless parameters of the model. If all constants $A-G$ are much less than unity, the energy levels of operator H_{eff} will be grouped into polyads. We shall now apply the above described analytical scheme to the Hamiltonian (6).

1. Construction of an effective vibrational Hamiltonian. We shall rewrite the vibrational Hamiltonian (6) using the creation-destruction vibrational operators a_k and a_k^+, where $a_k = (Q_k + iP_k)/2^{1/2}$, ($k$ = 1, 2) and we shall use the standard technique of canonical transformations for reducing it to an even form.[87]

Being limited for simplicity only by the first non-disappearing contributions from all terms introduced into the Hamiltonian (6) we obtain:[32,33]

$$H_{\text{eff}}/\hbar\omega = H_0 + [\alpha_1 + \alpha_2(J+0.5)]J_x + \gamma J_x^2 + \delta J_z^2, \quad (7)$$

where J_x and J_z are the pseudomomentum operators determined using the creation-destruction vibrational operators as

$$J_x = (a_1^+ a_2 + a_2^+ a_1)/2, \quad J_z = (a_1^+ a_1 - a_2^+ a_2)/2, \quad (8)$$

while parameters α_1, α_2, γ and δ are expressed by the known method through the constants $A-G$. All terms which are constant within the vibrational polyad are introduced into H_0. The operator J = 0.5 $(a_1^+ a_1 + a_2^+ a_2)$ is associated with the number of the vibrational polyad with a ratio of $N = 2J$ and is the motion integral.

The method described for constructing an effective vibrational Hamiltonian is far from being the only method. Moreover it is often more expedient to regard the Hamiltonian (7) as purely phenomenological and to determine the parameters contained in it from the experiment as in the case of algebraic models.

2. The classical limit. The construction of the classical limit for the quantum system is generally quite a complex operation resting on the theory of generalised coherent states.[88,89] In our case this operation is markedly simplified and amounts to a trivial replacement of the pseudomomentum operators by their quasi-classical expressions

$$J_x = L\cos\varphi\sin\vartheta, \quad J_z = L\cos\vartheta, \quad L = J + 1/2, \quad (9)$$

where L is the length of the pseudomomentum vector. Since the value l is conserved during motion, the phase space is a normal two-dimensional sphere. By omitting the term H_0 which is insignificant in our case we finally obtain the following expression for the function H_{kl}:

$$H_{kl} = (\alpha_1 + \alpha_2 L)L\cos\varphi\sin\vartheta + \gamma L^2\cos^2\varphi\sin^2\vartheta + \delta L^2\cos^2\vartheta. \quad (10)$$

3. Qualitative analysis. We shall study the behaviour of stationary points of function H_{kl} on change in N. They are important because closed closely localised trajectories are associated with the stationary points of the minimum or maximum type. Under certain conditions regular sequences of localised quantum states correspond to these trajectories. Thus from a study of the stationary points of the function H_{kl} it is possible to study the possible types of localised quantum states and their change on excitation.

We shall restrict ourselves to an examination of only Hamiltonians of a common form, when no additional limitations apart from those caused by the symmetry of the system were applied to the parameters. The stationary points of the Hamiltonian function (10) and their corresponding total energy values are presented in Table 1, and their behaviour with increase in L is schematically illustrated in Fig. 2. It is apparent from Table 1 and Fig. 2 that at low L values corresponding to the real excitation of the system the function H_{kl} has only two nondegenerate stationary points a and b, one of which is the maximum, the other being the minimum. With increase in energy such a position is preserved whilst L does not exceed a certain critical value $L\P$. When $L > L\P$, the dynamics of the model studied undergo a qualitative change, which is reflected as a change in the number and nature of the stationary points of function H_{kl}. The values of parameter L at which this occurs are called bifurcational, and the process itself is a bifurcation. The diagrams similar to that shown in Fig. 2 in which changes in the system of stationary points of the function are depicted on change in its parameters are called bifurcational diagrams and provide a convenient method for describing systems in which certain qualitative changes may arise when the parameters are continuously changing.

Table 1. Coordinates, energies and conditions for the existence of stationary points (SP) of the function H_{kl}.[33]

SP	φ	ϑ	Energy	Conditions for the existence
a	0	$\pi/2$	$E_a = \alpha L + \gamma L^2$	at all L
b	π	$\pi/2$	$E_b = -\alpha L + \gamma L^2$	at all L
$c_{1,2}$	$\pi[1-\text{sgn}(r_1)]/2$	$\pm\arcsin\lvert r_1\rvert$	$E_{c_1} = E_{c_2} = \delta L^2 + \alpha^2/4(\delta-\gamma)$	$\lvert r_1\rvert < 1$
$d_{1,2}$	$\pm\arccos\lvert r_2\rvert$	$\pi/2$	$E_{d_1} = E_{d_2} = -\alpha^2/4\gamma$	$\lvert r_2\rvert < 1$

Notations: $\alpha = \alpha_1 + \alpha_2 L$, $r_1 = (\alpha_1 + \alpha_2 L)/2L(\delta-\gamma)$, $r_2 = -(\alpha_1 + \alpha_2 L)/2L\gamma$.

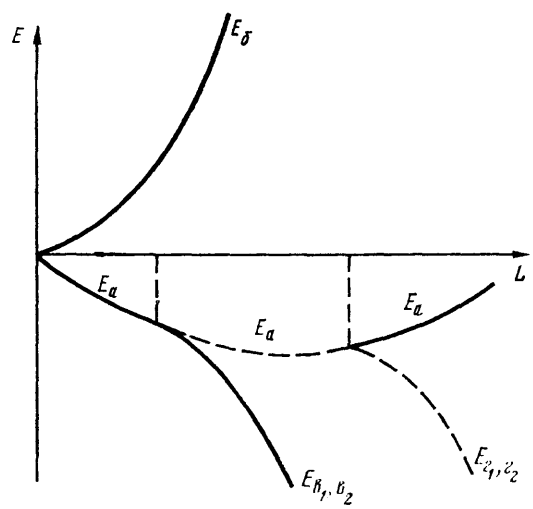


Figure 2. Bifurcational diagram describing the changes with increase in energy of the system of stationary points of the Hamiltonian function (10) for the case of the H_2O molecule.[30]

The system of two harmonic oscillators associated with quadratic potential and kinetic interactions is the simplest system described by the Hamiltonian (6). This system is described by a Hamilton function (10) with $\gamma = \delta = 0$ and is equivalent to two non-interacting harmonic oscillators with slightly different wavenumbers.

Its spectrum is a polyad structure with polyads of a purely normal type, and their structure does not alter with increase in energy. It is apparent from Table 1 that in the case examined with function H_{kl} there are only two non-degenerate stationary points *a* and *b* for all values of *L*. This implies that in the above model the upper and lower parts of the vibrational polyads are constructed from regular sequences of the non-degenerate energy levels which is in total agreement with the results of accurate quantum-mechanics calculations.

We shall now consider the anharmonicity of oscillators which corresponds to the selection of a nontrivial value of coefficient δ. Analysis of the stationary points shows that when $L = L\P = [\alpha_1/2\delta]$ bifurcation occurs in the system. When $L < L\P$ the function H_{kl} has two non-degenerate stationary points *a* and *b*. As in the previous example the vibrational polyads are of the normal type. When $L > L\P$ one of the stationary points is split into two degenerate stationary points of the same type as the point of their origin, and one saddle point. The appearance of two degenerate stable stationary points leads to the formation of a regular sequence of double degenerate energy levels in the vibrational polyads. In this case that end of the vibrational polyads at which the double degenerate energy levels appeared will be better described by a local vibration model, whereas the other end of the polyad will continue to correspond to the normal vibration model.

We shall examine the question of what is the physical nature of the double degenerate localised quantum states arising as a result of the bifurcation. With increase in energy let the distances between the adjacent energy levels of the initial oscillators decrease systematically, which is a typical situation in molecular problems. In this case the double degenerate localised quantum states are formed in the lower part of the vibrational polyads, and the states themselves correspond to vibrations with an extremely asymmetrical energy distribution between the oscillators, i.e. they are well studied local modes.[2,3]

Thus the qualitative analysis of the function H_{kl} gives a simple and clear picture of the formation of local modes from normal vibrations on excitation. It shows that the formation of local modes with increase in energy is a typical phenomenon and is not dependent on the specific values of the Hamiltonian parameters. However one should note that the experimental observation of rearrangements associated with this process in the specific molecules may be made difficult by too great or small values of $L\P$.

Within the framework of the approach examined there are no significant differences between normal and local vibrations. Both are examples of localised quantum states with wavefunctions localised close to the stable stationary points of function H_{kl}. Thus the states described above are a natural generalisation of local and normal vibrations.

Two new effects appear when all coefficients of the effective vibrational Hamiltonian differ from zero: 1) a new type of localised quantum states corresponding to stationary points *d* may arise, and 2) localised quantum states existing only in a limited energy range may appear.

The results obtained from the use of a qualitative approach to the analysis of experimental spectra of stretching vibrations in H_2O, SO_2, and O_3 molecules and vibrations of the CH and CD bonds in C_2H_2 and C_2D_2 molecules taken from literature data are presented in Table 2.[33]

The small values of $L\P$ for C_2H_2 and H_2O molecules are in good agreement with the fact that the vibrational polyads in these molecules have a clearly expressed local nature beginning from the lowest part itself. The vibrational polyads in the C_2D_2 and SO_2 molecules belong to the normal type, which is also in good agreement with the $L\P$ values for these molecules. The ozone molecule spectrum is of greatest interest. Using this as an example it is possible to follow the transition from vibrational polyads of a normal type at low *N* values to the mixed type of vibrational polyads when $N \geqslant 3$. It should be emphasised that the accuracy of the results obtained from the qualitative analysis increases with increase in *N*. At low *N* values one can expect that they agree only qualitatively with the experimental data. In this case the vibrational polyad rearrangements predictable by the theory are more sharply manifested the greater is the value of *N*. Taking into account the comments made the results obtained from analysis of the experimental spectrum presented in Table 2 should be recognised as being unexpectedly good.

Table 2. Analysis of the bifurcations of effective vibrational Hamiltonians of certain molecules.[33]

Molecule	Region of existence of stationary points	
	c	d
H_2O	$L>0.4$	$5.9<L<36.5$
SO_2	$L>6.5$	$L>13.7$
O_3	$L>0.6$	$L>10.8$
C_2H_2	$L>0.4$	Absent
C_2D_2	$L>3.2$	$L>22.8$

The transition from the normal to the mixed polyads in the model spectrum of molecule C_2D_2 may serve as a classical example of the rearrangement of vibrational polyads. A sufficiently large value of $L\P$ corresponding to $N = 6$ leads to a clearly pronounced sharp transition.

Thus we have achieved the objective set at the beginning of this chapter and have found a classical analogue of the quantum rearrangement. We have shown that bifurcations of the Hamilton function, expressed as a change in the number and nature of its extremal points, correspond to rearrangements of the vibrational polyads.

Qualitative changes in the Hamilton function with increase in energy lead to qualitative changes in the phase picture of the system studied and hence to a change in possible forms of its dynamic behaviour. Of great interest in this regard are earlier studies in which a strategy is developed which in the case of two vibrations allows phase pictures of vibrational polyads to be constructed from experimental spectra.[90–94]

In concluding the discussion of the qualitative theory of vibrational polyads and their rearrangements one should note the work in which all kinds of typical elementary rearrangements of vibrational polyads are found in a system of two associated anharmonic oscillators,[33] and a study in which a generalisation of the theory to the case of an arbitrary number of vibrations is presented.[95]

IV. Localisation in the vicinity of isolated periodic orbits: "Scars" of the periodic orbits in the wavefunctions and low resolution spectra

In the systems of interest to us a transition from regular to chaotic dynamics is typical with increase in energy. In this case the volume of the phase space filled by regular trajectories approaches zero. However even in the region of totally chaotic dynamics in the phase space a large number of isolated and unstable periodic orbits is preserved. Since the extent of the volume of the phase space occupied by them is equal to zero, it would appear that they should not appear as quantum properties. In fact the unstable periodic orbits are not only markedly reflected in the quantum properties but also determine them to a significant extent especially at high energies.

The first theory associating the properties of isolated periodic orbits with the quantum characteristics of the system was developed mainly in the work by Gutzwiller, Balian, and Bloch. A good review of this theory and a comparatively comprehensive list of early studies may be found in the literature.[96] The central result of this theory is the formula:

$$n(E)=\bar{n}(E)+\sum_r\sum_j a_{rj}(E)\cos\{j[S_r(E)-\mu_r]\}, \qquad (11)$$

linking the quasiclassical density of states $n(E)$ with the characteristics of isolated periodic orbits. Here $\bar{n}(E)$ is the average density of the Thomas–Fermi states which can be determined by the volume of the phase space enclosed within the isoenergetic surface with energy E, the index r denotes different primitive periodic orbits, the sum with respect to j takes into account the contribution from a multiple inversion at the primitive periodic orbits, while S_r and μ_r represent the action and the index of Maslov for the r-th primitive periodic orbit. It is important to understand that formula (11) establishes the conformity not between individual periodic orbits and quantum states but between the entire spectrum of the system and the combination of all of its periodic orbits in the classical limit.

In recent years attempts have been made to use the formula (11) to calculate quasiclassical spectra of a number of simple model systems both in the regular and chaotic regions. Of the more successful applications one should note that it has been used to resolve the problem described by Kepler[97] regarding the quantisation of free particle motion on a pseudosphere,[98] and in different billiards,[99,100] and the calculation of the H atom spectrum in a magnetic field.[101–105] The generalisation of this formula by introducing into it the contributions from classically forbidden complex periodic orbits, which enable the tunnel distributions to be calculated,[106–109] is of significant interest.

A more general application of the formula (11) for calculating the spectra encounters certain difficulties. The most serious of these problems is the absence of sufficiently general and effective methods to search for all periodic orbits in a chosen energy region, the exponential growth in the number of isolated periodic orbits with increase in their period and the very slow convergence of the series (11). Nevertheless the method based on its use is at present the only sequential approach to the quasiclassical calculation of the spectrum in the field of chaotic dynamics.

In formula (11) contributions remain only from the periodic orbits with periods less than the somewhat fixed time T, although it gives a value $n(E)$ obtained in experiments with a fixed resolution $\Delta E = h/T$ with respect to energy. An interesting consequence of such a rough approximation assuming experimental verification is the confirmation that the quasiclassical density of the states is a multiperiodic energy function and that its oscillation periods are determined by periods of motion with respect to the periodic orbits. Such oscillations of the state densities were in fact observed in spectra of a number of simple systems.[51–59] One should note that the existence of the narrow resolution of different structures in the spectrum indicates that at high energies in the system studied regions of quasiregular motion occur against a background of largely chaotic dynamics.

Low resolution spectra: the dynamic theory. If unstable isolated periodic orbits play such an important role in the formation of chaotic spectra, the question arises as to whether it is possible to obtain information on dynamically existing periodic orbits directly from the spectra, and if so, how? The natural answer to this question is provided by the dynamic theory of spectra,[110,111] which we shall illustrate by the example of the electronic emission spectra.

The process of electron excitation of molecules is often regarded as an instantaneous Franck-Condon transfer of the wave function Φ of the principal vibrational level of the original electronic state into a certain ultimate electronic state in which Φ is already a wave packet describing a nonstationary state. The emission spectrum from this nonstationary state contains information on the dynamics of energy redistribution between different degrees of freedom of the molecule.

The principal idea of the dynamic theory of the spectra resides in the transfer of information within the spectrum from the energy language to the temporal language by calculation of the correlation function $C(t) = <\Phi|\Phi(t)>$. In our case the link between $C(t)$ and the spectrum of infinitely high resolution has the form:

$$S(E)=(1/2\pi)\lim_{T\to\infty}\int_{-T}^{T} C(t)\exp(iEt/\hbar)\,dt, \qquad (12)$$

from where it follows that the information provided by the spectrum of infinitely high resolution is equivalent to that provided by the dynamics of the system studied over an infinitely long period. At high energies it is usually impossible to obtain spectra in which all lines have been totally resolved. Instead spectra with broad spectral contours with a more or less clearly pronounced vibrational structure are obtained. From the dynamic standpoint this implies that such spectra contain information on the dynamics of the system only over a certain final time interval, T. The corresponding spectral contour $S_T(E)$ is given by the formula:

$$S_T(E)=(1/2\pi)\int_{-T}^{T} C(t)\exp(iEt/\hbar)\,dt. \qquad (13)$$

We shall examine the excitation process in which the centre of the Gaussian wave packet, which corresponds to the wave function of the principal vibrational level of the lower electronic state, encounters one of the periodic orbits. The dynamics of the Gaussian wave packets in smooth potentials have been studied in considerable detail.[112] In our case the centre of the packet will move along the periodic orbit, while the packet itself will gradually spread more rapidly the more stable is the periodic orbit. In this case the function $|C(t)|$ will have the characteristics of damped vibrations. Its maxima are associated with the reversions of the wave packet to the starting point, whereas the systematic decrease in their height was caused by the spreading of the packet. Thus each dynamically significant periodic orbit generates in the correlation function a series

of equidistant maxima, their separations being equal to the transformation period along this periodic orbit.

The analysis shows that, in contrast to the high resolution spectra, the low resolution spectra in the chaotic region contain information not on individual states of the quantum system but on the dynamically significant isolated periodic orbits. Therefore it is possible to use the low resolution spectra to study the intramolecular redistribution of vibrational energy in the quasicontinuum.

Another approach to explain the appearance of isolated unstable periodic orbits in the low resolution spectra which is close in principle to the Feshbaich theory of resonances has been developed by other authors.[113–115]

The above-mentioned analytical scheme for the low resolution spectra based on the extraction of information on periodic orbits which they contain has been successfully used to interpret the spectra of the H atom in a magnetic field,[52–54,101–105,113–118] the molecular ion H_3^+,[115–121] Na_3,[116,122,123] O_3,[124,125] CO_2,[126] and HCN[127–129] molecules.

Another interesting manifestation of unstable periodic orbits in the properties of quantum systems was found by Heller in a study of wavefunctions of highly excited states of the quantum billiard "Stadium" consisting of two hemispheres connected by segments of straight lines.[130–132] The classical limit "Stadium" is an example of a totally chaotic system at all levels. Therefore one would expect that in accordance with the quasiclassical analysis and the principle of concordance its wavefunctions will be strongly delocalised. The real position was found to be much more interesting. Analysis of the surfaces of the level of the function $[\Psi_k]^2$ showed that the wavefunctions of many excited states clearly have a tendency to be localised close to the periodic orbits. Heller named this effect as the scars of the periodic orbits in the wavefunctions. Such scars were subsequently found also in other systems including those with smooth potentials.[133] The theoretical basis of this effect from different standpoints may be found in earlier reports.[131,134–137] However the scars of the periodic orbits in the configurational space have not been widely studied. Study of the scars in the phase space with the aid of the quantum cross sections by Poincare for the distribution functions of Wigner[138] or Husimi[139] was found to be markedly more fruitful. Both of these approaches have been compared,[137,140] and it was concluded that the use of the Husimi distribution function was preferable.

Thus the unstable periodic orbitals separate certain special states in the chaotic region which are typical representatives of localised quantum states with the wavefunctions localised in the vicinities of these orbits. From the extent of the localisation of wavefunctions of such states it is possible to develop effective methods for their calculation. As an example one should note the variation method as the basis of Gaussian wavefunctions with the adjacent centres and in the corresponding periodic orbit[113–115,119,141,142] analogous to the stabilisation method used in the calculation of the positions of the resonances and which allows information to be obtained on the class of localised quantum states of interest to us without calculating all lower-lying states.

Another effective approach to the study of localised quantum states under discussion is the use of the adiabatic approximation for separating slow motion along a periodic orbital and rapid vibrations perpendicular to the orbit.[117,133] Such a separation operates more efficiently the less unstable is the corresponding periodic orbit, i.e. the longer the trajectory which will stay in the vicinity of its origin. It was found that only adiabatically stable, attracting periodic orbitals, which possess the same property, lead to scars, and that any trajectory having started in the vicinity of such an orbit, before vacating it will certainly intersect the projection of the periodic orbit on to the configurational space.[133,143] One should note that adiabatically stable periodic orbits may be totally unstable in the Lyapunov sense.

One should also note the method of calculation based on the quasiclassical quantisation of unstable periodic orbits[144,145] which is successfully used to explain the low resolution spectra of the H_3^+ ion.[121]

Nonlinear normal vibrations at which all generalised coordinates at any time period are proportional to one of them and which in the small energy limit is reduced to the usual normal vibrations[146–149] are the most simple periodic motions in nonlinear mechanical systems permitting systematic study. The number of nonlinear normal vibrations is dependent not only on the number of degrees of freedom in the system studied but also on its symmetry. Thus with the CH_4 molecule the number of linear and nonlinear normal vibrations is equal to 9 and 63 respectively.[147]

From a sequential study of the evolution and bifurcation of the system of nonlinear normal vibrations with increase in energy, it is possible to find all periodic orbits of the system originating from the normal linear vibrations. Such periodic orbits and the quantum states localised near them are termed regular orbits.[150] In addition to them irregular periodic orbits may exist in the system which are genetically unassociated with any of the linear normal vibrations. Irregular periodic orbits are of significant interest, since the localised quantum states, the properties of which cardinally differ from those of the localised quantum states associated with the regular periodic orbits, correspond to them.

In recent years it has become more evident that "scars" of periodic orbits in the wavefunctions are only the most simple example of a broad class of effects, which could have been determined as the manifestation of different elements of the phase picture of the system (the structure of the phase space) in its quantum properties. Apart from the above-mentioned, scars from such elements of the phase picture as families of unstable periodic orbits,[115–121,151–153] resistant and nonresistant invariant varieties of periodic orbits,[152,153,160] invariant tori, the dimensionality of which is less than the number of corresponding degrees of freedom,[122–123] homo- and heterocyclic structures,[154,155] and separatrix varieties (see Refs. 152, 155–157, 140 and literature cited in these articles) and cantori (see Refs. 158, 159, 140 and the literature cited in these articles) have so far been observed in the wavefunctions. In particular one should note the manifestations of the cantori, the noteable "bottlenecks" playing an important role in the intramolecular redistribution of energy.

V. Spatial localisation of the basis functions: bound states in a continuous spectrum

As a clear example illustrating the effectiveness of studying the localisation of quantum states in the space of the basis functions we shall discuss the effect of excitation capture in the continuous spectrum caused by the existence of quasibound states in a continuum. In its mathematical form this effect is analogous to such widely known quantum-optical effects as superradiant radiation in a system of identical double-level systems (the Dikke model)[161] and the coherent capture of the occupancies in the N-level systems containing metastable states or interacting with a certain continuum in the presence of intense multimodal laser radiation (see Refs. 162–187

and the literature cited in these articles). In contrast to quantum optics the effect of excitation capture in the theory of nonradiative intramolecular transitions has been studied in considerably less detail,[201,202] although the basic principle that bound states exist in a continuum was substantiated quite a long time ago.[188–191] Such a position is associated with the fact that in the objectives of intramolecular dynamics there are no natural controlling parameters analogous to the intensity of irradiation and to the frequency difference of the resonance in quantum optics, which could have been changed as desired and continuously in order to satisfy the conditions essential for the expression of the effect under discussion.

(Quasi)stationary states in the continuous spectrum may also arise during the decay of quantum systems in stable outer fields.[192–196] In this case the outer field strength plays the role of the continuous controlling parameter. A good example of such an effect is the narrowing of the autoionisation widths of the Rydberg states in the regions of their quasi-intersections which arises as a result of the destructive interference between different decay channels (see Refs. 194–196 and the references cited in these papers).

In a recent series of studies the possibility that (quasi)bound states of a purely intramolecular nature could exist in a continuum was demonstrated. Such states naturally arise during the decay of a coherently excited group of discrete (quasi)degenerate levels interacting with one or several continua. An analogous effect may also arise during the interaction of several continua.[203,204] In a discussion of the theory of this effect we will not give a concrete definition of the physical nature of the discrete states and the continuum; this enables us to obtain results applicable to a very broad range of processes.

We shall examine N degenerate discrete states interacting with a single continuum by means of potential V. We shall assume that the wavefunctions of the discrete states $\{\varphi_k,\ k = 1, \ldots, N\}$ and the continuum φ_E were selected as actual, whereas the interaction V has matrix elements differing from zero only between the states of the discrete and continuous spectra ($V_{kn} = V_{EE'} = 0$, $V_{ke} = 0$) and the matrix elements are not dependent on E. Such assumptions are normal in the theory of nonradiative transitions.[205]

In a description of the decays it is convenient from the start to exclude from examination the states of the continuous spectrum. One of the simplest ways of achieving this is to construct an effective Hamiltonian acting in the subspace of discrete states and implicitly taking into account their interaction with the states of the continuum. Such an effective Hamiltonian may usually be reduced to the form:

$$H=H_0-i\alpha W, \tag{14}$$

where H_0 is the unperturbed Hamiltonian describing the discrete states in the absence of a continuum, W is the effective potential describing their interaction with each other by means of the continuum, while $\alpha > 0$ is a certain parameter characterising the intensity of this interaction. In our case the operators H_0 and W are actual symmetrical matrices with a dimensionality of $N \times N$, and the matrix W was positively determined.

We shall examine the decay of the N-fold degenerate level within the generalised Weisskopf–Wigner formalism.[206,207] Let only the discrete states be coherently excited at the initial moment of time,

$$\Phi(0)=\sum a_k(0)\varphi_k, \tag{15}$$

which corresponds to the situation realised in different physical experiments. The variation in the amplitude vector $\mathbf{a}(t)$ as a function of time is determined by the equation

$$i\dot{\mathbf{a}}(t)=\mathrm{H}\mathbf{a}(t), \tag{16}$$

where the matrix elements of the effective Hamiltonian have the form

$$H_{kn}=-i\alpha\gamma_{kn},\quad \gamma_{kn}=(\gamma_k\gamma_n)^{1/2},\quad \gamma_k=\pi V_{kE}V_{Ek}>0. \tag{17}$$

Here we have used the atomic system of units ($\hbar = 1$) and have set the energy of the degenerate level = 2 and introduced the designation γk for the initial halfwidth characterising the decay rate of the k-th state in the absence of other states. The dynamics of our system is most simply described on the basis of the wavefunctions of the effective states, which are eigenfunctions of operator H. The eigenvalues $\lambda_n = E_n - iG_n$ correspond to them, where E_n determines the position, and G_n determines the halfwidth of the n-th effective state. In our case the spectrum of the matrix h has a very simple form:

$$\lambda_1=\mathrm{Tr}(H)=-i\alpha\sum\gamma_k,\qquad \lambda_2=\ldots=\lambda_N=0. \tag{18}$$

A number of important physical corollaries result from formula (18).

1. The interaction between the degenerate states via the continuum does not reduce their degeneracy.

2. As a result of such an interaction the $N-1$ bound state and only one unbound state with halfwidth G_1 and wavefunction Ψ_1 which were predetermined by the expressions are formed:

$$\Gamma_1=|\mathrm{Tr}(H)|=\alpha\sum\gamma_k,\qquad \Psi_1=\sum(\alpha\gamma_k/\Gamma_1)^{1/2}\varphi_k. \tag{19}$$

Thus we arrive at a very surprising result, i.e. interference between different decay pathways of a coherently excited system of degenerate states each of which in the absence of the other states would have decayed at its own particular rate determined by the halfwidth leads to a situation in which only one rapid channel of decay remains. All remaining decay routes are found to be closed. the effect under discussion is universal and is not dependent either on the number of states in the group or on the magnitude of the halfwidth γk.

3. The probability that the system examined will remain coupled up to the time moment t is given by the equation

$$P(t)=A\exp(-2\Gamma_1 t)+B, \tag{20}$$

where

$$A=\left[\sum(\alpha\gamma_k/\Gamma_1)^{1/2}a_k(0)\right]^2,\qquad B=1-A. \tag{21}$$

From (20) and (21) it follows that relaxation in the process of excitation of the effective states Ψ_k with $k = 1$ leads to the capture of excitation in the continuous spectrum. Thus initial relaxation is significantly dependent on the nature of the physical process (polarised irradiation, short and ultrashort laser pulses, nonradiative transitions, etc.) used for its creation, and the effect under discussion may be used to control both the rate and the direction of the chemical process by localisation of the excitation in a given group of states. It could have been used in particular for the local heating of individual fragments of molecules such as various functional groups and ligands.[208]

4. We shall discuss how the effect examined alters in the case of the disorganisation of the group of quasidegenerate levels. It has already been shown that the interaction between the group of

quasidegenerate states and the continuum leads to two interesting effects which can be seen in Fig. 3 and Fig. 4,[198] in which the dependence of the effective states of two model systems with an initial equidistant arrangement of the energy levels (normal vibrational polyads) and with equal zero halfwidths ($\gamma_1 = \ldots = \gamma_N = \gamma$) on the α axis and the halfwidths are schematically represented. It can be seen that interaction with the continuum leads to the contraction of the group of interacting states and to the redistribution of the widths in favour of a single effective state. In this case instead of the bound states in the continuous spectrum long-lived resonance states are formed with lifetimes which contrary to expectations increase with increase in the intensity of the interaction between the original states φ_k and the continuum.

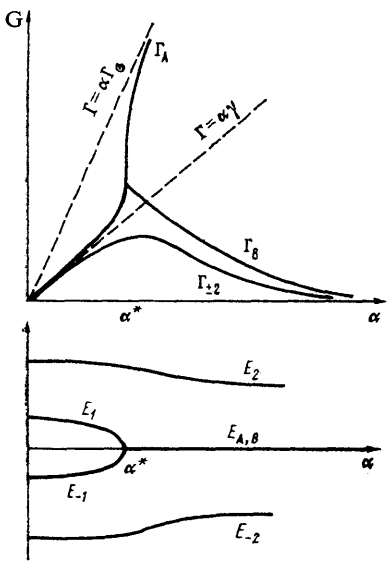


Figure 3. Changes in the positions $\{E_k\}$ and halfwidths $\{G_k\}$ of resonance states in the equidistant N-level system with increase in parameter α, characterising the intensity of the interaction of the coupled states with the continuum. All levels have identical zero halfwidths equal to $\alpha\gamma$, $G_\sigma = N\gamma$. Case $N = 4$.[198]

In general the interaction of N discrete states with the continuum leads to the formation of two different types of resonance state. Firstly the A-resonances the widths of which increase with increase in the interaction between discrete states and the continuum, which lead to their diffusion in the continuous spectrum in the limit $\alpha\to\infty$, and secondly the B-resonances, which in the same limit are transformed into exceptionally long-lived quasistationary states. It is possible to show that the number of A-resonances coincides with the rank of matrix W, which in turn is determined by the number of different decay channels of the system.[198–200] In the Weisskopf–Wigner model the rank of matrix W is equal to unity, which explains the formation of only one A-resonance during the decay. The results obtained have been generalised for the case of the decay of the system in certain of the interacting continua.[199]

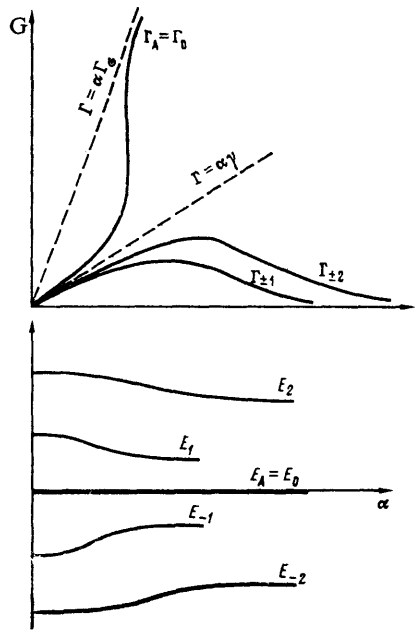


Figure 4. As for Fig. 3, but for case $N = 5$.[198]

VI. Conclusion

The examples considered in this review show that classical concepts play an extremely important role in the theory of highly excited quantum states.

Firstly they serve as the basis for the construction of effective numerical methods of calculation, the most well-known examples being the numerous variants of the quasiclassical method. Moreover information on the characteristics of classical dynamics may be successfully used to increase the efficiency of the standard quantum-mechanical methods of calculation such as the variation method (the selection of the optimum basis) and the adiabatic approximation (the selection of optimum variables).

Secondly the classical concepts serve as a source of both ideas for the design of particular experimental studies and concepts used to interpret the experimental data in the high energy range of the system.

Another important conclusion from the above analysis is the perception of that role played by the concept of localised quantum states by means of which it is possible to examine a set of the most diverse phenomena from common positions.

Thus many rearrangements of vibrational polyads with increase in energy in the transitional range of the spectrum are associated with a change in the nature of the localisation of vibrations on excitation. By studying localised quantum states in the quasicontinuum range it is possible to find and study systematically special relatively stable dynamic regimes and also to observe how they change with increase in energy. Localisation in the continuous spectrum leads to the formation of long-lived resonances and bound states.

A study of the localised vibrational states is of significant interest also because it provides a means of exploring a route to perform selective chemical reactions. From general considerations it is clear that the possibility of controlling a chemical reaction should apparently be closely associated with the possibility of preparing a

molecule in certain special states which have different probabilities for the various reaction pathways. Currently the localised vibrational states are the most practicable candidates for this role.

References

1. E B Wilson, J C Denius, P C Cross *Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra* (Translated into Russian), Mir, Moscow, 1960
2. A A Ovchinnikov, N S Erikhman *Usp. Fiz. Nauk*, 1982, **138** 289
3. M S Child, L Halonen *Adv. Chem. Phys.*, 1984, **57** 1
4. O S Van Roosmalen, F Iachello, R D Levine, A E L Dieperink *J. Chem. Phys.*, 1983, **79** 2515
5. M E Kellman *Chem. Phys. Lett.*, 1983, **99** 437
6. M E Kellman *Chem. Phys. Lett.*, 1983, **103** 40
7. O S Van Roosmalen, I Benjamin, R D Levine *J. Chem. Phys.*, 1984, **81** 5986
8. I Benjamin, R D Levine *Chem. Phys. Lett.*, 1985, **117** 314
9. F Michelot, J Moret-Bailly *J. Phys. Fr.*, 1987, **48** 51
10. M E Kellman *J. Chem. Phys.*, 1988, **83** 3843
11. A Leviatan *J. Chem. Phys.*, 1989, **91** 1706
12. J Hornos, F Iachello *J. Chem. Phys.*, 1989, **90** 5284
13. T A Holme, R D Levine *Chem. Phys.*, 1989, **131** 169
14. M Iwai, R D Levine *Phys. Rev. A*, 1990, **42** 3991
15. A Lichtenberg, M Lieberman *Regular and Stochastic Dynamics* (Translated into Russian), Mir, Moscow, 1984
16. G M Zaslavskii *Stokhastichnost Dinamicheskikh Sistem* (The Stochastic State of Dynamic Systems), Nauka, Moscow, 1984
17. V S Anishchenko *Slozhnye Kolebaniya v Prostykh Sistemakh* (Complex Vibrations in Simple Systems), Nauka, Moscow, 1990
18. W G Harter, C W Patterson, F J DaPaixao *Rev. Mod. Phys.*, 1978, **50** 37
19. W G Harter, H W Galbraith, C W Patterson *J. Chem. Phys.*, 1978, **69** 4888
20. W G Harter, C W Patterson, H W Galbraith *J. Chem. Phys.*, 1978, **69** 4896
21. C W Patterson, H W Galbraith, B Krohn, W G Harter *J. Mol. Spectrosc.*, 1979, **77** 457
22. W G Harter, C W Patterson *J. Chem. Phys.*, 1984, **80** 4241
23. W G Harter *J. Chem. Phys.*, 1985, **85** 5560
24. W G Harter *Comp. Phys. Rep.*, 1988, **8** 319
25. I M Pavlichenkov, B I Zhilinskii *Chem. Phys.*, 1985, **100** 339
26. B I Zhilinskii, I M Pavlichenkov *Zh. Eksp. Teor. Fiz.*, 1987, **92** 387
27. I M Pavlichenkov, B I Zhilinskii *Ann. Phys. (N. Y.)*, 1988, **184** 1
28. C Jaffe, P Brumer *J. Chem. Phys.*, 1980 **73** 5646
29. E L Siebert, III, W P Reinhardt, J T Hynes *J. Chem. Phys.*, 1982, **77** 3583
30. V B Pavlov-Verevkin, B I Zhilinskii *Khim. Fizika*, 1987, **6** 1459
31. V B Pavlov-Verevkin, B I Zhilinskii *Khim. Fizika*, 1988, **7** 1299
32. V B Pavlov-Verevkin, B I Zhilinskii *Opt. Spektrosk.*, 1988, **64** 46
33. V B Pavlov-Verevkin, B I Zhilinskii *Chem. Phys.*, 1988, **128** 429
34. J T Muckerman, M S Child *Chem. Phys. Lett.*, 1988, **153** 477
35. Z Li, L Xiao, M E Kellman *J. Chem. Phys.*, 1990, **92** 2251
36. L Xiao, M E Kellman *J. Chem. Phys.*, 1990, **93** 5805
37. D A Sadovskii, B I Zhilinskii *Mol. Phys.*, 1988, **65** 109
38. V B Pavlov-Verevkin, D A Sadovskii, B I Zhilinskii *Europhys. Lett.*, 1988, **6** 573
39. D A Sadovskii, B I Zhilinskii, J P Champion, G Pierre *J. Chem. Phys.*, 1990, **92** 1523
40. P Robinson, K Holbrook *Unimolecular Reactions* (Translated into Russian), Mir, Moscow, 1975
41. *Statistical Theories of Spectra: Fluctuations* (Edited by C E Porter), Academic, New York, 1965
42. M Mehta *Random Matrices and the Statistical Theory of Energy Levels*, Academic, New York, 1967
43. T A Brody, J Flores, J B French, et al. *Rev. Mod. Phys.*, 1981, **53** 385
44. *Lect. Notes Phys*, 1986, **263**
45. T Zimmermann, L S Cederbaum, H D Meyer, H Köppel *J. Phys. Chem.*, 1987, **91** 4446
46. G M Zaslavskii *Usp. Fiz. Nauk*, 1979, **129** 211
47. G M Zaslavskii *Phys. Rep.*, 1981, **80** 157
48. M V Berry *Proc. R. Soc. London, A*, 1987, **413** 183
49. P V Elyutin *Usp. Fiz. Nauk*, 1988, **155** 397
50. B Eckhardt *Phys. Rep.*, 1988, **163** 205
51. W R S Garton, F S Tomkins *Astrophys. J.*, 1969, **158** 839
52. A Holle, G Wiebusch, J Main, et al. *Phys. Rev. Lett.*, 1986, **56** 2594
53. J Main, G Wiebusch, A Holle, K H Welge *Phys. Rev. Lett.*, 1986, 57 2789
54. A Holle, J Main, G Wiebusch, et al. *Phys. Rev. Lett.*, 1988, **61** 161
55. A Carrington, R M Kennedy *J. Chem. Phys.*, 1984, **81** 91
56. E Abramson, R W Field, D Imre, et al. *J. Chem. Phys.*, 1985, **83** 453
57. M Broyer, G Delacretaz, G-Q Ni, et al., *J. Chem. Phys.*, 1989, **90** 4620
58. D E Freeman, K Yoshino, J R Esmond, W H Parkinson *Planet. Space Sci.*, 1984, **32** 239
59. X Yang, C A Rogaski, A M Wodtke *J. Chem. Phys.*, 1990, **92** 2111
60. I C Percival *J. Phys. B*, 1973, **6** L229
61. M Tabor *Adv. Chem. Phys.*, 1981, **46** 73
62. D W Noid, M L Koszykowski, R A Marcus *Ann. Rev. Phys. Chem.*, 1981, **32** 267
63. *Lect. Notes Phys.*, 1979, **93**
64. *Chaotic Behaviour in Deterministic Systems* (Edited by G Iooss, R H G Helleman, R Stora), North-Holland, Amsterdam, 1983
65. *Chaotic Behaviour in Quantum Systems* (Edited by G Casati), Plenum Press, New York, 1985
66. N L Balazs, B K Jennings *Phys. Rep.*, 1984, **104** 347
67. M Hillery, R F O'Connell, M O Scully, E P Wigner *Phys. Rep.*, 1984, **106** 121
68. T Mückenheim *Phys. Rep.*, 1986, **133** 337
69. J H Jensen, Q Niu *Phys. Rev. A*, 1990, **42** 2513
70. K Husimi *Proc. Phys. Math. Soc. Japan*, 1940, **22** 264
71. K Takahashi *J. Phys. Soc. Japan*, 1986, **55** 762
72. J Kurchan, P Lebeouf, M Saraceno *Phys. Rev. A*, 1989, **40** 6800
73. M Shapiro, G Goelman *Phys. Rev. Lett.*, 1984, **53** 1714
74. J Reichl *Europhys. Lett.*, 1988, **6** 669
75. R Ramaswamy, S Swaminathan *Europhys. Lett.*, 1987, **4** 127
76. S W McDonald, A N Kaufman *Phys. Rev. A*, 1988, **37** 3067
77. K S J Nordholm, S A Rice *J. Chem. Phys.*, 1974, **61** 203
78. E J Heller *Phys. Rev. A*, 1987, **35** 1360

79. E B Stechel *J. Chem. Phys.*, 1985, **82** 364
80. E B Stechel *Lect. Notes Phys.*, 1986, **263** 182
81. J C Lorque, V B Pavlov-Verevkin *J. Chem. Phys.*, 1990, **93** 520
82. F Iachello, R D Levine *Europhys. Lett.*, 1987, **4** 389
83. G Hose, H S Taylor *J. Chem. Phys.*, 1982, **76** 5356
84. G Hose, H S Taylor *J. Chem. Phys.*, 1983, **78** 5845
85. G Hose, H S Taylor, A Tip *J. Phys. A*, 1984, **17** 1209
86. R M Stratt, C N Handy, W H Miller *J. Chem. Phys.*, 1979, **71** 3311
87. Yu S Makushkin, V G Tyuterev *Metody Vozmuchshenii i Effektivnye Gamil'toniany v Molekulyarnoi Spektroskopia* (Perturbation Methods and Effective Hamiltonians in Molecular Spectroscopy), Nauka, Novosibirsk, 1984
88. L G Jaffe *Rev. Mod. Phys.*, 1982, **54** 407
89. A M Perelomov *Obobshchennye Kogerentnye Sostoyanye i ikh Premeneniya* (Generalised Coherent States and their Use), Nauka, Moscow, 1987
90. M E Kellman, E D Lynch *J. Chem. Phys.*, 1986, **85** 7216
91. M E Kellman, E D Lynch *J. Chem. Phys.*, 1988, **88** 2205
92. L Xiao, M E Kellman *J. Chem. Phys.*, 1989, **90** 6086
93. M E Kellman, L Xiao *Chem. Phys. Lett.*, 1989, **162** 486
94. M E Kellman, L Xiao *J. Chem. Phys.*, 1990, **93** 5821
95. B I Zhilinskii *Chem. Phys.*, 1989, **137** 1
96. M V Berry *Lect. Notes Phys.*, 1979, **93** 171
97. M C Gutzwiller *J. Phys. Chem.*, 1988, **92** 3154
98. N L Balazs, A Voros *Phys. Rep.*, 1986, **143** 109
99. M V Berry *Ann. Phys.*, 1981, **131** 163
100. M Sieber, F Steiner *Physica D*, 1990, **44** 248
101. M L Du, J B Delos *Phys. Rev. A*, 1988, **38** 1896
102. M L Du, J B Delos *Phys. Rev. A*, 1988, **38** 1913
103. D Wintgen *Phys. Rev. Lett.*, 1987, **58** 1589
104. D Wintgen, H Friedrich *Phys. Rev. A*, 1987, **36** 131
105. D Wintgen *Phys. Rev. Lett.*, 1988, **61** 1803
106. W H Miller *J. Phys. Chem.*, 1979, **83** 960
107. R Balian, G Parisi, A Voros *Lect. Notes Phys.*, 1979, **106** 337
108. A Voros *Ann. Inst. Henry Poincare*, 1983, **39** 211
109. J M Robbins, S C Creagh, R G Littlejohn *Phys. Rev. A*, 1989, **39** 2838
110. E J Heller *Potential Energy Surfaces and Dynamics Calculations* (Edited by D G Truhlar), Plenum Press, New York, 1981, p. 103
111. E J Heller *Acc. Chem. Res.*, 1981, **14** 368
112. R G Littlejohn *Phys. Rep.*, 1986, **138** 193
113. H S Taylor, J Zakrzewski, S Saini *Chem. Phys. Lett.*, 1988, **145** 555
114. H S Taylor, J Zakrzewski *Phys. Rev. A*, 1988, **38** 3732
115. J M Gomez Llorente, J Zakrzewski, H S Taylor, K C Kulander *J. Chem. Phys.*, 1989, **90** 1505
116. J M Gomez Llorente, H S Taylor *Phys. Rev. A*, 1990, **41** 697
117. E Pollak *Philos. Trans. R. Soc. London, A*, 1990, **332** 343
118. E Pollak *J. Chem. Phys.*, 1988, **89** 1195
119. J M Gomez Llorente, J Zakrzewski, H S Taylor, K C Kulander *J. Chem. Phys.*, 1988, **89** 5959
120. J M Gomez Llorente, E Pollak *J. Chem. Phys.*, 1989, **90** 5406
121. O Brass, J Tennyson, E Pollak *J. Chem. Phys.*, 1990, **92** 3377
122. J M Gomez Llorente, H S Taylor *Phys. Rev. Lett.*, 1989, **62** 2096
123. J M Gomez Llorente, H S Taylor *J. Chem. Phys.*, 1989, **91** 953
124. B R Johnson, J L Kinsey *Phys. Rev. Lett.*, 1989, **62** 1607
125. B R Johnson, J L Kinsey *J. Chem. Phys.*, 1987, **89** 7638
126. R Schinke, V Engel *J. Chem. Phys.*, 1990, **93** 3252
127. S C Farantos, J M Gomez Llorente, O Hahn, H S Taylor *J. Chem. Phys.*, 1990, **93** 76
128. S C Farantos, M Founargiotakis *Chem. Phys.*, 1990, **142** 345
129. S C Farantos, J M Gomez Llorente, O Hahn, H S Taylor *Chem. Phys. Lett.*, 1990, **166** 71
130. E J Heller *Phys. Rev. Lett.*, 1984, **53** 1515
131. E J Heller *Lect. Notes Phys.*, 1986, **263** 162
132. P W O'Connor, E J Heller *Phys. Rev. Lett.*, 1988, **61** 2288
133. B Eckhardt, G Hose, E Pollak *Phys. Rev. A*, 1989, **39** 3776
134. E B Bogomolny *Physica D*, 1988, **31** 169
135. E Pollak *J. Chem. Phys.*, 1984, **80** 3613
136. M V Berry *Proc. R. Soc. London, A*, 1989, **423** 219
137. M Feingold, R G Littlejohn, S B Solina, et al. *Phys. Lett. A*, 1990, **146** 199
138. J S Hutchinson, R E Wyatt *Chem. Phys. Lett.*, 1980, **72** 378
139. Y Weissman, J Jortner *J. Chem. Phys.*, 1982, **77** 1486
140. M J Davis *J. Phys. Chem.*, 1988, **92** 3124
141. A Hazi, H S Taylor *Phys. Rev. A*, 1970, **1** 1109
142. J H Frederick, E J Heller *J. Chem. Phys.*, 1987, **87** 6592
143. E Pollak *Chem. Phys.*, 1981, **61** 305
144. K Stefanski, E Pollak *J. Chem. Phys.*, 1987, **87** 1079
145. K Stefanski, E Pollak *Chem. Phys.*, 1989, **134** 37
146. L I Manevich, Yu V Mikhlin, V N Pilipchuk *Metod Normal'nykh Kolebanii dlya Sushchestvenno Nelineinykh Sistem* (A Method of Normal Vibrations for Significantly Linear Systems), Nauka, Moscow, 1989
147. J Montaldi, M Roberts, I Stewart *Lect. Notes Phys.*, 1988, **278** 695
148. J Montaldi, M Roberts, I Stewart *Nonlinearity*, 1990, **3** 695
149. J Montaldi, M Roberts, I Stewart *Nonlinearity*, 1990, **3** 731
150. M Founargiotakis, S C Farantos, G Contopoulos, C Polymilis *J. Chem. Phys.*, 1989, **91** 1389
151. P Leboeuf, M Saraceno *Phys. Rev. A*, 1990, **41** 4614
152. R M Benito, F Borondo, J H Kim, et al. *Chem. Phys. Lett.*, 1989, **161** 60
153. R L Waterland, J M Yuan, C C Martens, et al. *Phys. Rev. Lett.*, 1988, **61** 2733
154. A M Ozorio de Almeida *Nonlinearity*, 1989, **2** 519
155. M Saraceno *Ann. Phys.*, 1990, **199** 37
156. T Geisel, G Radons, J Rubner *Phys. Rev. Lett.*, 1986, **57** 2883
157. G Radons, T Geisel, J Rubner *Adv. Chem. Phys.*, 1989, **73** 891
158. R S MacKay, J D Meiss, I C Percival *Physica, D*, 1984, **13** 55
159. D Bensimon, L P Kadanoff *Physica, D*, 1984, **13** 82
160. B Eckhardt, G Hose, E Pollak *Chem. Phys. Lett.*, 1990, **174** 325
161. A V Andreev, V I Emel'yanov, Yu A Il'inskii *Kooperativnye Yavleniya v Optike: Sverkhizluchenie, Fazovye Perekhody* (Cooperative Phenomena in Optics: Superradiant Radiation), Nauka, Moscow, 1988
162. B L Beers, L Armstrong, Jr., *Phys. Rev. A*, 1975, **12** 2447
163. R M Whitley, C R Stroud *Phys. Rev. A*, 1976, **14** 1498
164. J D Stettler, C M Bowden, N M Witriol, J H Eberly *Phys. Lett. A*, 1979, **73** 171
165. F T Hioe, J H Eberly *Phys. Rev. Lett.*, 1981, **47** 838
166. P Lambropoulos, P Zoller *Phys. Rev. A*, 1981, **24** 379
167. K Rzaeiwski, J H Eberly *Phys. Rev. Lett.*, 1981, **47** 408
168. M Crance, L Armstrong *J. Phys. B*, 1982, **15** 3199
169. P E Coleman, P L Knight *J. Phys. B*, 1982, **15** L235
170. D A Cardimona, M G Raymer, C R Stroud, Jr. *J. Phys. B*, 1982, **15** 55
171. S Swain *J. Phys. B*, 1982, **15** 3405

172. P M Radmore, P L Knight *J. Phys. B*, 1982, **15** 561
173. P M Radmore *Phys. Rev. A*, 1982, **26** 2252
174. Z Deng *Opt. Commun.*, 1983, **48** 284
175. Z Deng *J. Opt. Soc. Am. B*, 1984, **1** 874
176. P M Radmore, P L Knight *Phys. Lett. A*, 1984, **102** 180
177. Z Deng *Phys. Lett. A*, 1984, **105** 43
178. E Kyröla *J. Phys. B*, 1986, **19** 1437
179. A Lami, N K Rahman *Phys. Rev. A*, 1986, **33** 782
180. A Lami, N K Rahman *Phys. Rev. A*, 1986, **34** 3908
181. S L Haan, G S Agarwal *Phys. Rev. A*, 1987, **35** 4592
182. F T Hioe, C E Carroll *Phys. Rev. A*, 1988, **37** 3000
183. V S Smirnov, A M Tumaikin, V I Yudin *Zh. Eksp. Teor. Fiz.*, 1989, **96** 1613
184. C A Glosson, C D Cantrell *Phys. Rev. A*, 1990, **41** 2898
185. M P Sharma, D A Cardimona, A Gavrielides *Phys. Rev. A*, 1990, **41** 5237
186. M Pont, M Gavrila *Phys. Rev. Lett.*, 1990, **65** 2362
187. K Burnett, P L Knight, B R M Piraux, V C Reed *Phys. Rev. Lett.*, 1991, **66** 301
188. J Von Neumann, E Wigner *Phys. Z*, 1929, **30** 465
189. F H Stillinger, D R Herrick *Phys. Rev. A*, 1975, **11** 446
190. F H Stillinger, D R Herrick *J. Chem. Phys.*, 1975, **62** 4360
191. B Gazdy *Phys. Lett. A*, 1977, **61** 89
192. H Friedrich, D Wintgen *Phys. Rev. A*, 1985, **31** 3964
193. H Friedrich, D Wintgen *Phys. Rev. A*, 1985, **32** 3231
194. D A Harmin *Phys. Rev. A*, 1984, **30** 2413
195. J Y Liu, P McNicholl, D A Harmin, et al. *Phys. Rev. Lett.*, 1985, **55** 189
196. C Chardonnet, D Delande, J C Gay *Phys. Rev. A*, 1989, **39** 1066
197. V B Pavlov-Verevkin *Phys. Lett. A*, 1988, **129** 168
198. A V Churakov, T Yu Michailova, V B Pavlov-Verevkin, V I Pupyshev *Phys. Lett. A*, 1990, **144** 86
199. F Remacle, M Munster, V B Pavlov-Verevkin, M Desouter-Lecomte *Phys. Lett.*, 1990, **145** 265
200. V G Zelevinskii, V V Sokolov *Fizika Atomnogo Yadra: Materialy 24 Zimnei Shkoly LIYaF* (Physics of the Atomic Nucleus: Material Presented at the 24th Winter School), Konstantinov Institute of Nuclear Physics, Leningrad, 1989, p. 3
201. G A Voth *J. Chem. Phys.*, 1988, **88** 5547
202. R D Gilbert, R N Porter *J. Chem. Phys.*, 1988, **89** 3057
203. Z Deng, J H Eberly *Phys. Rev. A*, 1986, **34** 2492
204. R S Burkey, C A Glosson, C D Cantrell *Phys. Rev. A*, 1989, **39** 2978
205. E S Medvedev, V I Osherov *Teoriya Bezyzluchatel'nykh Perekhodov v Mnogoatomnykh Molekulakh* (Theory of Nonradiative Transitions in Multiatomic Molecules), Nauka, Moscow, 1983
206. W Weisskopf, E Wigner *Z. Phys.*, 1930, **63** 54
207. M Bixon, J Jortner, Y Dothan *Mol. Phys.*, 1969, **17** 109
208. W P Reinhardt, C Duneczky *J. Chem. Soc., Faraday Trans. 2*, 1988, **84** 1511

Translated from *Uspekhi Khimii* **61** 29–47 (1992) U.D.C. 541.127.1

The dynamic effects of the solvent in electron transfer reactions

L D Zusman
Institute of Inorganic Chemistry, Siberian Division of the Russian Academy of Sciences, Novosibirsk

ABSTRACT. The theories of electron transfer reactions in polar solvents, which describe the dynamic effects of the solvent manifested in these reactions, are examined. The theoretical and the available experimental literature data for these effects are compared.

The bibliography includes 85 references.

Contents

I. Introduction 15
II. Theories of electron transfer reactions based on the structureless dielectric approximation 15
III. Conclusion 23

I. Introduction

The mechanism of the elementary step in an electron transfer reaction in the liquid phases is as follows. There are two electronic states corresponding to the location of the electron on the electron donor or acceptor. The energies of these electronic states depend on the polarisation of the solvent and the intramolecular degrees of freedom of the donor and the acceptor. The thermal fluctuations in the polarisation of the medium and in the intramolecular degrees of freedom of the reactants lead to the modulation of the energies of the electronic states and sometimes the energy levels intersect. At this instant the electron tunnels from the donor to the acceptor, after which the polarisation of the medium and the intramolecular degrees of freedom of reactants relax to the new equilibrium position.

The theory of the elementary step in electron transfer reactions originated from the classical study by Marcus,[1] who was able to obtain an expression for the free energy of activation for the reaction. This energy is equal to the free energy which the medium and the intramolecular degrees of freedom of the donor and the acceptor must receive in order to attain the point of intersection of the energy levels of the electron. However, Marcus[1] was unable to calculate the pre-exponential factor in the expression for the reaction rate constant. The first calculation of this factor was achieved[2,3] on the basis of the quantum-mechanical perturbation theory using Fermi's famous "golden rule".[4] Within the framework of this theory, the pre-exponential factor in the expression for the rate constant proved to be proportional to the square of the resonance integral characterising the degree of overlap of the donor and acceptor orbitals. If the resonance integral is sufficiently large or the dynamics of the medium sufficiently slow, the perturbation theory ceases to be applicable and it is necessary to set up a theory going beyond the framework of this approximation.

Such a transition to the region of strong interaction was achieved in studies[5–10] where it was shown that, for a sufficiently large resonance integral, the rate of reaction is controlled by the dynamics of the polarisation of the solvent and, in the case of Debye solvents, is proportional to the frequency of the longitudinal relaxation of the solvent polarisation ν_L. This effect of the proportionality of the reaction rate constant to the frequency ν_L has been called the "dynamic effect of the solvent". It was first confirmed experimentally in studies[11–24] where a linear correlation was demonstrated between ν_L in a series of Debye solvents and the rate constant for electron transfer between the reactants dissolved in these solvents. Arguments have been adduced[25] in support of the fact that the dynamic effect of the solvent is manifested in the electron exchange reaction between benzonitrile and its radical-anion in a series of Debye solvents.[26] A similar conclusion has been reached[27] concerning the electron transfer reaction between anthracene and its radical-anion in a mixture of two Debye solvents with different proportions of the latter.[28] The inverse proportionality of the rate constant for electron transfer to the solvent viscosity, predicted by the theory,[5–10] has been confirmed.[29,30]

The dynamic effects of the solvent are observed not only in Debye solvents, having one Debye relaxation time of the polarisation of the medium, but also in solvents of the type of alcohols, which have two and more polarisation relaxation times.[15,17,20,21,31–35] The theories of electron transfer in such solvents will be examined in the present review together with those of the dynamic effect of the solvent in simpler solvents of the Debye type.

A large group of solvents of the type of glycerol have a continuous distribution of relaxation times of the Cole–Davidson type. The dynamic effects of the solvent in such media have a number of characteristic features distinguishing them from the effects in Debye solvents and also in alcohols. The theories of electron transfer in solvents of the glycerol type will also be examined in the present review.

The dynamic effects of the solvent are not limited to the influence of the reorientation relaxation of the solvent, many effects being associated with the translational motion of the solvent dipoles. These questions will be likewise examined in the present review.

II. Theories of electron transfer reactions based on the structureless dielectric approximation

The electron transfer reactions in a polar medium can be described as transitions between two electronic states at the instant when the energy levels of these states intersect under the influence of thermal fluctuations of the medium. It has been shown[39] that the difference between the energies of these states is

$$-\delta H(t)=H_2(t)-H_1(t)=E_0-E(t), \quad (1)$$

where $H_1(t)$ and $H_2(t)$ are the energies of the first and second electronic states fluctuating in a period t,

$$E(t)=-\int \Delta\mathbf{D}(\mathbf{r})\delta\mathbf{P}(\mathbf{r},t)d\mathbf{r}, \quad (2)$$

where $\Delta\mathbf{D}(\mathbf{r}) = \mathbf{D}_2(\mathbf{r}) - \mathbf{D}_1(\mathbf{r})$ is the difference between the electrostatic inductions of the first and second states, and

$$\delta\mathbf{P}(\mathbf{r},\ t)=\mathbf{P}(\mathbf{r},\ t)-\mathbf{P}_1(\mathbf{r}), \quad (3)$$

where $\mathbf{P}(\mathbf{r},\ t)$ is the polarisation of the solvent and $\mathbf{P}_1(\mathbf{r})$ the equilibrium polarisation of the solvent in the first electronic state;

$$E_0=J_2-J_1+E_r, \quad (4)$$

where J_1 and J_2 are the free energies of the first and second states and E_r is the solvent reorganisation energy:

$$E_r=\frac{c_0}{8\pi}\int \Delta\mathbf{D}(\mathbf{r})^2 d\mathbf{r}. \quad (5)$$

Here c_0 is the familiar Pekarov multiplier:

$$c_0=\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_S},$$

and ε_∞ and ε_S are the high-frequency and static dielectric constants respectively.

It has also been shown[39] that $E(t)$ fluctuates in conformity with a Gaussian random process. All the properties of Gaussian processes are known to be expressed in terms of a binary correlation function of a random variable. By virtue of the fluctuation-dissipative theorem, in the given case this correlation function is expressed as follows in terms of the complex dielectric constant of the solvents $\varepsilon(\mathbf{q}, \omega)$ at a frequency ω and for a wave vector $\mathbf{q}$:

$$K(\tau)=\langle E(\tau)E(0)\rangle=\frac{kT}{32\pi^5}\int |\Delta\mathbf{D}_q|^2\frac{\varepsilon''(\mathbf{q},\omega)}{\omega|\varepsilon(\mathbf{q},\omega)|^2}$$

$$\exp(-i\omega\tau)d\mathbf{q}\,d\omega, \quad (6)$$

where k is the Boltzmann constant and T the absolute temperature. The angular brackets in Eqn. (6) denote averaging with respect to the random fluctuations in the polarisation of the medium and

$$\Delta\mathbf{D}_q=\int \Delta\mathbf{D}(\mathbf{r})\exp(-\mathbf{qr})d\mathbf{r} \quad (7)$$

is the spatial Fourier transform of the difference between the inductions $\Delta\mathbf{D}(\mathbf{r})$.

Eqns. (1) and (6) are the initial expressions for the construction of the theory of electron transfer in a polar solvent.

1. Theories of electron transfer reactions in solvents with one Debye relaxation time of the polarisation of the medium

We shall consider the simplest case where the solvent in which the reaction takes place is of the Debye type, i.e. its complex dielectric constant assumes the form

$$\varepsilon(\omega)=\varepsilon_\infty+\frac{\varepsilon_S-\varepsilon_\infty}{1-i\omega\tau_D}. \quad (8)$$

On substituting Eqn. (8) in Eqn. (6), we find that the correlation function of the fluctuations of the electronic energy levels assumes the simplest form

$$K(\tau) = 2kTE_r\exp(-\nu_L|\tau|), \quad (9)$$

where $\nu_L = (E_S/E_\infty)(1/\tau_D)$ is the frequency of the longitudinal relaxation of the solvent polarisation, describing the relaxation of the medium under the conditions of a constant charge polarising it.

It has been shown[5,6] that, when the correlation function of the fluctuations of the energy levels of the electron has the form of Eqn. (9), then motion along the coordinate $E(t)$, which in the given instance is the reaction coordinate, has the character of diffusion with two parabolic terms $U_1(E)$ and $U_2(E)$ corresponding to the first and second electronic states:

$$U_1(E) = J_1 + \frac{E^2}{4E_r}, \quad U_2(E) = J_2 + \frac{(E-2E_r)^2}{4E_r}. \quad (10)$$

The transitions between these electronic terms are described by the following system of kinetic equations for the partial populations $\rho_1(E, t)$ and $\rho_2(E, t)$:[5,6]

$$\dot{\rho}_1(E,t)=-\frac{2\pi V^2}{\hbar}\delta(E-E_0)[\rho_1(E,t)-\rho_2(E,t)]+$$
$$+\nu_L\left[1+E\frac{\partial}{\partial E}+\Delta^2\frac{\partial^2}{\partial E^2}\right]\rho_1(E,t), \quad (11)$$
$$\rho_2(E,t)=\frac{2\pi V^2}{\hbar}\delta(E-E_0)[\rho_1(E,t)-\rho_2(E,t)]+$$
$$+\nu_L\left[1+(E-2E_r)\frac{\partial}{\partial(E-2E_r)}+\Delta^2\frac{\partial^2}{\partial(E-2E_r)^2}\right]\rho_2,$$

where $\Delta^2 = 2kTE_r$.

The partial populations $\rho_1(E, t)$ and $\rho_2(E, t)$ have the physical significance of the probabilities of finding an electron in the first or second electronic state respectively when the reaction coordinate assumes a value E. The first term on the right-hand sides of the equations describes the tunnelling of the electron from the donor to the acceptor at the point of intersection of the electronic terms E_0. The rate of such tunnelling is

$$K(E)=\frac{2\pi V^2}{\hbar}\delta(E-E_0), \quad (12)$$

where V is the resonance integral between the electron donor and acceptor, $\delta(E - E_0)$ the Dirac delta-function, and $\hbar$ the Planck constant. The second terms on the right-hand sides of Eqns. (11) describe diffusion in terms of the potentials $U_1(E)$ and $U_2(E)$ for the diffusion coefficient $\Delta^2\nu_L$.

A general solution of Eqns. (11) has been found[5,6] by the method of Green's functions and it has been shown that, in the limit of high activation energies for the reaction, $E_{a1}/kT \gg 1$ and $E_{a2}/kT \gg 1$ and that, for sufficiently long solvation times $t \gg \nu_L^{-1}$, the kinetics of the transitions are exponential as a function of time. It is possible to introduce the rates of the forward (W_{12}) and reverse (W_{21}) transitions respectively, for which the following expressions have been obtained:[5,6]

$$W_{12}=\frac{W_{12}^{NA}}{1+W_{12}^{NA}/W_{12}^{D}}$$

$$W_{21}=\frac{W_{21}^{NA}}{1+W_{12}^{NA}/W_{12}^{D}}, \quad (13)$$

where W_{12}^{NA} is the rate of the forward non-adiabatic electron transfer reaction, W_{21}^{NA} the rate of the reverse non-adiabatic electron transfer reaction, and W_{12}^{D} the rate of the forward reaction determined by diffusion along the electronic term consisting of two portions of diabatic terms (Fig. 1). W_{12}^{D} is identical with the familiar solution of the Kramers problem[40] concerning the diffusional overcoming of a sharp barrier, for which the following expression has been obtained:[5,6]

$$W_{12}^{D} = \nu_L \frac{|E_0||E_0 - 2E_r|}{|E_0| + |E_0 - 2E_r|} \frac{1}{(2\pi\Delta^2)^{1/2}} \exp\left(-\frac{E_0^2}{4E_r kT}\right). \qquad (14)$$

W_{12}^{NA} and W_{21}^{NA} are defined by the usual expressions of the Levich–Dogonadze–Kuznetsov theory:[2,3]

$$W_{12}^{NA} = \frac{\sqrt{2\pi}}{\hbar\Delta} V^2 \exp\left(-\frac{E_0^2}{4E_r kT}\right),$$
$$W_{12}^{NA} = \frac{\sqrt{2\pi}}{\hbar\Delta} V^2 \exp\left[-\frac{E_0 - 2E_r)^2}{4E_r kT}\right]. \qquad (15)$$

It is seen from Eqn. (13) that, if the rate of the non-adiabatic reaction is sufficiently low ($W_{12}^{NA} \ll W_{12}^{D}$), then the electron tunnelling stage is rate-limiting and

$$W_{12} = W_{12}^{NA},$$
$$W_{21} = W_{21}^{NA}. \qquad (16)$$

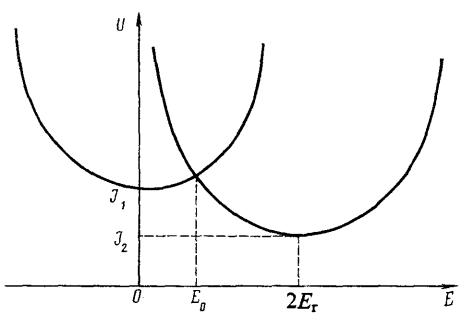


Figure 1. Electronic terms: J_1 = free energy of the first electronic state; J_2 = free energy of the second electronic state; E_0 = point of intersection of the electronic terms; E_r = energy of the reorganisation of the solvent.

On the other hand, if the tunnelling stage is rapid, i.e. $W_{12}^{NA} \gg W_{12}^{D}$, then diffusion along the electronic term is rate-limiting and

$$W_{12} = W_{12}^{D},$$
$$W_{21} = \frac{W_{21}^{NA}}{W_{12}^{NA}} W_{12}^{D} = \exp\left(\frac{J_2 - J_1}{kT}\right) W_{12}^{D}. \qquad (17)$$

As can be seen from Eqn. (14), in this case the rate of reaction is proportional to the frequency of the longitudinal relaxation of the solvent polarisation ν_L. This prediction of the theory has been confirmed experimentally in a number of studies.[11–24]

Eqn. (14) has been revised by the present author,[7] who obtained a somewhat different expression for W_{12}^{D}:

$$W_{12}^{D} = \frac{\nu_L}{\pi} \sqrt{\frac{E_r}{\pi kT}} \sin\left(\frac{\pi E_0}{2E_r}\right) \exp\left(-\frac{E_0^2}{4E_r kT}\right). \qquad (18)$$

If the reaction proceeds in the inverted regime $\Delta J > E_r$, where $\Delta J = J_2 - J_1$ is the driving force of the reaction, then, as shown by Gennett et al.,[41] not only the rate of the diffusional overcoming of the barrier W_{12}^{D} but also the rates of the non-adiabatic reactions W_{12}^{NA} and W_{21}^{NA} depend on ν_L for not very low values of the latter. In this case Eqns. (15) for W_{12}^{NA} and W_{21}^{NA} cease to be applicable and more complex expressions must be used for them.[41] However, with decrease in ν_L, even in the inverted regime, the validity of Eqns. (15) is restored starting from a certain instant and the rate of reaction depends on the solvent dynamics only in the limit where diffusion along the electronic term is rate-limiting.

Eqns. (13) are applicable for not unduly high values of the resonance integral V. The inequalities

$$V \ll kT, \qquad (19)$$

$$\frac{2\pi V^2}{kT\hbar\omega_L}\left(\frac{\pi kT}{E_p}\right)^{1/2} \ll 1, \qquad (20)$$

where ω_L is the frequency characterising the rate of movement of the electron-medium system along the reaction coordinate E over the length of the free path, serve as a criterion of their applicability. The following relation has been obtained[42] for ω_L:

$$\omega_L^2 = \left(\frac{2\varepsilon_S + \varepsilon_\infty}{3\varepsilon_\infty g}\right)\omega_f^2, \qquad (21)$$

where ω_f is the average thermal rate of free rotation of the solvent dipoles[43] and g is the Kirkwood factor.[43]

On the other hand, if the inequality (20) breaks down and the Landau–Zener adiabaticity parameter

$$k_{el} = \frac{\pi V^2}{kT\hbar\omega_L}\left(\frac{\pi kT}{E_r}\right)^{1/2}$$

becomes sufficiently large, i.e. $k_{el} \gg 1$, then instead of Eqn. (13) it is necessary to employ the following formulae:[42]

$$W_{12} = \frac{W_{12}^{WA}}{1 + W_{12}^{WA}/W_{12}^{D}},$$
$$W_{21} = \frac{W_{21}^{WA}}{1 + W_{12}^{WA}/W_{12}^{D}}, \qquad (22)$$

where

$$W_{12}^{WA} = \frac{\omega_L}{2\pi}\exp(-E_0^2/4E_r kT),$$
$$W_{12}^{WA} = \frac{\omega_L}{2\pi}\exp\left[\left(-\frac{(E_0 - 2E_r)^2}{4E_r kT}\right]\right. \qquad (23)$$

Eqns. (23) express none other than the rates of reaction within the framework of the transition state theory. Thus Eqns. (22) imply that the reaction proceeds in two stages. Initially the system reaches the top of the barrier by diffusion and then moves dynamically in the immediate vicinity of the top of the barrier at a certain thermal velocity proportional to the frequency ω_L. Throughout this time, the system is on the lower adiabatic electronic term, which is constructed in the usual way from the diabatic terms defined by Eqn. (10).

Using the method of molecular dynamics, the electron transfer reaction has been modelled numerically in a model solvent which is typical of a series of polar aprotic solvents being investigated experimentally at the present time. It was shown that Eqns. (22) agree better than Eqn. (13) with the results of numerical modelling. This apparently means that the inequality (20) breaks down in the model systems. Indeed, substitution of the parameters used in the above study[44] shows that the Landau–Zener parameter k_{el} is large in these systems.

Formulae (13) and (22) were obtained for condition (19). This condition means that the barrier, which the system overcomes by moving along the reaction coordinate, is nearly triangular. If the inequality (19) is reversed, i.e.

$$V \gg kT, \tag{24}$$

then the barrier overcome becomes nearly parabolic and the expression for the rates of reaction assume the following form:[6]

$$W_{12} \frac{\nu_L}{4\pi} \left(\frac{2E_r}{V}\right)^{1/2} \left(\frac{|E_0||E_o - 2E_r|}{E_r^2}\right)^{3/4} \exp\left\{ -\left[\frac{(E_0)^2}{4E_r} - V\left(\frac{|E_0||E_o - 2E_r|}{E_r^2}\right)^{1/2}\right] \frac{1}{kT} \right\},$$
$$W_{21} = W_{12} \exp \frac{\Delta J}{kT}. \tag{25}$$

It also follows from Eqn. (25) that the rates of the forward and reverse reactions must be proportional to ν_L, i.e. in this limit too the theory[6] predicts the dynamic effect of the solvent. We may draw attention to the fact that, subject to condition (24), the free energy of activation for the reaction is not equal to the Marcus value $E_{a1} = E_0^2/4E_r$ but is smaller than the latter by the amount $V(|E_0||E_0 - 2E_r|/E_r^2)^{1/2}$. This quantity is exactly equal to the splitting of the adiabatic electronic terms at the point of intersection of the diabatic terms E_0.

Eqns. (13), (22), and (25) were derived on the assumption of high activation energies. The non-activated ($E_{a1} = 0$, $E_{a2} = 0$) or low-barrier ($E_{a1}/kT \ll 1$, $E_{a2}/kT \ll 1$) electron transfer reactions are also of considerable interest. The solutions of Eqns. (11) for such processes are non-exponential as a function of time. Strictly speaking, it is therefore impossible to introduce time-independent rates of reaction. Nevertheless, numerical analysis of the solution of Eqns. (11) carried out by Rips and Jortner[45] shows that in the range $\nu_L t < 4$, the kinetics of the transitions are nearly exponential and one can introduce the rates of the forward and reverse reactions W_{12} and W_{21} as an approximation.

It has been shown[46] that in both the normal ($\Delta J < E_r$) and the inverted ($\Delta J > E_r$) regimes the rate of reaction can be controlled by the solvent dynamics, whereupon it is proportional to ν_L. This agrees well qualitatively with the results of experiments[31–35] in which a linear correlation was found for non-activated intramolecular electron transfer reactions between the rate of reaction and the lowest solvent relaxation frequency. However, it is noteworthy that the experiments[31–35] were carried out in alcohols, which are not Debye solvents. On the other hand, the prediction[46] that the rate of reaction is proportional to the lowest solvent relaxation frequency was based on an erroneous study[47] in which an attempt was made to extend the present author's results[5,6] to non-Debye solvents. The conclusion[46,48] that the theory and experiment[31–35] agree is therefore controversial. We shall return to the discussion of these experiments below.

The theories examined above were based on the approximation of a linear medium first introduced by Ovchinnikov and Ovchinnikova.[49] The present author[10] was able to extend the treatment outside the framework of this approximation having shown that in the more general situation the rate of reaction may be proportional to ν_L.

All the theories of electron transfer examined hitherto fail to take into account the reorganisation of the intramolecular degrees of freedom of the reactants and reaction products. The first attempt to take into account the reorganisation of the intramolecular degrees of freedom of reactants and products and to estimate its influence on the dynamic effect of the solvent in the rate of reaction was undertaken by Ovchinnikova.[50] As a result of the allowance for the reorganisation of the intramolecular degrees of freedom, electronic transitions are seen to occur not only at the point of intersection of the electronic terms E_0 but also over the entire range of values of the reaction coordinate E. Eqns. (11) were extended by Ovchinnikova[50] as follows:

$$\dot{\rho}_1(E,t) = -K_{12}(E)\rho_1(E,t) + K_{21}(E)\rho_2(E,t) + \nu_L\left[1 + E\frac{\partial}{\partial E} + \Delta^2\frac{\partial^2}{\partial E^2}\right]\rho_1(E,t),$$
$$\dot{\rho}_2(E,t) = -K_{21}(E)\rho_2(E,t) + K_{12}(E)\rho_1(E,t) + \nu_L\left[1 + (E-2E_r)\frac{\partial}{\partial(E-2E_r)} + \Delta^2\frac{\partial^2}{\partial(E-2E_r)^2}\right]\rho_2, \tag{26}$$

where the following expressions were used for $K_{12}(E)$ and $K_{21}(E)$:

$$K_{12}(E) = \frac{\omega_Q}{2\pi}\exp\left[-\frac{(E_0 - E + E_i)^2}{4E_i kT}\right],$$
$$K_{21}(E) = \frac{\omega_Q}{2\pi}\exp\left[-\frac{(E_0 - E - E_i)^2}{4E_i kT}\right]. \tag{27}$$

Here $K_{12}(E)$ is the characteristic frequency of intramolecular vibrations and E_i is the energy of the reorganisation of the intramolecular degrees of freedom. Eqns. (27) were obtained on the assumption that the intramolecular vibrations are classical, i.e. subject to the condition $kT \gg h\omega_Q$. However, Ovchinnikova[50] was not able to solve Eqn. (26). This was done later.[7] Nevertheless, Ovchinnikova[50] reached the generally correct conclusion that intramolecular vibrations hinder the observation of the dynamic effect of the solvent in the rate of electron transfer.

The influence of intramolecular degrees of freedom of the reactants on the rate of electron transfer has also been considered.[51,52] In the theory of Marcus and co-workers,[51,52] the intramolecular vibrations were assumed to be classical ($kT \gg \hbar\omega_Q$) and the theory was based, as in Ovchinnikova's study,[50] on

Eqn. (28), where, however, no account was taken of the reverse reaction. The authors used Eqn. (27) for $K_{12}(E)$ and assumed that the partial rate of the reverse reaction $K_{21}(E)$ was identically equal to zero. They postulated that the reverse reaction may be disregarded for $\Delta J \gg kT$. Generally speaking, this is correct for the reaction as a whole, but the condition $K_{21}(E) \equiv 0$ constitutes a much stronger limitation than $\Delta J \gg kT$. It implies that the reverse reaction is neglected for any value of the coordinate of the medium E.

On the other hand, analysis of the simpler Eqns. (11) shows that $K_{21}(E) \neq 0$ contributes not only to the rate of the reverse reaction W_{21} but also to that of the forward reaction W_{12}. This contribution is fully comparable to the contribution of the forward partial reactions specified by the rate $K_{12}(E)$. This contribution to W_{12} does not vanish in the limit where $\Delta J \gg kT$. Therefore the hypothesis that $K_{21}(E) \equiv 0$ makes the treatment inconsistent with the physics of the process and the formulae presented by Sumi and Marcus[51] for the case where $E_{a1} \gg kT$ hardly describe the reaction adequately or even approximately. As regards the non-activated reaction with $E_{a1} \ll kT$, the conclusion[51,52] that on reorganisation of the intramolecular degrees of freedom and in the limit $\nu_L \to 0$ the reaction kinetics become highly non-exponential while the average reaction time τ_a may be much shorter than ν_L^{-1} and in the limit $\nu_L \to 0$ may cease to depend on ν_L is believeable. Indeed, subject to the condition $E_{a1} \ll kT$, the analysis of Eqns. (11) carried out by Rips and Jortner[46] shows that the hypothesis that $K_{21}(E) \equiv 0$ in the limit where $\Delta J/kT \gg 1$ becomes more acceptable. The prediction[52] that, when account is taken of the intramolecular degrees of freedom of the reactants, the rate of reaction at $\nu_L \to 0$ should be proportional to ν_L^{α}, where α may depend on the ratio E_i/E_r and varies in the range $0 < \alpha < 1$, is also of interest.

The intramolecular electron transfer in dimethylaminobenzonitrile and in diethylaminobenzonitrile has been investigated[53] in a series of solvents. In conformity with the authors' predictions,[51,52] it was observed that the kinetics of the reactions involving these compounds are markedly non-exponential. It has also been shown[53] that the average reaction time τ_α is shorter for these compounds than the longitudinal relaxation time of the solvent ν_L^{-1}. These data confirm the theory developed by Marcus and co-workers.[51,52]

The conclusion that, when account is taken of the intramolecular degrees of freedom of the reactants the rate of reaction as $\nu_L \to 0$ should be proportional to ν_L^{α} was invoked[52] to account for the observed[54] proportionality between the rate of reaction and ν_L^{β}. However, the reactions investigated by McGuire and McLendon[54] were carried in glycerol—a solvent of the non-Debye type. It is therefore not clear at present what lies behind the proportionality of the rate of reaction to ν_L^{β}—the presence of intramolecular degrees of freedom of the reactants or the nature of the solvent (its not being a Debye solvent). Below, we shall return to the discussion of the results of McGuire and McLendon.[54]

The theories considered above describe the reorganisation of the intramolecular degrees of freedom on the assumption that $kT \gg \hbar\omega_Q$. A theory has been developed[55] for electron transfer where account is taken of the reorganisation of the intramolecular degrees of freedom, but, in contrast to Marcus and co-workers,[50–52] it is assumed that the intramolecular vibrations are quantised, i.e. subject to the conditions $kT \ll \hbar\omega_Q$. The author[55] began his treatment with the kinetic equations (26) where, in contrast to Eqn. (27), the following expressions were used for $K_{12}(E)$ and $K_{21}(E)$:

$$K_{12}(E) = \frac{2\pi V^2}{\hbar} \sum_{n=-\infty}^{\infty} \lambda_n \delta(E_0 + n\hbar\omega_Q - E),$$
$$K_{21}(E) = \frac{2\pi V^2}{\hbar} \sum_{n=-\infty}^{\infty} \lambda_n \delta(E_0 - n\hbar\omega_Q - E), \qquad (28)$$

where λ_n is the Franck–Condon factor for the intramolecular oscillator.[56] Eqns. (28) imply that the transitions do not occur solely at the point of intersection of the E_0 terms but also at the points $E_0 + n\hbar\omega_Q$ and $E_0 - n\hbar\omega_Q$ and are accompanied by the emission or absorption of n quanta.

With the aid of a method analogous to that used by the present author,[5,6] Helman[55] found a solution to Eqn. (26) with the coefficients defined by Eqn. (28) and obtained expressions for the reaction rates W_{12} and W_{21}, generalising Eqns. (13). Thus in the limit corresponding to high activation energies, $E_{a1}/kT \gg 1$ and $E_{a2}/kT \gg 1$, Helman[55] obtained expressions for W_{12} and W_{21} identical with Eqns. (13), where

$$W_{12}^{NA} = \frac{\sqrt{2\pi}}{\hbar\Delta} V^2 \lambda_0 \exp\left(-\frac{E_0^2}{4E_r kT}\right),$$
$$W_{21}^{NA} = \frac{\sqrt{2\pi}}{\hbar\Delta} V^2 \lambda_0 \exp\left[-\frac{(E_0 - 2E_r)^2}{4E_r kT}\right]. \qquad (29)$$

It is seen from Eqns. (13) and (29) that, for the observation of the dynamic effect of the solvent, the following criterion must be satisfied:

$$\frac{2\pi V^2}{\hbar}\lambda_0 \gg \lambda_L \frac{|E_0|\,|E_0 - 2E_r|}{|E_0| + |E_0 - 2E_r|}. \qquad (30)$$

Since $\lambda_0 < 1$, the observation of the dynamic effect of the solvent in the presence of intramolecular degrees of freedom of the reactants requires larger values of the resonance integral V than in the case where the degree of reorganisation of these degrees of freedom is small or is altogether absent. The result of Helman's study[55] was reproduced by Onuchic et al.[57] Results similar to Helman's[55] were also obtained subsequently in later studies.[58,59] The solution found by Helman[55] was refined by the present author.[7]

All the theories examined hitherto describe reactions occurring under homogeneous conditions. The theories of reactions occurring on the electrode are constructed similarly. The present author[60] began with Eqn. (26), where, in contrast to Eqn. (27), the partial rates $K_{12}(E)$ and $K_{21}(E)$ are defined by the following expressions:

$$K_{12}(E) \int \frac{\rho(\varepsilon)}{n_e} f(\varepsilon) K_{12}(\varepsilon, E)\, d\varepsilon,$$
$$K_{21}(E) = \int \frac{\rho(\varepsilon)}{n_e} [1 - f(\varepsilon)] K_{21}(\varepsilon, E)\, d\varepsilon. \qquad (31)$$

Here $f(\varepsilon)$ is the Fermi distribution of electrons in the electrode, $K_{12}(\varepsilon, E)$ and $K_{21}(\varepsilon, E)$ are the partial rate of the forward and reverse electron transfer from the energy level ε in the electrode to the energy level in the reactant, and $\rho(\varepsilon)$ is the density of electronic

states in the electrode. The general expressions quoted by the present author[7,61] are valid for the rates $K_{12}(\varepsilon, E)$ and $K_{21}(\varepsilon, E)$. In view of the very cumbersome nature of these formulae, we do not quote them here.

The kinetic equations (26), with the partial rates $K_{12}(E)$ and $K_{21}(E)$ expressed in the form of Eqns. (31), were solved[60] with the aid of the method used previously;[7] the following formulae were obtained for the rates of reaction W_{12} and W_{21}:

$$W_{12} = \frac{\overline{K}_{12}}{1 + \overline{K}_{12}/W_{12}^{eD}}, \qquad W_{21} = \frac{\overline{K}_{21}}{1 + \overline{K}_{12}/W_{12}^{eD}}, \tag{32}$$

where

$$\overline{K}_{12} = \frac{1}{\sqrt{2\pi}\Delta}\int K_{12}(E)\exp\left(-\frac{E^2}{2\Delta^2}\right)dE, \qquad \overline{K}_{12} = \frac{1}{\sqrt{2\pi}\Delta}\int K_{21}(E)\exp\left(-\frac{E^2}{2\Delta^2}\right)dE, \tag{33}$$

$$W_{12}^{eD} = \frac{\nu_L}{\pi}\left(\frac{E_r}{\pi kT}\right)^{1/2}\sin\left(\frac{\pi E_0'}{2E_r}\right)\exp\left[-\frac{(E_0')^2}{4E_r kT}\right], \tag{34}$$

$$E_0' = e\xi - kT\ln(c_{z-1}/c_z) + E_r. \tag{35}$$

Here e is the electronic charge, Z and $Z-1$ are the charges on the reactant and the reaction product respectively, c_Z and c_{Z-1} are their concentrations, and ξ is the electrode overpotential. Eqns. (32) are analogous to Eqns. (13) describing homogeneous reactions.

Knowing Eqns. (32) for the reaction rates, it is possible to find the transient current of the reaction:[60]

$$i = i_0\left[1 - \exp\left(\frac{e\xi}{kT}\right)\right], \tag{36}$$

where

$$i_o = -\frac{ec_z}{2\kappa}\frac{\nu_L}{\pi}\left(\frac{E_r}{\pi kT}\right)^{1/2}\sin\left(\frac{\pi E_0'}{2E_r}\right)\exp\left[-\frac{(E_0')^2}{4E_r kT}\right]\times$$

$$\times\ln\left\{1 + \pi\left(\frac{\pi kT}{E_r}\right)^{1/2}\frac{\overline{K}_{12}^0}{\nu_L}\frac{\exp[(E_0')/4E_r kT]}{\sin(\pi E_0'/2E_r)}\right\}. \tag{37}$$

In deriving Eqn. (37), it was assumed that

$$\overline{K}_{12} = \exp(-2\kappa r)\,\overline{K}_{12}^0, \tag{38}$$

where the parameter κ^{-1} characterises the scale of the decay of the electronic resonance integral between the reactant and the electrode with distance from the electrode. Eqn. (38) is usually a satisfactory approximation.

It is evident from Eqns. (36) and (37) that, when the resonance integral is fairly small and the inequality

$$\overline{K}_{12}^0 \ll \frac{\nu_L}{\pi}\left(\frac{E_r}{\pi kT}\right)^{1/2}\sin\left(\frac{\pi E_0'}{2E_r}\right)\exp\left[-\frac{(E_0')^2}{4E_r kT}\right], \tag{39}$$

holds, then the second term in the logarithmic expression is small. Expanding the logarithm in series in terms of this small parameter, one can obtain

$$i_0 = -\frac{ec_z}{2\kappa}\overline{K}_{12}^0. \tag{40}$$

This agrees exactly with the results of the non-adiabatic Dogonadze–Kuznetsov theory.[62] On the other hand, if the resonance integral is fairly large or the solvent exhibits a fairly slow polarisation relaxation, i.e. the inequality

$$\overline{K}_{12}^0 \gg \frac{\nu_L}{\pi}\left(\frac{E_r}{\pi kT}\right)^{1/2}\sin\left(\frac{\pi E_0'}{2E_r}\right)\exp\left[-\frac{(E_0')2}{4E_r kT}\right], \tag{41}$$

which is the opposite of the inequality (39), holds, then the following result can be readily obtained from Eqn. (37):

$$i_o = -\frac{ec_z}{2\kappa}\frac{\nu_L}{\pi}\left(\frac{E_r}{\pi kT}\right)^{1/2}\sin\left(\frac{\pi E_0'}{2E_r}\right)\exp\left[-\frac{(E_0')^2}{4E_r kT}\right]\times$$

$$\times\ln\left\{\pi\left(\frac{\pi kT}{E_r}\right)^{1/2}\frac{\overline{K}_{12}^0}{\nu_L}\frac{\exp[(E_0')/4E_r kT]}{\sin(\pi E_0'/2E_r)}\right\}. \tag{42}$$

It follows from Eqn. (42) that, similarly to the processes occurring under homogeneous conditions, the reaction at the electrode subject to condition (41) is controlled by the solvent dynamics and its rate as well as the current are proportional to ν_L in this limit. This theoretical prediction has been confirmed experimentally.[13–15,18–23]

Eqns. (32)–(42) describe the kinetics of the reaction occurring in the region of the normal overpotentials ξ, i.e. subject to the condition $|e\xi| \ll E_r$. For the non-activated region, where $e\xi > -E_r$, and also in the region of anomalous overpotentials, where $e\xi \simeq -E_r$, an approach different from that used previously[7] is required.

Such an approach to the problem of electron transfer from the reactants to the electrode has been developed.[63] The authors began with Eqns. (26), where $K_{12}(E)$ was specified by Eqn. (31) and $K_{21}(E)$ was assumed to be identically equal to zero. They used the variational principle, with the aid of which they found expressions for the rate of reaction on the electrode in both normal and non-activated regions and also in the anomalous range of overpotentials. However, as already mentioned in discussing the studies of Marcus and co-workers,[51,52] the approximation $K_{21}(E) \equiv 0$ is incorrect in the normal region and the formulae of Morgan and Wolynes[63] therefore describe the reaction incorrectly in this case. For normal overpotentials, Eqns. (32)–(42) should be used. As mentioned in the discussion of homogeneous reactions, in the non-activated and anomalous regions, the approximation $K_{21}(E) \equiv 0$ becomes reasonable and the formulae obtained by the above workers[63] for these situations are more believable. The theory of Morgan and Wolynes[63] predicts that, in solvents with a fairly slow relaxation of the polarisation of the medium in the anomalous and non-activated ranges of overpotentials and also in the normal region, the reaction is controlled by the solvent dynamics and its rate is proportional to ν_L. The formulae of the above workers[63] supplement the present author's theory,[60] because they describe the reaction in other ranges of overpotentials.

Thus in both homogeneous and heterogeneous electron transfer reactions in Debye solvents with a fairly slow relaxation of the medium, the reaction begins to be controlled by the solvent

dynamics and the rate of reaction is proportional in this limit to ν_L. This conclusion is qualitatively consistent with the available experimental data.

2. Theories of electron transfer reactions in solvents with two (or more) relaxation times of the polarisation of the medium

The dielectric properties of many solvents of the type of alcohols, where the molecules are linked by a network of hydrogen bonds, are not described by the simple equation (8). The following relation is applicable to such solvents:[64]

$$\varepsilon(\omega)=\varepsilon_\infty+(\varepsilon_S-\varepsilon_\infty)\sum_{i=1}^{N} f_i(1-i\omega\tau_i)^{-1}, \tag{43}$$

where τ_i are quantities differing greatly in magnitude.

If Eqn. (43) is now substituted in Eqn. (6), the correlation function for the fluctuations of the electronic energy levels becomes

$$K(\tau) = 2kTE_\tau\left[\sum_{i=1}^{N}\delta_i\exp(-\nu_i|\tau|)\right], \tag{44}$$

where the correlation times ν_i^{-1} and the coefficients δ_i are expressed in some way in terms of f_i and τ_i. The coefficients δ_i satisfy the relation

$$\sum_{i=1}^{N}\delta_i=1. \tag{45}$$

A general theory of homogeneous electron transfer reaction, applicable to solvents with an arbitrary dielectric losses spectrum and therefore valid for any correlation function $K(\tau)$, has been constructed.[65] This theory is based on the summation of series in powers of V^2 by Padé's method of approximants. It has been shown that the kinetics of transitions with high reaction activation energies are exponential. The following general expressions have been obtained[65] for the rates W_{12} and W_{21}:

$$W_{12}=\frac{W_{12}^{NA}}{1+W_{12}^{NA}/W_{12}^{S}}, \qquad W_{21}=\frac{W_{21}^{NA}}{1+W_{12}^{NA}/W_{12}^{S}}, \tag{46}$$

where W_{12}^{NA} and W_{21}^{NA} are again defined by Eqns. (15) and it has been found that the rate W_{12}^{S} is given by

$$(W_{12}^{S})^{-1}=\int_0^\infty d\tau\left\{\frac{1}{[1-M^2(\tau)]^{1/2}}\exp\left[\frac{E_0^2}{\Delta^2}\frac{M(\tau)}{1+M(\tau)}\right]-1\right\}+$$
$$+\exp\left(\frac{\Delta J}{kT}\right)\int_0^\infty d\tau\left\{\left(\exp\left[\frac{(E_0-2E_\tau)}{\Delta^2}\frac{M(\tau)}{1+M(\tau)}\right]\right)\Big/\right.$$
$$\left.\Big/(1-M^2(\tau))^{1/2}-1\right\}, \tag{47}$$

where

$$M(\tau)=\frac{K(\tau)}{K(0)}. \tag{48}$$

Eqns. (46) extend Eqns. (13) to reactions occurring in media with an arbitrary dielectric constant $\varepsilon(q, \omega)$ and they are therefore applicable to electron transfer reactions in solvents where the correlation function $K(\tau)$ has an arbitrary form.

Eqns. (46) have also been obtained independently by Hynes[42] with the aid of the theory of stable states and Padá's method of approximants, used, however, in a somehwat different way than in the present author's study,[65] and by Sparpaglione and Mukamel,[66,67] while Fonseca[68] showed that Eqns. (46) are not restricted by the approximation involved in Padá's method of approximants but represent an exact solution for reactions in which correlation functions of type (44) play a significant role.

Eqns. (46) as well as Eqns. (13) are applicable only subject to conditions (19) and (20). On the other hand, if the Landau–Zener adiabaticity parameter k_{el} becomes fairly large, i.e. $k_{el} \gg 1$, then, as shown by Hynes,[42] it is essential to use the following expressions instead of Eqns. (46):

$$W_{12}=\frac{W_{12}^{WA}}{1+W_{12}^{WA}/W_{12}^{S}}, \qquad W_{21}=\frac{W_{21}^{WA}}{1+W_{12}^{WA}/W_{12}^{S}}, \tag{49}$$

where W_{12}^{WA} and W_{21}^{WA} are defined by Eqns. (23).

Eqns. (49) constitute an extension of Eqns. (22) to cases where the reactions take place in media with an arbitrary dielectric constant $\varepsilon(q, \omega)$. If all the correlation times ν_i^{-1} are of the same order of magnitude, only short times $|\tau| \ll \nu_i^{-1}$ contribute to the integral (47). Therefore, having expanded the correlation function in series in terms of the parameter $|\tau|$ and having substituted $K(\tau) = K(0) + K'(0)|\tau|$ in Eqn. (47) and then having evaluated this integral, we obtain finally[42,66]

$$(W_{12}^{S})^{-1}=-\frac{K(0)}{K'(0)}\left[\frac{1}{|E_0|}+\frac{1}{|E_0-2E_\tau|}\right]\sqrt{2\pi}\Delta\exp\left(\frac{E_0^2}{4E_\tau kT}\right). \tag{50}$$

The result represented by Eqn. (50) differs from Eqn. (14) only in the replacement of ν_L by $-K'(0)/K(0)$, i.e. for the case where all the correlation times have the same order of magnitude we can describe the reaction with the aid of an effective frequency of polarisation fluctuations:

$$\nu_{ef}=-\frac{K'(0)}{K(0)}. \tag{51}$$

Having substituted Eqn. (44) in Eqn. (51), we obtain a simple relation:

$$\nu_{ef}=\sum_{i=1}^{N}\nu_i\delta_i. \tag{52}$$

By virtue of the relation between ν_i, δ_i and f_i, τ_i, formula (52) can be rewritten in another form:

$$\nu_{ef}=\frac{\varepsilon_S}{\varepsilon_\infty}\sum_{i=1}^{N}f_i\tau_i^{-1}. \tag{53}$$

Eqn. (53) was first obtained by Hynes[42] for two relaxation times of the medium and was then extended to the case of N relaxation times.[69] Admittedly, in the latter study[69] it was claimed erroneously

that Eqns. (52) and (53) differ, although it can be shown that they are equivalent. Furthermore, one should note that Helman[69] obtained an expression for W_{12}^{S} somewhat different from Eqn. (50), which in our view is associated with two causes. Firstly, Helman[69] adopted initial postulates different from those used by Sparpaglione and Mukamel[66] and Hynes[42] and, secondly, he developed[69] an incorrect approximation for the evaluation of one of the final integrals.

Eqn. (52) for the case of two relaxation times has also been found by another method.[70] The results represented by Eqns. (46) and (49) have been obtained subject to condition (19). If the inequality (19) is reversed, then the rate of reaction assumes a form analogous to that defined by Eqn. (25) with the sole difference that ν_L has now been replaced by ν_{ef}.

As already mentioned, Eqns. (50)–(53) were derived on the assumption that all the correlation times ν_i^{-1} have the same order of magnitude. On the other hand, if one of the times $\nu_1^{-1} \gg \nu_2^{-1}, \ldots, \nu_N^{-1}$, then the situation is less clear. There exists only the theory of electron transfer in solvents with two markedly different relaxation times.[72] Furthermore, electron transfer in the case with several markedly different relaxation times for the solvent has been investigated by the numerical evaluation of integrals (47) in two studies.[73,74] Fonseca[68] also investigated electron transfer by numerical methods.

The theoretical and experimental data for electron exchange between metallocenes in a number of alcohols have been compared[73] on the basis of Eqns. (49) and (47). It was shown that these formulae account for a large part of the rate of electron transfer between metallocenes in alcohols.

As already mentioned, the present author[72] developed a theory of electron transfer in solvents with two markedly different relaxation times of the medium. The linear correlation observed[31–35] between the rate of reaction and the lowest relaxation frequency of the solvent was explained by this theory. This explanation of the experimental data[31–35] differs from that quoted for the same data in another study,[46] which was based on Helman's erroneous investigation.[47]

Eqns. (46) were derived on the assumption that the reaction proceeds under homogeneous conditions. Reactions occurring at an electrode in solvents of the type of alcohols have been studied in only one investigation,[75] where the relaxation of the solvent was modelled by two relaxation times. These results[75] are analogous to those of the present author.[72] The theory developed in the latter investigation[72] explained qualitatively the experimental data.[15,20,21]

3. Theories of electron transfer reactions in solvents with a continuous distribution of relaxation times of the polarisation of the medium

In many solvents of the type of glycerol, the dielectric properties cannot be described by either the simple Debye model [Eqn. (8)] or by the more complex Eqn. (43). In such solvents, there is a continuous distribution of the relaxation times of the polarisation and the Cole–Davidson equation is applicable to them:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{(\varepsilon_S - \varepsilon_\infty)}{(1 - i\omega\tau_0)^\beta}, \tag{54}$$

where τ_0 is the characteristic relaxation time and β is the Cole–Davidson parameter, which satisfies the inequality $0 < \beta \leqslant 1$.

The microscopic mechanism underlaying Eqn. (54) is at present obscure. There are two hypotheses concerning the nature of this relation. According to the first, the solvent is microscopically homogeneous and Eqn. (54) holds at each point in it. According to the second hypothesis, the solvent is microscopically inhomogeneous and Debye's model [Eqn. (8)] holds at each point in it but with a Debye time τ which varies randomly from point to point. Under these conditions, Eqn. (54) is applicable only on the macroscopic scale and is obtained by averaging Eqn. (8) over the distribution of the Debye times $g(\tau)$, which has the following form according to Bötcher and Bordewijk:[76]

$$g(\tau) = \begin{cases} \dfrac{\sin(\pi,\beta)}{\pi\tau}\left(\dfrac{\tau}{\tau_0 - \tau}\right)^\beta & (\tau < \tau_0), \\ 0 & (\tau > \tau_0). \end{cases} \tag{55}$$

The theory of electron transfer in glycerol type solvents has been constructed in accordance with two hypotheses concerning the nature of the relaxation of the polarisation of the medium. If the first hypothesis concerning the nature of Eqn. (54) is adopted as a basis, then electron transfer can be described within the framework of the formalism of Sparpaglione and Mukamel[66] and the reaction rates are defined by Eqns. (46), where $M(\tau)$ is found with the aid of Eqns. (48), (6), and (54). The integrals (47) have been evaluated with the aid of Eqn. (54) in a study[74] where the expression

$$W_{12}^{S} = \frac{\sqrt{2}\beta[8kTE_r]^{1/2-1/\beta}}{\Gamma(1/\beta - 1/2)\,[4\Gamma(\beta+1)\,\varepsilon_\infty/\varepsilon_S]^{1/\beta}} \times \\ \times [|E_0|^{1-2/\beta} + |E_0 - 2E_r|^{1-2/\beta}]^{-1}\tau_0^{-1}\exp\left(-\frac{E_0^2}{4E_r kT}\right), \tag{56}$$

where $\Gamma(x)$ is a gamma-function,[77] was obtained in the limit corresponding to high activation energies for the reaction.

The theory employing the second hypothesis concerning the nature of Eqn. (54) as a basis has been developed by Rips and Jortner.[78,79] They showed that the reaction kinetics are described by the following formula:

$$n_1(t) = \int_0^\infty \exp[-W_{12}(\tau)]\,g(\tau)\,d\tau, \tag{57}$$

where $n_1(t)$ is the population of the first electronic state and $W_{12}(\tau)$ is defined by Eqn. (13). In the derivation of Eqn. (57), it was assumed that the reverse reaction may be neglected.

On the basis of Eqn. (57), Rips and Jortner[78,79] predicted that, in the reaction regime controlled by the solvent dynamics, the rate of reaction is given by

$$W^{DC} = W_{12}^{NA}\left(\frac{\varepsilon_S}{\varepsilon_\infty}\frac{\hbar E_r}{4\pi V^2\tau_0}\right)^\beta. \tag{58}$$

Two conclusions follow from Eqn. (58). Firstly, the rate of reaction depends on the characteristic relaxation time of the medium τ_0 less than in the case of Debye solvents. Secondly, the rate of reaction in this limit is proportional to $V^{2(1-\beta)}$ when account is taken of Eqn. (15).

The available experimental data on intramolecular electron transfer[80] support the theory of Rips and Jortner[78,79] rather than that of Sparpaglione and Mukamel.[74] Indeed, the observed[80] dependence of the rate of reaction on τ_0 is described satisfactorily by

Eqn. (58) when τ_0 is varied within the limits of two orders of magnitude. The dependence of the rate of reaction on V, described by Eqn. (58), also agrees well with experiment.

As already mentioned, McGuire and McLendon[54] likewise observed the proportionality of the rate of reaction to $\tau_0^{-\beta}$. The reaction which they investigated[54] occurred in glycerol—a solvent of the Cole–Davidson type. Rips and Jortner[78,79] therefore explained this proportionality by Eqn. (58). However, since the proportionality of the rate of reaction to $\tau_0^{-\beta}$ was deduced[54] on the basis of indirect considerations, the reliability of the interpretation of these results[54] within the framework of the theory of Rips and Jortner[78,79] is at present unclear.

4. The dynamic effect of the diffusion polarisation of the solvent in the rate of electron transfer

The theories of electron transfer reactions examined above took into account only the reorientation relaxation of the polarisation of the solvent. On the other hand, in certain solvents the rate of relaxation of the polarisation via the self-diffusion of the dipoles of the medium may be comparable to the rate of relaxation of the polarisation associated with the reorientation of the solvent molecules. The theory of electron transfer taking into account both pathways to the relaxation of the solvent polarisation has been developed.[81] It was shown that the rate of reaction is expressed by the formula

$$W_{12} = \frac{W_{12}^{NA}}{1+W_{12}^{NA}/W_{12}^{DII}}, \tag{59}$$

where

$$W^{DII} = \tilde{\nu}_{ef}\frac{|E_0||E_0-2E_r|}{|E_0|+|E_0-2E_r|}\frac{1}{(2\pi\Delta^2)^{1/2}}\exp\left(-\frac{E_0^2}{4E_rkT}\right), \tag{60}$$

and

$$\tilde{\nu}_{ef} = \nu_L + \frac{\epsilon_S}{\epsilon_\infty}D\frac{c_0}{64\pi^4E_r}\int|\Delta D_q|^2q^2dq. \tag{61}$$

In Eqn. (61), D is the self-diffusion coefficient of the solvent molecules and ΔD_q is defined by Eqn. (7).

Eqn. (59) is applicable only for $V \ll kT$. Subject to the condition $V \gg kT$, a formula has been obtained[81] for the rate of reaction differing from Eqn. (25) only in the replacement of ν_L by $\tilde{\nu}_{ef}$. A formula for $\tilde{\nu}_{ef}$, convenient for making estimates, was also obtained in the above study:[81]

$$\tilde{\nu}_{ef} = \nu_L + \frac{\varepsilon_S}{\varepsilon_\infty}D\frac{2.048(R_2^3+R_1^3)R}{R(R_2+R_1)R_1^2R_2^2-2R_1^3R_2^3}. \tag{62}$$

It is valid for $R \geqslant R_1 + R_2$, where R_1 and R_2 are the radii of the reactants and R is the distance between them.

The estimates made in the above study[81] by Eqn. (62) show that in solvents such as methanol and nitrobenzene, where the diffusion coefficients of the solvent molecules are fairly large and the values of ν_L are fairly small, the contribution of the diffusion-dependent solvent polarisation to $\tilde{\nu}_{ef}$ may become dominant.

III. Conclusion

The dynamic effects of the solvent examined in this review have been described within the framework of the continuous model of a structureless dielectric. At the same time, if the dimensions of the reactants are comparable to those of the solvent molecules, the structureless dielectric approximation becomes poor and it is necessary to construct a theory of electron transfer on a basis which takes into account the molecular structure of the solvent models.

There exist at the present time two approaches to allowance for the molecular structure of the solvent in devising a theory of electron transfer. The first of these (phenomenological) is based on the fact that the relaxation time of the centre of gravity of the fluorescence spectrum of a polar molecule dissolved in the given solvent coincides with ν_S^{-1}, where ν_S^{-1} is the effective frequency of the fluctuations in the polarisation of the medium, which enters into the preexponential factor for the reaction rate constant. This approach has been developed in a number of studies.[36–38]

The second approach to allowing for the molecular structure of the solvent in the electron transfer theory is based on different approximations of the theory of the liquid state. In particular, it is represented by a study,[82] where it was shown that, in a continuous description of the solvent, it is possible to overestimate the activation energy for the reaction. However, in the same investigation an important conclusion was reached: if the energy of the reorganisation of the solvent is regarded not as a theoretically calculated parameter but as an adjustable parameter derived from experimental data, then the expressions for the reaction rate constants obtained within the framework of the continuous approximation can provide an excellent description of the reaction kinetics.

Finally, we may note that the dynamic effect of the solvent may be manifested not only in electron transfer reactions but also in the more general charge transfer reactions,[83–85] but a detailed discussion is outside the scope of the present review.

References

1. R A Marcus *J. Chem. Phys.*, 1956, **24**(5) 979
2. V G Levich *Physical Chemistry: An Advanced Treatise* (Edited by H Henderson, W Yost), Acad. Press, New York, 1970, p. 985
3. R R Dogonadze, Z D Urushadze *J. Electroanal. Chem.*, 1971, **32**(2) 235
4. L D Landau, E M Lifshits *Kvantovaya Mekhanika* (Quantum Mechanics), Nauka, Moscow, 1974, 752 pp
5. L D Zusman *Teor. Eksp. Khim.*, 1979, **15**(3) 227
6. L D Zusman *Chem. Phys.*, 1980, **49**(2) 295
7. L D Zusman *Chem. Phys.*, 1983, **80**(1) 29
8. I V Alexandrov *Chem. Phys.*, 1980, **51**(3) 449
9. D F Calef, P G Wolynes *J. Phys. Chem.*, 1983, **87**(18) 3387
10. L D Zusman *Kinet. Katal.*, 1986, **27**(4) 775
11. W Harrer, G Grampp, W Yaenicke *Chem. Phys. Lett.*, 1984, **112**(3) 263
12. G Grampp, W Yaenicke *J. Chem. Soc., Faraday Trans.*, 1985, **81**(2) 1035
13. M J Weaver, T Gennett *Chem. Phys. Lett.*, 1985, **113**(2) 213
14. T Gennett, D F Milner, M J Weaver *J. Phys. Chem.*, 1985, **89**(13) 2787

15. G E McManis, M N Golovin, M J Weaver *J. Phys. Chem.*, 1986, **90**(24) 6563
16. G E McManis, A K Mishra, M J Weaver *J. Chem. Phys.*, 1987, **86**(10) 5550
17. R M Nielson, G E McManis, M N Golovin, M J Weaver *J. Phys. Chem.*, 1988, **92**(12) 3441
18. A Kapturkiewicz, B Behr *J. Electroanal. Chem.*, 1984, **179**(2) 187
19. A Kapturkiewicz, M Opallo *J. Electroanal. Chem.*, 1985, **185**(3) 15
20. M Opallo, A Kapturkiewicz *Electrochim. Acta*, 1985, **30**(10) 1301
21. M Opallo *J. Chem. Soc., Faraday Trans.*, 1986, **82**(1) 339
22. A Kapturkiewicz, W Yaenicke *J. Chem. Soc., Faraday Trans.*, 1987, **83**(1) 2727
23. G Grampp, A Kapturkiewicz, W Yaenicke *Ber. Bunsenges. Phys. Chem.*, 1990, **94**(2) 439
24. W R Fawcett, A F Colby *J. Electroanal. Chem.*, 1989, **270**(3) 103
25. L D Zusman *Teor. Eksp. Khim.*, 1984, **20**(3) 362
26. B A Kowert, L Marcoux, A J Bard *J. Am. Chem. Soc.*, 1972, **94**(16) 5538
27. L D Zusman *Elektrokhimiya*, 1989, **25**(7) 957
28. K Suga, S Aoyagui *Bull. Chem. Soc. Jpn.*, 1973, **46**(3) 755
29. X Zhang, J Leddy, A J Bard *J. Am. Chem. Soc.*, 1985, **107**(12) 3719
30. X Zhang, H Yang, A J Bard *J. Am. Chem. Soc.*, 1987, **109**(7) 1916
31. D Huppert, H Kanety, E M Kosower *J. Chem. Soc., Faraday Trans.*, 1982, **74**(2) 161
32. E M Kosower, D Huppert *Chem. Phys. Lett.*, 1983, **96**(4) 433
33. D Huppert, P M Rentzepis *J. Phys. Chem.*, 1988, **92**(19) 5466
34. D Huppert, V Ittah, E M Kosower *Chem. Phys. Lett.*, 1988, **144**(1) 15
35. D Huppert, V Ittah, A Masad, E M Kosower *Chem. Phys. Lett.*, 1988, **150**(3) 349
36. M A Kahlow, T J Kang, P F Barbara *J. Chem. Phys.*, 1988, **88**(4) 2373
37. M A Kahlow, T J Kang, P F Barbara *J. Phys. Chem.*, 1987, **91**(26) 6452
38. T J Kang, M A Kahlow, D Giser, et al. *J. Phys. Chem.*, 1988, **92**(23) 6800
39. L D Zusman *Zh. Eksp. Teor. Fiz.*, 1975, **69**(11) 1558
40. H A Kramers *Physica*, 1940, **7**(4) 284
41. M Morillo, R I Cukier *J. Chem. Phys.*, 1988, **89**(11) 6736
42. J T Hynes *J. Phys. Chem.*, 1986, **90**(16) 3701
43. C Brot *Dielectric and Related Molecular Processes*, Chem. Soc., London, 1975, p. 1
44. D A Zichi, G Ciccotti, M Ferrario *J. Phys. Chem.*, 1989, **93**(17) 6261
45. I Rips, J Jortner *J. Chem. Phys.*, 1988, **88**(2) 818
46. I Rips, J Jortner *J. Chem. Phys.*, 1987, **87**(11) 6513
47. A B Helman *Chem. Phys.*, 1983, **79**(2) 235
48. I Rips, J Jortner *J. Chem. Phys.*, 1987, **87**(4) 2090
49. A A Ovchinnikov, M Ya Ovchinnikova *Zh. Eksp. Teor. Fiz.*, 1969, **56**(4) 1278
50. M Ya Ovchinnikova *Teor. Eksp. Khim.*, 1981, **17**(5) 651
51. H Sumi, R A Marcus *J. Chem. Phys.*, 1986, **84**(9) 4894
52. W Nadler, R A Marcus *J. Chem. Phys.*, 1987, **86**(7) 3906
53. D Huppert, S D Rand, P M Rentzepis, et al. *J. Chem. Phys.*, 1981, **75**(12) 5714
54. M McGuire, G McLendon *J. Phys. Chem.*, 1986, **90**(12) 2549
55. A B Helman *Chem. Phys.*, 1982, **65**(3) 271
56. M D Frank-Kamenetskii, A V Lukashin *Usp. Fiz. Nauk*, 1975, **116**(2) 193
57. J N Onuchic, D N Beratan, J J Hopfield *J. Phys. Chem.*, 1986, **90**(16) 3707
58. J N Onuchic *J. Chem. Phys.*, 1987, **86**(7) 3925
59. J Jortner, M Bixon *J. Chem. Phys.*, 1988, **88**(1) 167
60. L D Zusman *Chem. Phys.*, 1987, **112**(1) 53
61. L D Zusman *Chem. Phys. Lett.*, 1982, **86**(5/6) 547
62. R R Dogonadze, A M Kuznetsov *Elektrokhimiya*, 1971, **7**(2) 172
63. J D Morgan, P G Wolynes *J. Phys. Chem.*, 1987, **91**(4) 874
64. S K Garg, C P Smyth *J. Phys. Chem.*, 1965, **69**(4) 1294
65. L D Zusman *Teor. Eksp. Khim.*, 1983, **19**(4) 413
66. M Sparpaglione, S Mukamel *J. Phys. Chem.*, 1987, **91**(15) 3938
67. M Sparpaglione, S Mukamel *J. Chem. Phys.*, 1988, **88**(5) 3263
68. T Fonseca *J. Chem. Phys.*, 1989, **91**(5) 2869
69. A B Helman *Chem. Phys.*, 1989, **133**(2) 271
70. A A Belousov, A M Kuznetsov *Elektrokhimiya*, 1987, **23**(12) 1675
71. Yu I Dakhnovskii, A A Ovchinnikov *Khim. Fiz.*, 1986, **5**(5) 649
72. L D Zusman *Chem. Phys.*, 1988, **119**(1) 51
73. G E McManis, M J Weaver *J. Chem. Phys.*, 1989, **90**(2) 912
74. M Sparpaglione, S Mukamel *J. Chem. Phys.*, 1988, **88**(7) 4300
75. L D Zusman *Elektrokhimiya*, 1988, **24**(9) 1212
76. C J F Bötcher, P Bordewijk *Theory of Electric Polarization*, Elsevier, Amsterdam, 1978, Vol. 2, 200 pp
77. I S Gradshtein, I M Rzhik *Tablitsy Integralov Summ, Ryadov i Proizvedenii* (Tables of Integrals, Sums, Series, and Products), Fizmatgiz, Moscow, 1963, 1100 pp
78. I Rips, J Jortner *Chem. Phys. Lett.*, 1987, **133**(5) 411
79. I Rips, J Jortner *Chem. J. Quant. Chem.*, 1987, **21**(2) 313
80. H Heitele, M E Michel-Beyerle, P Finckh *Chem. Phys. Lett.*, 1987, **138**(2) 237
81. L D Zusman *Khim. Fiz.*, 1988, **7**(10) 1347
82. D F Calef, P G Wolynes *J. Chem. Phys.*, 1983, **78**(1) 470
83. G Van der Zwan, J T Hynes *J. Chem. Phys.*, 1982, **76**(6) 2993
84. G Van der Zwam, J T Hynes *Chem. Phys. Lett.*, 1983, **101**(4) 367
85. L D Zusman *Chem. Phys.*, 1990, **144**(1) 1

Translated from *Uspekhi Khimii* **61** 48–74 (1992) U.D.C. 541.14+547.557

The photochemistry of phenyl azide

M F Budyka, M M Kantor, M V Alfimov
Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka

ABSTRACT. The literature data on the photochemical reactions of phenyl azide under different conditions are reviewed. Its photoinitiated autocatalytic chain decomposition reaction is examined in detail. Questions relating to the structure and properties of intermediates formed during photolysis of aryl azides and the mechanism of formation of azo compounds are discussed. The existing information on photoinitiated chain reactions of alkyl and aryl azides is briefly considered.

The bibliography includes 93 references.

Contents

I. Introduction 25
II. Triplet nitrene and the formation of azo compounds 25
III. Photoinitiated autocatalytic chain decomposition of aromatic azides 29
IV. Different routes in the photochemical reactions of aryl azides 31
V. Photochemical chain reactions of azides 36

I. Introduction

In the present review the photochemical reactions of phenyl azide (PhA)—the simplest compound from amongst the fairly extensive class of aromatic azides—are discussed. The photochemistry of aromatic azides has been widely studied in connection with the use of these compounds in photoresists and vesicular light-sensitive materials and as photoaffinity labels in biology.

By analysing the photochemical reactions of PhA it is possible to derive some idea of the typical properties of this whole class of aromatic azides. Moreover, Waddell, et al. recently published a series of articles[1–8] in which photoinitiated autocatalytic chain decomposition (PACD) was described. As a result of detailed studies the mechanism of reaction and structure of the intermediate products were proposed, and the maximum apparent quantum yield of photodissociation of PhA (Φ_{-PhA}) was 15 300.[7]

The high quantum yield of dissociation and also their kinetic analysis led the authors to claim "a molecular explosion observed for the first time in solution".[7] Information about the PACD reaction is given in a number of reviews[9,10] but so far it has not been possible to confirm that this reaction takes place, despite the fact that direct attempts have been made to do this.

Processes with a quantum yield $\Phi > 1$ are of interest both for the theoretical and practical points of view; so information about the PACD reaction of aromatic azides is examined in this review. Since the basis of this reaction is assumed to be the interaction of triplet phenylnitrene (PhN) with PhA and the final product is azobenzene, it is logical to start this review with the findings on the properties of PhN in the mechanism for formation of azobenzene. The synthetic and applied aspects of the chemistry of azides have been discussed in a recent review.[11]

II. Triplet nitrene and the formation of azo compounds

Triplet PhN was first detected by Wasserman, et al.[12] in 1962 during the photolysis of vitrified solutions of PhA and other azides in poly(chlorotrifluoroethylene) at 77 K using EPR. The parameter D which was calculated from the spectrum and which characterises the magnitude of the interaction between the unpaired spins was determined as 0.99 cm^{-1}, less than $D = 1.625$ cm^{-1} for t-butylnitrene, which suggested that there is considerable delocalisation of one unpaired electron around the aromatic ring of PhN.[13] The parameter E, which characterises the difference in the distribution of spins about the molecular axes, was close to zero for both nitrenes ($E < 0.002$ cm^{-1}).

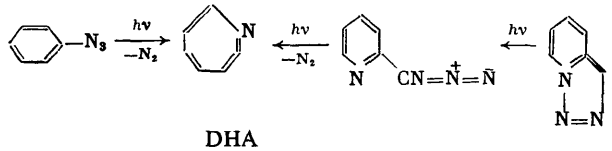
The hyperfine structure of the spectra of nitrenes generated in crystals of the corresponding azides,[14] the effect of substituents in PhN on the spectrum, and quantum-chemical calculations[15] confirmed the structure proposed for triplet PhN. A pair of electrons is situated in an *sp* orbital along the C–N axis, one unpaired electron occupies a molecular orbital enveloping the aromatic π-system, and the second electron is localised on an orthogonal *p* orbital of the nitrogen atom.

On the basis of EPR data Reiser, et al.[16] attributed the electronic absorption spectra obtained in 1965 under similar conditions of photolysis (77 K, organic matrix) to triplet nitrenes. Confirmation of this assignment was obtained from the following evidence:[17] the spectrum did not depend on the type of matrix (vitreous hydrocarbons, ether, ethanol, and their mixtures); the spectrum belonged to a single compound, since an isobestic point occurred on the spectrosocpic curves; quantum yields of photodissociation of about 0.5 were obtained for all the azides studied; the spectrum disappeared on heating the matrix to its softening point (90 K); the spectra had characteristic features relating to the occurrence of an "aromatic system with an open shell", for example, the spectrum of phenylnitrene (λ_{max} 314 and 402 nm) was similar to the spectrum of the aniline radical (λ_{max} 309 and 400 nm).

Subsequently similar spectra were obtained at 77 K by other authors,[18,19] and in all cases they were attributed to triplet PhN. Quantum-chemical calculations of the transition energies and oscillator strength corresponded satisfactorily to the experimental spectra of PhN.[18]

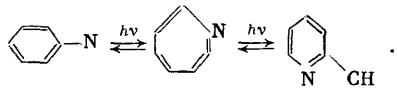
However, in 1978 Chapman, et al.[20] in studying the photolysis of phenyl azide in an argon matrix or in thin films at 8 K using IR spectroscopy demonstrated that the photolysis product under these conditions is dehydroazepine (DHA), which was detected from the

characteristic intense absorption due to the heterocumulated bonds in the IR region at 1895 cm^{-1} (close to the absorption of the spectroscopic model $-C_6H_5-\overline{C}=\overset{+}{N}=CH_2$ with ν_{CNC} = 1930 cm^{-1}). Its spectrum was also demonstrated by counter-synthesis from triazolopyridine:



DHA

At the same time an analysis of the photolysis products of PhA obtained under similar conditions (12 K) using EPR showed that triplet PhN was also present in the mixture,[21] and on subsequent irradiation it was converted to triplet 2-pyridylcarbene. Photolysis in the direction triazolopyridine→pyridylcarbene→phenylnitrene suggested that the nitrene and carbene were interconverted via dehydroazepine:[22]



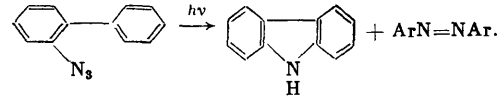
Hence the electronic absorption spectrum that was recorded in four studies[16–19] may belong not only to triplet PhN but also to a mixture of products. However, this assertion is contradicted by studies on the T_1-T_0 luminescence of PhN and its derivatives,[19,23] in which it was shown that the luminescence spectrum of triplet PhN is a mirror reflection of the absorption spectrum of the photolysis products of PhA and the latter coincides with the spectrum of luminescence excitation. Hence it was concluded that the absorption spectrum belongs to a single compound, namely, triplet PhN.

Thus, low-temperature studies have provided an ambiguous answer to the question as to what are the primary photodissociation products of PhA. It would appear that the inconsistency in the results may be due in part to the different conditions of the studies: 4–8 K in an argon matrix[20–22] or 77 K in an organic matrix.[16–19,23] Moreover, taking into account the revealed ability of PhN and DHA to undergo photochemical interconversion, the final result may depend to a significant extent on the intensity, duration, and spectroscopic range of incident light (see below).

The possibility that a number of intermediates are formed was also suggested by the results from a preparative study of the photochemical reactions of PhA and other azides and from flash photolysis of azides at room temperature.

In 1966 Doering and Odum[24] established that the final photolysis product of PhA in the presence of amines was a substituted 2-amino-3*H*-azepine. Subsequently Splitter and Calvin[25] concluded that the azepine was formed from singlet PhN on the basis of the evidence that in triplet sensitisation with *p*-dimethylaminobenzaldehyde the yield of 2-diethylamino-3*H*-azepine, for example, decreased from 34 to 2% while the yield of aniline increased from 70–80%.

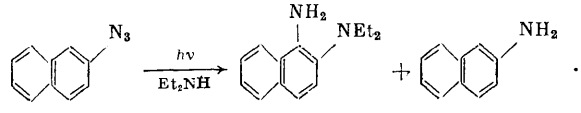
For singlet 2-biphenylnitrene the main reaction is cyclisation to carbazole, the yield of which amounted to 74% in the direct photolysis of azide, while at the same time about 12% azo compound was isolated:[26]



Quenchers of triplet excitation increased the yield of carbazole, reducing the yield of azo compound at the same time, while triplet sensitisers had the reverse effect. It followed from this that triplet nitrene is formed from triplet azide rather than singlet nitrene.

A study of the photolysis of 10^{-2} M solutions of PhA in alcoholic and hydrocarbon solvents showed that a polymer and product derived from insertion of solvent into the molecule are formed from singlet PhN, while aniline and azobenzene are formed from triplet PhN.[27] From the effect of the chemical nature of the solvent, the composition of the solvent mixture, and the added amounts of triplet sensitisers on the molar ratio of the reaction products it was estimated that in the photolysis of PhA only 12–13% PhN is directly generated in the ground triplet state.

A further type of reaction of singlet nitrene—formation of aromatic diamines with migration of the nitrogen atom of the azide group to the neighbouring position of the aromatic ring—occurred during photolysis of 2-azidonaphthalene in diethylamine. 2-Aminonaphthalene, which is probably formed in parallel from triplet nitrene, is also isolated:[28]



The method of flash photolysis at room temperature was first applied in 1966 to studies on the reactions of aromatic azides.[29] In the irradiation of a 5 × 10^{-4} M solution of 1-azidoanthracene in ethanol, 4 μs after the flash a spectrum was recorded that had a characteristic absorption at 342 nm, similar to that found previously at 77 K and attributed to triplet nitrene. The lifetime of nitrene was about 5 μs.

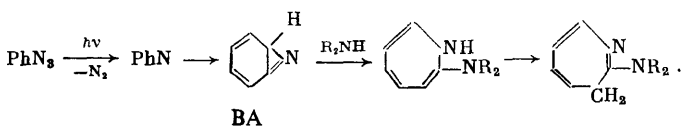
Other aromatic azides have been investigated in detail and the kinetics of certain reactions of nitrenes have been studied.[30] Reiser, et al.[30] maintained that for substituted phenyl azides, 1-azidonaphthalene, and also 1-azidoanthracene, the electronic absorption spectra of the intermediates that were recorded using flash photolysis matched the spectra of the corresponding triplet nitrenes obtained by irradiation of rigid matrices at 77 K, but the actual spectra were not depicted. Unsubstituted PhA was not studied and information on singlet intermediates was also absent.

This information was obtained subsequently by Sundberg, et al.[31] In the flash photolysis of a 10^{-4} M solution of PhA in hexane, an intermediate with an absorption spectrum in the region up to 300 nm was formed. The main reaction product was an unidentified polymeric compound, but the possibility that trace quantities of aniline and azobenzene were formed was not excluded. The presence of oxygen had no effect on the monomolecular kinetics of the increase in the unidentified absorption at a wavelength of 366 nm,

and $\tau_{1/2} \sim 5$ μs (22 °C) was found. It was suggested that the intermediate with this lifetime and spectroscopic properties ($\lambda < 300$ nm) has the stucture of a bicyclic azirine (benzazirine, BA), which is an isomer of singlet PhN.

The structure of BA as an intermediate in the formation of azepines was first proposed for thermal reactions of PhA and then extended to photochemical reactions.[32]

It was shown by Sundberg, et al.[31] that in the flash photolysis of PhA in the presence of dibutylamine, BA reacts with the amine with a rate constant of $k = 9.7 \times 10^5$ M^{-1} s^{-1} (hexane) and 3.5×10^7 M^{-1} s^{-1} (acetonitrile), and the primary product of this reaction—2-dibutylamino-1*H*-azepine—was detected, which then rearranged to the final 3*H*-isomer:

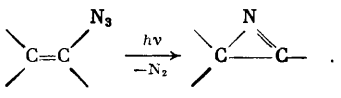


BA

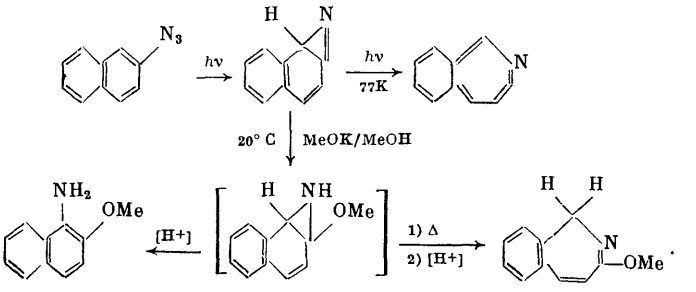
The yield of azepine by flash photolysis (from the increase in absorption) was 85%, and the recorded quantum yield for its formation during stationary photolysis $\Phi = 0.42$. The latter figure is in good agreement with the value of the quantum yield of photodissociation of PhA ($\Phi_{-PhA} = 0.53$),[33] if it is assumed that both flash and stationary photolysis give the same percentage (85%) conversion of azide to azepine. Moreover, this is in agreement with the estimate of Reiser and Leyshon[27] that 12–13% of phenylnitrene is generated in the triplet state, which does not give an azepine.

After dehydroazepine was detected amongst the photolysis products of PhA at 8 K, the reaction scheme involving bicyclic azirine became a subject of criticism.[20] DHA instead of BA was proposed as the isomer of singlet PhN and intermediate in the reactions of PhA. Chapman and Le Roux[20] related the prejudice against DHA to the results of quantum-chemical calculations[34] which showed that the structure of DHA must be less stable than that of BA or even singlet nitrene. However, the low-temperature studies of photolysis of Ph and the isomeric pyridyl diazomethanes provided clear evidence for the existence of such structures.[22]

On the other hand, supporters of the benzazirine structure doubted the validity of making direct use of the results of low-temperature studies to interpret the data obtained at a normal temperature. Moreover, evidence in favour of the BA structure was provided, for example, by the preparative isolation of azirines in the photolysis of vinyl azides:[35]



For naphthyl azides the formation of azirines was demonstrated in photolysis in argon matrices (12 K) from the appearance of bands in the region of 1708–1738 cm^{-1} in the IR spectra, and on further photolysis the azirines were converted to dehydroazepines (bands at 1910–1930 cm^{-1}).[36] At 20 °C photolysis of 2-naphthyl azide (and 2-anthryl azide) in methanol in the presence of potassium methoxide gave different final products depending on the subsequent conditions of treatment. On neutralisation directly after irradiation, 1-amino-2-methoxynaphthalene was formed, while on boiling the irradiated mixture or keeping it at 20 °C for several hours, methoxybenzazepine was isolated.[37] Rigaudy, et al.[37] suggested that a fairly stable intermediate with an aziridine structure is formed by photolysis, since the strongly alkaline medium inhibits its rapid isomerisation. These latter two studies are combined in the following scheme:



Thus, in contrast to phenyl azide, for condensed aryl azides the formation of aziridine structures during photodissociation has been demonstrated experimentally.

Without going further into the experimental details, it may be concluded that, despite the possible variants of the isomeric intermediates and the assertion that the same intermediates are formed at both 77 K and 20 °C,[30] at least for phenyl azide the majority of the results suggest that direct photolysis at room temperature mainly gives singlet PhN while low-temperature photolysis yields mainly triplet PhN.

We shall now turn to an examination of the data on the mechanism of formation of azo compounds in the decomposition of aromatic azides. Frequently the authors have confined themselves solely to an assertion that triplet nitrene takes part in this reaction without specifying the scheme in any detail. Nevertheless, three main reaction routes can be distinguished:[38–40]

dimerisation of nitrene in the triplet state:

$$2Ar-\dot{N}^{\cdot} \rightarrow Ar-N=N-Ar\ ,$$

reaction of triplet nitrene with the initial azide:

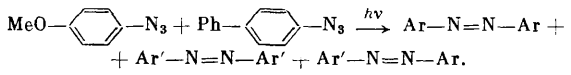
$$Ar-\dot{N}^{\cdot} + ArN_3 \xrightarrow[-N_2]{} Ar-N=N-Ar\ ,$$

dimerisation of aminyl radicals followed by oxidation of diarylhydrazine by nitrene:

$$Ar-\dot{N}^{\cdot} \xrightarrow{[H]} ArNH^{\cdot} \longrightarrow Ar-NH-NH-Ar \xrightarrow{2ArN} \rightarrow Ar-N=N-Ar + 2ArNH\ .$$

In terms of the PACD reaction under consideration, it is definitely the second scheme, in which the formation of an intermediate that decomposes to two nitrenes, namely, propagation (branching) of the chain (see below) is assumed, that is the specific reaction route of the greatest interest (in the first and third schemes chain termination occurs). There are a number of ambiguous results obtained by different authors which can either be used in support of a reaction between triplet nitrene and azide, to refute such a reaction, or included in an explanation of experimental results for a scheme that does not involve nitrenes.

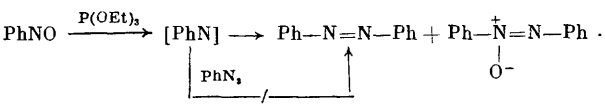
Thus, in the photolysis of a mixture of two azides—azidoanisole and azidodiphenyl—in benzene at 20 °C, almost equal quantities (about 30%) of all three possible azo compounds were formed:[41]



The formation of an asymmetric azo compound in this case may be due to the dimerisation of two different nitrenes that are formed simultaneously during photolysis, but the reaction of a single nitrene with another azide cannot be excluded.

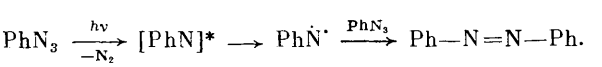
However, later findings on the thermolysis of a mixture of azides—the same *p*-azidoanisole and 1-methyl-3,5-diphenyl-4-azidopyrazole—at 80 °C testify against a reaction between nitrene and azide.[42] The temperature was selected in such a manner that the first azide was stable and only the second azide decomposed. These are the most favourable conditions for proving that a crossed reaction occurs between one nitrene and another azide. Despite the fact that *p*-azidoanisole was present in fivefold excess, the authors did not manage to detect any appreciable quantities of the product of this reaction.

Attempts were made to detect the reaction of nitrene with a suitable azide by generating the nitrene through reaction of a nitroso compound with triethyl phosphite.[43] It was found in this case that when PhA was added to the reaction mixture with nitrosobenzene, PhA did not undergo reaction and the main reaction products were azoxybenzene and tar, azobenzene being formed in trace amounts:

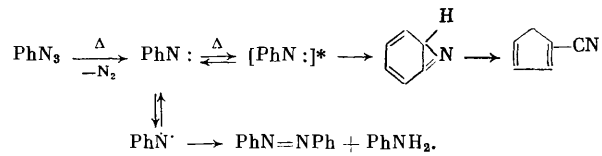


Although it was shown for a number of nitroso compounds that deoxygenation occurs via a nitrene intermediate,[44] in general it may not take place in this manner.[45] Therefore the possibility that it may nevertheless occur for other azides and/or other reaction conditions with nitrene giving an azo compound should not be completely ruled out.

The feasibility of this reaction occurring in the gas phase was demonstrated by Lehman and Berry.[46] The spectrum of PhN was recorded in the region of 340–370 nm on flash photolysis of PhA vapour in the presence of an inert gas—a quencher of excess excitation (rapid isomerisation occurred when the gas was not added). Azobenzene was formed (yield 6%) with a pseudo-monomolecular rate constant of 5×10^4 s^{-1}, from which the rate constant of the bimolecular reaction between PhN and PhA was determined as $k_{II} = 1.3 \times 10^{-12}$ cm^3 s^{-1}. The authors[46] note that because of the very high rate of reaction between PhN and PhA it was not possible to determine the rate of dimerisation of PhN, since higher concentrations of the latter were needed for this.



On the other hand, in an earlier study[47] of the pyrolysis of PhA in the gas phase (300–670 °C) it had been concluded from the dependence of the yield of azobenzene and aniline (and cyanocyclopentadiene) on the rate of admission of PhA into the hot zone (a decrease in yield of the first two with an increase in rate, namely, concentration, of reactant) that azobenzene was formed by the dimerisation of triplet PhN rather than as a result of a reaction with PhA:



It would appear that thermal generation achieved considerably higher concentrations of PhN than by photolysis.

On irradiaiton of a degassed 10^{-4} M solutions of 1-azidonaphthalene in hexane with low-intensity light, a mixture of amines was formed and the azo compound was not detected.[30] However, the latter was obtained as the main product by slow thawing of matrices irradiated at 77 K and by flash photolysis of solutions of this azide in organic solvents. The kinetics of the increase in absorption of azonaphthalene at a wavelength of 400 nm corresponded to second-order, and the rate constant for recombination of triplet nitrene was determined as $k = 5.5 \times 10^8$ M^{-1} s^{-1}. It was shown in the same study that on flash photolysis of a solution of 1-azidoanthracene in ethanol with light of reduced intensity, when only about 5% of the azide was converted to nitrene, the kinetics of the disappearance of nitrene corresponded to first-order with $\tau_{1/2}$ of 5 μs, from which the bimolecular constant for reaction between nitrene and azide was obtained ($k = 5 \times 10^8$ M^{-1} s^{-1}).[30]

At the same time, as was mentioned above, in studying the reactions of PhA using flash photolysis, Sundberg, et al.[31] did not observe the spectrum of triplet PhN at normal temperatures. The primary reaction product (not more than 30 μs after the flash) was benzazirine[31]—an isomer of singlet PhN—or dehydroazepine, as Chapman, et al. maintain.[20]

Thus, an azo compound may be formed by reaction of an azide and nitrene (which does not have to be in the triplet state),[48] but if an alternative exists for the formation of the azo compound, the nitrene reacts in a different manner.

With regard to the labile compound formed as an intermediate in the reaction between nitrene and azide, its structure was first suggested as a tetraazadiene derivative[41] ("tetrazene"), and it was assumed that it decomposes to an azo compound and nitrogen.

Subsequently, in a review Smith[38] extended this idea by the introduction of 1,2- and 1,4-isomers of substituted tetraazadiene, where the possibility of the latter decomposing to two nitrene molecules had already been admitted. Smith[38] noted that at a given ratio of the rate constants of the intermediate reactions dissociation of aryl azide will occur with first-order kinetics and it will not be possible to distinguish the formation of the azo compound by dimerisation of nitrene or by reaction of nitrene with azide. The data published by that time on the thermolysis of aryl azides suggested that the kinetics of the disappearance of azide are always first-order regardless of whether the final product is an azo compound or another product.[38]

III. Photoinitiated autocatalytic chain decomposition of aromatic azides

Let us examine the literature data of Waddell, et al. on the PACD reaction of aryl azides.

The first report on the PACD reaction of phenyl azide appeared in 1982.[1] For the photodissociation of PhA at 77 K in 3-methylpentane a value of $\Phi_{-PhA} = 0.49$ was determined (in good agreement with the results of Reiser and Marley).[33] It transpired, however, that the values of Φ_{-PhA} in solution were markedly dependent on the concentration of PhA, the solvent, and the presence of oxygen. A value of $\Phi_{-PhA} = 300$ was obtained for a 0.03 M solution of PhA in acetonitrile, and the yield decreased sharply on dilution, in the presence of oxygen, or by the addition of 2,3-dimethylbutene or tetracyanoethylene. The quantum yield of considerably greater than unity was also obtained for substituted PhA in degassed solutions: $\Phi = 210$ for *o*-tolyl azide (0.069 M), while $\Phi = 60$ for *p*-tolyl azide (0.066 M).

The authors reported that at the initial stage of photolysis in the spectroscopic curves an isobestic point was maintained at 261 nm, the absorption due to PhN at 250 nm decreased, and the absorption due to azobenzene in the region 270–360 nm increased. The latter was the sole reaction product with short irradiation times and a low conversion of PhA, on further irradiation there was considerable tar formation. It was shown by Reiser and Leyshon[27] that under similar conditions—photolysis of hydrocarbon solutions of PhA to 2% conversion—the main products are azobenzene and tar in equal ratio.

In order to explain the experimental phenomena, the authors took as a basis the possibility suggested by Horner, et al.[41] that nitrene reacts with azide to form an intermediate tetrazene. However, it was assumed that in accordance with Smith,[38] only the 1,2-isomer of the latter decomposes to azobenzene and nitrogen, while 1,4-diphenyltetraazadiene (DPTA) yields a molecule of nitrogen and two PhNs, thus propagating the chain reaction:

$$\mathrm{PhN} + \mathrm{PhN_3} \longrightarrow \mathrm{Ph{-}\overset{+}{N}{=}N{-}Ph} + \mathrm{Ph{-}N{=}N{-}N{=}N{-}Ph},$$
$$\mathrm{N{=}\bar{N}}$$

$$\mathrm{Ph{-}\overset{+}{N}{=}N{-}Ph} \longrightarrow \mathrm{Ph{-}N{=}N{-}Ph} + \mathrm{N_2},$$
$$\mathrm{N{=}\bar{N}}$$

$$\mathrm{Ph{-}N{=}N{-}N{=}N{-}Ph} \rightarrow 2\mathrm{PhN} + \mathrm{N_2}.$$

The formation of two PhNs directly by reaction of PhN with PhA without intermediates was also assumed:

$$\mathrm{PhN} + \mathrm{PhN_3} \rightarrow 2\mathrm{PhN} + \mathrm{N_2}.$$

The authors cited the formation of stable complexes between 1,4-diaryltetraazadiene and transition metal ions[49] as well the mass spectrometric reaction of the PhN anion with PhA to form the DPTA anion[50] as confirmation of the existence of the tetraazadiene structure.

An attempt was made[2] to demonstrate the involvement of DPTA as an intermediate in the decomposition of PhA by nanosecond laser photolysis (excitation wavelength 266 nm, pulse 10 ns) in a continuous-flow cuvette. It transpired that the spectroscopic properties of the intermediate were virtually the same for dilute and concentrated solutions. The spectrum was preserved with virtually no changes throughout the whole of the timescale studied—from 15 ns to 5.45 μs—whether oxygen was present or not.

Feilchenfeld and Waddell[2] conclude on the basis of the lifetimes that were determined that the spectrum observed in the region of 330–500 nm belongs to a single compound, and citing studies already reviewed on the photolysis of azides at 77 K[17] and 20 °C[30] and their own results at 77 K[3] they attribute the spectrum to triplet PhN. We should note that only the spectroscopic region and not the spectrum itself matches the results of Reiser, et al.,[17] while PhA was not investigated at all in the other study.[30] The reasons for the absence of a reaction between PhN and oxygen are not discussed, although reactions of this type usually takes place at a considerable rate.

A parallel study was made of the spectrum of the intermediate derived from phenyl isocyanate, which loses a CO molecule on photolysis and also yields phenyl nitrene:

$$\mathrm{PhNCO} \xrightarrow{h\nu} \mathrm{PhN} + \mathrm{CO}.$$

The spectra of the intermediates from both compounds as well as the lack of dependence of the shape of the spectrum on the concentration of PhA while the quantum yield of photodissociation of PhA changed by a factor of 10 made it possible for Feilchenfeld and Waddell[2] to conclude that there was no spectroscopic evidence for the formation of diphenyltetraazadiene as an intermediate (the spectroscopic region of 250–550 nm and a period of time up to 6 μs after a flash).

This conclusion was supported[3] by a study of the PACD reaction of phenyl isocyanate. A quantum yield of greater than unity was observed for this compound also, but formation of a tetraazadiene-type of structure from it is impossible. An estimate was made of the number of branches (length of chain n) of the autocatalytic chain on the basis of the ratio $2^n = \Phi/\Phi_0$, where Φ_0 is the quantum yield of dissociation at infinite dilution. For phenyl isocyanate $\Phi_0 = 0.057$, which is an order less than the corresponding value for PhA; but similar values of n were obtained at similar concentrations for both compounds.[3] When $[PhN_3] = 0.03$ M, $n = 9.2$; while when [PhNCO] = 0.015 M, $n = 7.35$. Unfortunately, a "crossed" experiment was not carried out. The spectra of PhA and phenyl isocyanate differ sufficiently for a particular reactant to be excited selectively: for PhA $\lambda_{max} = 250$ nm ($\varepsilon = 1 \times 10^4$ M^{-1} cm^{-1}) with a long-wavelength limit of the spectrum at about 292 nm, for phenyl isocyanate $\lambda_{max} = 227$ nm ($\varepsilon = 1 \times 10^4$ M^{-1} cm^{-1}) with a long-wavelength limit at about 280 nm (both spectra in acetonitrile).[2] Involvement of one reactant in the reaction when the other is excited while retaining high quantum yields and the formation of azobenzene would act as a significant argument in support of the reactions detected by Waddell, et al.[1–8] However, there is no information about this in these studies.

Despite the conclusion[3] that the chain reaction occurs through the phenyl nitrene-sensitised decomposition of PhA or phenyl isocyanate to give two PhNs:

$$\mathrm{PhN} + \mathrm{PhN_3} \rightarrow 2\mathrm{PhN} + \mathrm{N_2},$$
$$\mathrm{PhN} + \mathrm{PhNCO} \rightarrow 2\mathrm{PhN} + \mathrm{CO},$$

intermediates such as diphenyltetraazadiene and its isomeric compounds were subsequently introduced again to explain the PACD reaction.[4,5]

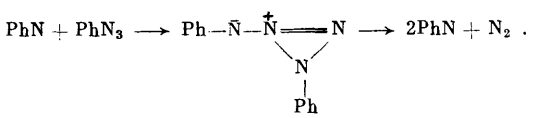
In one of these studies[4] the main focus of attention is a detailed analysis of the reaction products of PhA under different conditions. It is verified that the primary photoproduct in the irradiation of PhA in an inert atmosphere is (*E*)-azobenzene, which is then converted to the (*Z*)-isomer with a quantum yield of $\Phi = 0.14$. The data on the quantum yield of photodissociation of PhA differ somewhat from those reported previously,[1] when $\Phi_{-PhA} = 3$ at [PhA] = 3×10^{-5} M (acetonitrile, atmosphere of N_2) was recorded. In the later study[4] $\Phi_{-PhA} = 0.72$ when [PhA] = $10^{-5}-10^{-4}$ M; the latter figure is in closer agreement with the results of Reiser and Marley,[33] who found $\Phi = 0.53$.

In the presence of oxygen the primary product of the photolysis of PhA was established as nitrobenzene, which on further irradiation is converted to nitrobenzene and azobenzene. Since the value of Φ_{-PhA} in dilute solution did not depend on the presence of oxygen, it was concluded that azobenzene is formed under these conditions, probably by dimerisation of phenylnitrene. In concentrated solution oxygen significantly reduced the quantum yield of photodissociation of PhA, but when [PhA] > 3×10^{-3} M, $\Phi_{-PhA} > 1$ even in a solution saturated with oxygen.

In a later study[5] the range of concentrations of PhA studied was extended from 10^{-5} M to 0.218 M. Spectroscopic studies indicated that an isobestic point was maintained at 271 nm, i.e. in the opinion of Lee Go and Waddell,[5] the two-component nature of the system remained up to 40% conversion of PhA. High-performance liquid chromatography confirmed that the content of azobenzene increased linearly as the concentration of PhA decreased.

The quantum yield was determined up to a conversion of 3%; when [PhA] = 2.3×10^{-5} M, $\Phi_{-PhA} = 0.5$ was reported, while the maximum value of $\Phi_{-PhA} = 4330$ was obtained when [PhA] = 0.137 M. It was shown that the dependence of Φ_{-PhA} on the logarithm of the concentration of PhA is not linear but in fact has an exponential form, whereas the length of the chain n increases linearly with log [PhA].

In order to explain the autocatalytic chain reaction, the schemes already considered were supplemented with the possible intermediate formation of a triaza compound that decomposes to two phenylnitrenes and nitrogen:



The authors carried out an analogous process to this reaction with chain branching reactions during explosions in the gas phase and solid state, such as for metal azides. They note, however, that such reactions have not been recorded in solution. Since it was assumed in calculations of the chain length that the efficiency of the chain propagation stages is equal to unity (i.e., at the intermediate stages PhN is not lost through side reactions), the actual values of n could be even higher.

On repeated study of concentrated solutions of phenyl azide and phenyl isocyanate using pulsed laser photolysis, Feilchenfeld and Waddell[6] recorded a nonexponential decrease and oscillation of the induced optical density over the wavelength range 450–550 nm with a period of about 10 μs. For example, with a PhA concentration of 0.5 M, an increase in D_{450} occurred over a period of about 20 μs after a flash, then on the declining section of the curve there were six cycles of increase and decrease in optical density that were unaffected by the presence of oxygen. With a decrease in [PhA] the time for reaching a maximum value of D_{450} and the number of cycles decreased, and when [PhA] was 5×10^{-4} M the maximum of D was reached after 2–3 μs followed by a monoexponential decrease with a lifetime of 2.8 μs. A similar monoexponential decrease occurred for concentrated solutions in the presence of tetracyanoethylene.

Feilchenfeld and Waddell[6] concluded from these results and also the symbatic relationship between the decrease in the number of cycles on the oscillograms and the length of chain n and the decrease in concentration of PhA that they were detecting an oscillation in the content of triplet PhN in the reaction mixture.

The maximum value obtained—$\Phi_{-PhA} = 15300$ when [PhA] = 0.722 M in degassed acetonitrile and $\Phi_{-PhA} = 2280$ when [PhA] = 0.793 M in a solution saturated with oxygen—was subsequently reported.[7] An attempt was made to represent the PACD reaction of phenyl azide quantitatively. Four reactions form the basis of the kinetic scheme:

$$PhN_3 \xrightarrow{h\nu} PhN + N_2, \quad (1)$$

$$PhN + PhN_3 \xrightarrow{k_2} [Z] \longrightarrow 2PhN + N_2, \quad (2)$$

$$PhN + PhN_3 \xrightarrow{k_3} Ph{-}N{=}N{-}Ph + N_2, \quad (3)$$

$$2PhN \xrightarrow{k_4} Ph{-}N{=}N{-}Ph. \quad (4)$$

The scheme does not distinguish between the direct formation of two phenylnitrenes by reaction of PhN with PhA and the formation of an intermediate Z. On the basis of a quasi-steady-state condition for the PhN concentration with a fixed intensity of incident light I_0 and low conversions of PhA the following ratio was obtained:

$$\alpha = \beta + \lg\left[(k_2+k_3)^2\Phi_1 N_0/2k_4\right],$$

where: $\alpha = \lg\left[(\Phi-\Phi_1)^2/(1+2Q(\Phi-\Phi_1))\right]$,

$$Q = (k_2-k_3)/\left[2\Phi_1(k_2+k_3)\right],$$

$$\beta = \lg\left[[PhN_3]^2 V_0/(I_0(1-10^{-A}))\right],$$

Φ_1 is the quantum yield of reaction (1), $\Phi = \Phi_{-PhA}$, N_0 is the Avogadro number, V_0 is the volume of irradiated solution, and A is the optical density at the wavelength of incident light at an initial moment in time. All of the parameters in α and β were determined experimentally, with the exception of Q, whose value was found by trial and error. For degassed solutions a linear correlation between α and β was obtained with a gradient of unity when $Q = 0.0019$. For the complete series of 56 values of Φ_{-PhA} ranging from 0.3 to 15000 in solutions that were degassed or saturated with air and oxygen over a concentration range of 1.4×10^{-5} to 0.793 M, a linear correlation was also obtained, but with $Q = 0.0004$.

Costantino, et al.[7] consider that the excessively low values of Q indicate that the constants k_2 and k_3 are of virtually the same magnitude, which is not unexpected. The derived equation also accounts for the observed decrease in Φ_{-PhA} as the light intensity increases.

In the last of the series of publications by Waddell, et al.[8] on the PACD reaction, tetraazadiene is again rejected as an intermediate, and the species with the composition PhN is assumed to be the chain

carrier. In order to choose between four possibilities—singlet PhN, triplet PhN, benzazirine, or dehydroazepine—the authors studied the reactions of substituted phenyl azides and investigated triplet sensitisation†.

For all of the azides studied, the values of the quantum yields of photodissociation Φ were greater than 1. For example, at concentrations of 0.1 M, Φ = 81 for 4-bromo-PhA, Φ = 143 for 2,4,6-tribromo-PhA, and Φ = 434 for 4-nitro-PhA (for PhA itself, Φ = 1800 was found under similar conditions).[8] The quantum yields increased exponentially with the concentrations of the azides and at small degrees of conversion the corresponding azo compounds were established as photoproducts.

The following evidence illustrates that triplet nitrene is the intermediate that drives the chain:

for bromo-substituted PhAs, $\Phi \gg 1$, and it has been experimentally demonstrated for these compounds that because of accelerated intersystem crossing (heavy atom effect) they rapidly reach a triplet state;[51]

for nitro-PhA, $\Phi \gg 1$ also, and the formation of triplet nitrene has been demonstrated experimentally for this compound as well;[52]

in triplet-sensitised photodissociation of 4-nitro-PhA, $\Phi \gg 1$ also occurred regardless of the presence of n-butylamine in the mixture, whereas in direct photolysis the quantum yield decreased sharply on addition of the amine (a "singlet trap").

In summarising our review of the series of publications of Waddell, et al. on the photoinitiated autocatalytic chain decomposition (PACD) reaction of phenyl azide, it may be concluded that, despite the ambiguity of certain assumptions such as that concerning the spectrum of the intermediate in the photolysis of PhA at 20 °C, the actual existence of a chain reaction is not doubted by these authors.[1–8]

However, this cannot be said of other research workers, and we shall now turn to a discussion of their results.

IV. Different routes in the photochemical reactions of aryl azides

The first evidence for a lack of dependence of the quantum yield of photodissociation of aryl azides on their concentration was actually obtained much earlier than the first study on the PACD reaction. In 1968 Reiser and Marley[33] reported that over a concentration range from $10^{-5}-10^{-2}$ M the quantum yield of dissociation of 1-naphthyl azide was constant and equal to 1.00 ± 0.02.

† Raising the question in this way seems strange since the evidence cited by Waddell, et al.[1–7] that it is indeed triplet nitrene which is the chain carrier has already been examined above. It may be assumed that the article[8] was published in response to the criticism of Leyva, et al.[51] of the studies on the PACD reaction. Jenkins, et al.[8] refer to the formation, as demonstrated in two studies,[51,52] of triplet nitrenes in the photolysis of tribromo-PhA and 4-nitro-PhA at room temperature, but nothing is said about the lack of confirmation that triplet PhN is formed under similar conditions and hence the impossibility of it fulfilling the intended function. Moreover, it is shown by Liang and Schuster[52] that the azo compound is formed as a result of the dimerisation of 4-nitro-PhN rather than by a reaction with the azide (for further details, see below).

The first studies in which the disagreement with the results of Waddell, et al. is directly indicated were published in 1984. On irradiation of 1-azido-4-naphthylsulphonic acid with light at 310 nm the quantum yield of dissociation (0.66) did not depend on the concentration of azide, the presence of oxygen, or the presence of a second azide—*p*-azidobenzenesulphonic acid, which hardly absorbs at all at 310 nm and whose concentration exceeded that of the naphthyl azide by a factor of up to 100.[53]

We should note again that selective generation of one nitrene, let us say ArN, in the presence of another azide—Ar′N_3—and isolation of an asymmetric ("crossed") azo compound—ArN=NAr′—is a powerful argument in favour of a reaction between nitrene and azide. Geiger, et al.[53] give no information about the photolysis products, but they concluded that the second azide is not involved in a reaction with the nitrene obtained from the first azide.

The absence of a chain reaction could be due to the structural changes in the azides, but these changes should in fact have resulted in an intensification of the expected effect. Thus, acceptor substituents in PhA are known to increase the activity of the nitrene[54] and assist its formation in the triplet state at room temperature.[51,52] Replacement of the benzene ring by a naphthalene ring effects it in the same way.[30,37]

In the same year Shrock and Schuster[55] published the results of a detailed examination of the photochemical properties of PhA using flash photolysis with identification of the reaction products. In contrast to the results of Waddell, the yield of azobenzene depended only slightly on the degree of conversion of PhA and, what is more significant, decreased as the concentration of PhA increased—when [PhA] > 10^{-3} M virtually all of the PhA was converted to polymer. Changing from a stationary source of radiation to a laser also led to a marked reduction in yield, despite the fact that intermediates with concentrations 20 000 times higher were generated at the same time. The spectrum of the intermediate with λ_{max} at about 340 nm (hexane) which was formed less than 20 ns after a flash and with a lifetime of about 100 μs was attributed by the authors, also in contrast to Waddell, to a single intermediate, namely dehydroazepine, since this intermediate was not formed by triplet sensitisation, did not react with oxygen, and did not react with the standard singlet "trap"—diethylamine.

The somewhat contradictory nature of this study[55] should be noted. Shrock and Schuster report that PhA effectively quenched the triplet state of benzophenone with a rate constant of $k = 2 \times 10^9$ M^{-1} s^{-1} (acetonitrile) and considerable quantities of azobenzene were formed at the same time, but subsequently the low efficiency of photodissociation of PhA by triplet sensitisation is indicated—about 20% of the Φ_{-PhA} during direct photolysis—as well as low yields of azobenzene in the sensitised reaction. However, it was found previously[56,57] for concentrated solutions that the quenching constants had values that were lower by a factor of 10^3 and that every second sensitised molecule of PhA dissociates. In order to explain this discrepancy in their results, Shrock and Schuster[55] mention the values of $\Phi_{-PhA} \gg 1$ obtained by Waddell for concentrated solutions, but in calculations $\Phi = 0.5$ is used and the results of their own measurements of the quantum yield are not given. In interpreting the results the authors[55] believe that a reaction of triplet PhN (PhN^3) or its precursor occurs with PhA, and they refer to the studies of Waddell, but in contrast to the latter, they indicate that a polymer is formed as the final product rather than azobenzene:

$$PhN^3 + PhN_3 \xrightarrow[-N_2]{} [\dot{P}hN]_2 \xrightarrow[-nN_2]{nPhN_3} [PhN]_{n+2} .$$

In fact the only point of agreement between Shrock and Schuster[55] and Waddell, et al.[1-4] is that azobenzene is formed from triplet PhN.

The other study by Shrock and Schuster published at that time[58] on the photochemical properties of polynuclear azides did not shed light on this question. Certain arguments were put forward in favour of both the possibility of triplet nitrene reacting with azide and the formation at the same time of an intermediate that subsequently decomposes to the azo compound.

On irradiation of a mixture of two azides—PhA and 1- or 2-naphthyl azide (NA)—with low-intensity light of wavelength 350 nm, both azonaphthalene and the "crossed" asymmetric product, but not azobenzene, were obtained.

$$C_{10}H_7N_3 \xrightarrow[-N_2]{h\nu} C_{10}H_7N \xrightarrow[-N_2]{PhN_3} C_{10}H_7N{=}NC_{10}H_7 + C_{10}H_7N{=}NPh.$$

In contrast to the study of Horner, et al.[41] considered above, in which an asymmetric azo compound was also isolated, Shrock and Schuster[58] had a clearer result since light was absorbed by only one azide (NA). On laser photolysis (337 nm) the same mixture yielded only azonaphthalene, from which it was concluded that the rate of reaction of nitrene with azide is much lower than the rate of dimerisation of nitrene, the rate constant of which was determined as $k = 1 \times 10^9$ M^{-1} s^{-1} for 1-NA (but compare with the reaction of anthrylnitrene with anthryl azide:[30] $k = 5 \times 10^8$ M^{-1} s^{-1} and the reaction of PhN with PhA in the gas phase: $k = 1.3 \times 10^{-12}$ cm^3 s^{-1}).[46]

Interesting observations were made in analysing the products of stationary photolysis after standing in the dark. It transpired that the yields of azo compounds determined directly after photolysis gradually increased over a period of several hours, and in experiments with two azides this applied to both reaction products. Since the content of azides on standing in the dark did not change and the yield of azo compounds from laser photolysis remained constant and equal to that measured directly after irradiation, it was concluded that an additional quantity of azo compound is formed by decomposition of a fairly stable intermediate obtained by reaction between nitrene and azide. Shrock and Schuster,[58] with reference to the study of Waddell, et al.,[1] assumed that the intermediate had the structure of a tetraazadiene (tetraazine)[58] and defined the scheme for formation of the crossed azo compound as

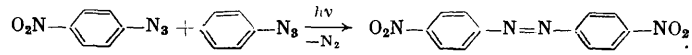
$$ArN + Ar'N_3 \longrightarrow$$

$$\longrightarrow [Ar{-}N{=}N{-}N{=}N{-}Ar'] \xrightarrow[-N_2]{} Ar{-}N{=}N{-}Ar'.$$

There is no spectroscopic or any other form of evidence for a tetraazadiene. Unfortunately, data on the quantum yields for formation of the azo compounds and photodissociation of the azides are also absent. On photolysis of solutions of pure PhA it was noted that the yield of azobenzene did not vary on standing in the dark.[55]

A direct refutation of the results of Waddell on the PACD reaction of aryl azides was made in subsequent studies of Schuster, et al.[59-61]

An investigation of the photochemical properties of 4-nitrophenyl azide showed that on irradiation of degassed acetonitrile or benzene solutions with low-intensity light the main reaction products were the azo compound (75%) and polymer, while the azo compound (>96%) was exclusively formed on laser photolysis[59] (a result that is in direct contradiction to that obtained by the same authors for PhA itself).[55] It followed from this that the azo compound was obtained by dimerisation of nitrophenyl azide; the experimental rate constant of dimerisation was $k = 1 \times 10^9$ M^{-1} s^{-1}. This conclusion was supported by an experiment with two azides. On irradiation of a mixture of PhA and 4-nitro-PhA under conditions where light was absorbed solely by the latter (313 nm), in contrast to the mixture of PhA and naphthyl azide,[58] neither a "crossed" azo compound nor azobenzene were formed, and only dinitroazobenzene—the dimerisation product of nitro-PhN—was isolated:



A quantum yield of $\Phi = 434$ was reported by Waddell, et al.[8] for concentrated (0.1 M) solutions of 4-nitro-PhA. Liang and Schuster[59] undertook a detailed examination of the dependence of Φ_{-N_2} on the concentration of azide. It transpired that over the concentration range 0.001–0.1 M azide, the quantum yield remained constant and equal to 0.7. A similar result was obtained for 3-nitro-PhA. It was therefore concluded[59] that there was no evidence to support the postulated PACD reaction of 4-nitro-PhA.

Another substituted PhA—4-dimethylaminocarbonylphenyl azide—was studied[60] by means of flash photolysis with the IR and electronic absorption spectra being recorded. Like PhA itself, irradiation of this azide in the presence of diethylamine resulted in the formation of a substituted 3*H*-azepine. On laser photolysis an intermediate was detected that was formed 20 ns after a pulse, and the kinetic curve for disappearance of this intermediate had an exponential form with a half-life of 1 μs, the rate of decay increasing in direct proportion to the content of amine. The spectroscopic properties—absorption in the UV region at 350–370 nm and in particular a band at 1887 cm^{-1} in the IR spectrum—provided clear evidence for the dehydroazepine structure of the intermediate. The characteristic band due to an azirine at 1730 cm^{-1} was absent. Since the kinetic and spectroscopic data and the reaction product accorded for dimethylaminocarbonyl-PhA and PhA,[55] Schuster, et al.,[60] by drawing a parallel between the properties of these two azides, concluded that the spectrum of DHA had been incorrectly attributed by Waddell, et al.[2] to triplet PhN and that the data on the "hypothetical molecular explosion in solution" should be carefully checked.

In order to explain the formation of 70% azo compound during stationary photolysis of dimethylaminocarbonyl-PhA in cyclohexane in the absence of an amine (and oxygen), it was suggested[60] that DHA may isomerise "with moderate efficiency" to triplet nitrene, probably via the singlet state.

The method of time-resolved IR spectroscopy was applied to PhA by Li, et al.[61] On laser photolysis of degassed heptane solutions of PhA, an intense band at 1887 cm^{-1} due to the cumulated double bonds of DHA was recorded, which shifted, in accordance with theory, to 1877 cm^{-1} when PhA enriched with ^{15}N isotope on the N(1) atom (joined into the ring) was used. The kinetics of the decrease in absorption of DHA had an exponential character, and the rate of decrease proved to be directly proportional to the concentration of PhA, from which the rate constant for reaction between PhA and DHA was obtained ($k = 7.5 \times 10^4$ M^{-1} s^{-1}). In the opinion of Li, et al.,[61] the reaction of DHA with PhA may, at least partly, account for the formation of tar (polymer) and the quantum yields of $\Phi_{-PhA} > 1$ in the photolysis of concentrated solutions of PhA. The lifetime of DHA (4.8 μs) was obtained by

extrapolation to zero concentration; this characterises the rate of irreversible conversion of DHA to triplet PhN‡.

In addition to PhA, 13 of its derivatives were also studied by Li, et al.[61] The formation of DHA was detected during photolysis at room temperature for all of them, with the exception of 4-dimethylamino-PhA. It had been demonstrated previously for the latter that singlet nitrene which is formed less than 25 ps after absorption of a quantum of light is completely converted to the triplet state over a period of 120 ps.[62] Relatively small quantities of DHA occurred for nitro- and iodo-substituted PhA because of the increase in the rate of intersystem crossing of singlet nitrene to the triplet state.

The possible occurrence of a chain reaction involving triplet PhN was examined.[61] The principal argument in favour of such a reaction was the increase in quantum yield of photodissociation to values of $\Phi \gg 1$ on increasing the concentration of PhA.[1-8] But Li, et al.[61] believed that at a high concentration it was doubtful whether any molecules of PhA would reach the triplet state PhN^3 after elimination of nitrogen. For example, they estimated that even when [PhA] = 0.05 M, less than one in twenty dissociated PhA molecules would be converted to PhN^3. This is also supported by the fact that with an increase in the concentration of PhA, the yield of azobenzene formed from PhN^3 decreases sharply. It was concluded[61] that the results obtained did not completely rule out the feasibility of a possible chain reaction but they limited its potential significance.

Thus, repeated studies of the properties of the intermediate formed during photolysis of PhA at room temperature clearly indicated a dehydroazepine structure rather than triplet phenylnitrene. However, the latter, according to the EPR data, is undoubtedly present in the photolysis products of PhA in rigid matrices at low temperatures. Leyva, et al.[51] proposed that competition between the two routes for conversion of singlet PhN—thermally activated isomerisation to DHA and temperature-independent intersystem crossing to PhN^3—leads to an almost complete change in reaction route on lowering the temperature from 20 °C to 77 K.

A study of the effect of temperature on the ratio of the final products of photolysis as well as the joint application of EPR, absorption and emission spectrosocpy supported this theory. It transpired that both intermediates—DHA obtained by laser photolysis of PhA in acetonitrile solution at 20 °C and PhN^3 obtained by photolysis in an EPA matrix (diethyl ether : isopentane : ethanol = 5 : 5 : 2) at 77 K—absorb in the region of 330–450 nm, which explains the certain amount of confusion in assigning the spectra. Nevertheless, the spectra are sufficiently clear for both intermediates to be distinguished: the spectrum of PhN^3 has distinct maxima at 490, 382, and 303 nm, which are absent in the spectrum of DHA (λ_{max} = 345 nm).

Leyva, et al.[51] demonstrated once again that the spectrum obtained at 77 K is actually that of PhN^3 rather than a mixture of products (in contrast to the previous findings of Reiser, et al.,[17] in which the spectrum of PhN^3 proved to be contaminated with DHA). Firstly, the EPR, absorption, and fluorescence spectra appeared and disappeared (on further photolysis) in the same way; secondly, the O–O bands in the latter two spectra were the same; and thirdly, the fluorescence excitation spectrum corresponded satisfactorily to the absorption spectrum (see the study of Smirnov and Brichkin).[23] The spectrum of DHA at 20 °C was unaffected by a change of solvent (benzene, hexane, acetonitrile), concentration of azide and wavelength of excitation (248 nm at 1×10^{-4} M and 308 nm at 1×10^{-3} M PhA), presence of oxygen.

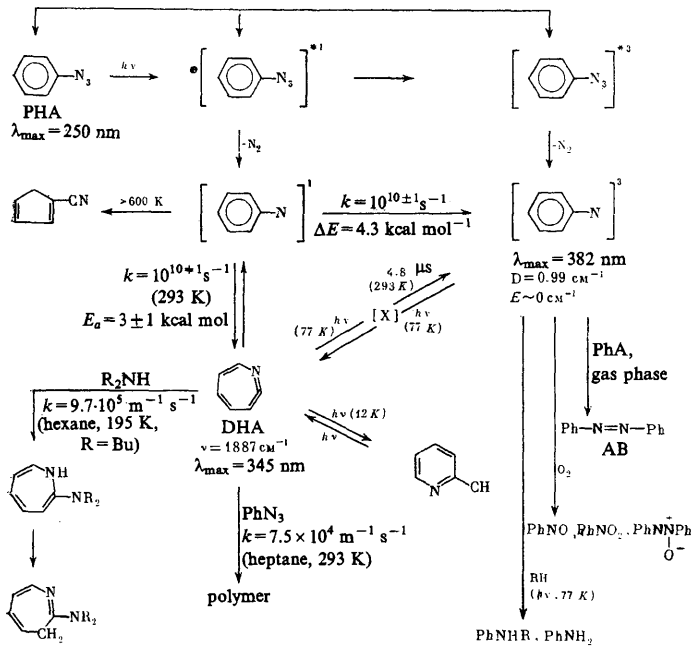
An attempt was made to generate PhN^3 by triplet sensitisation. At 77 K photolysis proved ineffective, while at 20 °C, despite the fact that the triplet states of sensitisers (benzophenone, 2,3-dimethylnaphthoquinone) were quenched by phenyl azide at a diffusion-controlled rate, the presence of PhN^3 could not be deduced from the spectra of the intermediates. This finding is in agreement with the study of Shrock and Schuster,[55] in which it was found that the quantum yield of photodissociation of PhA on triplet sensitisation was $\Phi < 0.1$, and with the study of Reiser, et al.,[30] in which the rate constant of reaction between 1-anthrylnitrene and the initial azide was determined as $k = 5 \times 10^8$ M^{-1} s^{-1}. Consequently, at the high concentrations of PhA necessary for flash photolysis experiments, even when small quantities of PhN^3 are formed the latter may rapidly disappear, so that it cannot be observed. Leyva, et al.[51] stated that these results did not support the mechanism of autocatalytic decomposition of PhA with triplet PhN as an initiator as proposed by Waddell, et al., and that they did not agree with the spectrum obtained by the latter authors[2] at 20 °C being attributed to triplet PhN. No data were given[51] on the quantum yields of dissociation of PhA.

The energy of activation of the isomerisation $PhN^1 \rightarrow$ DHA (E_a = 3 ± 1 kcal mol^{-1}), the rate constant of isomerisation at 20 °C ($k = 1 \times 10^{11\pm1}$ s^{-1}), and the temperature-independent rate constant of intersystem crossing ($k = 1 \times 10^{10\pm1}$ s^{-1}) were estimated[51] from the effect of temperature of the ratio of the photolysis products. The latter value is in good agreement with the recorded time of the singlet–triplet conversion of 4-dimethylamino-PhN ($\tau = 1.2 \times 10^{-10}$ s);[62] for the much more stable 1-pyrenylnitrene this value is substantially higher ($\tau \sim 3 \times 10^{-8}$ s).[63]

The results of the recent most exhaustive studies[51,61] supplemented with the data of earlier studies are combined in Scheme 1, which indicates the possible routes for (inter)conversion of intermediates in the photolysis of phenyl azide under different conditions.

‡Processes with first-order kinetics in the photolysis of solutions of pure PhA had already been observed previously. It would appear that the increase in absorption at a wavelength of 366 nm in the flash photolysis of a solution of PhA in hexane[31] characterises the formation of the product derived by reaction between DHA and PhA. In that case, starting with an apparent constant of about 1.4×10^2 s^{-1} and a PhA concentration of 1×10^{-4} M, the rate constant of the reaction between DHA and PhA can be determined as $k = 1.4 \times 10^6$ M^{-1} s^{-1}, which is somewhat higher than in heptane.[61] If the spectrum observed by Waddell, et al.[6] is that of DHA rather than triplet PhN, from the lifetime of the intermediate of $\tau = 2.8$ μs and a PhA concentration of 5×10^{-4} M, we obtain the rate constant of the reaction between DHA and PhA in acetonitrile ($k = 7 \times 10^8$ M^{-1} s^{-1}). The considerable increase in the rate of reaction between DHA and PhA on changing from hexane to acetonitrile is comparable to the increase in the rate of reaction of DHA with dibutylamine: $k = 9.7 \times 10^5$ M^{-1} s^{-1} (hexane) and 3.5×10^7 M^{-1} s^{-1} (acetonitrile).[31]

Scheme 1



Excitation of PhA leads to excited singlet PhA^{*1} and then to excited triplet PhA^{*3}. Both of the latter can dissociate to a nitrogen molecule and nitrene, and more will be said later about the relative proportion of these two reaction routes at different temperatures. Quantum-chemical calculations showed that in both of the excited states of PhA dissociation starts with movement of the terminal N(3) nitrogen atom out of the plane of the molecule, resulting in a decrease in the N—N—N angle, followed by cleavage of the N(1)—N(2) bond.[64] Since the quantum yield of dissociation $\Phi < 1$, there exists a route for the deactivation of excited singlet and/or excited triplet PhA.

Depending on the reaction conditions, singlet phenylnitrene PhN^1 is converted to the triplet state or isomerises to dehydroazepine DHA, and at high temperatures its isomerisation to cyanocyclopentadiene has been recorded[47,65] (one of the possible isomers is shown in Scheme 1). Singlet PhN (the protonated form) is also likely to be responsible for the formation of substituted aminophenols during photolysis in acetic acid,[24] similar products being formed in the protolytic decomposition of PhA.[66] Moreover, certain substituted phenylnitrenes ArN^1 are capable of reacting with amines R_2NH to give hydrazines $ArNHNR_2$.[59,67]

In the presence of amines DHA can be converted to a susbtituted 3*H*-azepine, form a polymer on reacting with azide[61] or by self-polymerisation,[68] and isomerise photochemically or by a slow thermal process to PhN^3 (for the possible intermediate "X" in this process, see below).

Triplet phenylnitrene PhN^3 on reacting with hydrogen donors can be converted to aniline and/or a substituted aniline or dimerise to azobenzene (AB). In the gas phase AB is also formed by the reaction of PhN^3 with PhA;[46] in solution this process occurs for anthrylnitrene,[30] but it has been demonstrated for substituted phenyl azides that an azo compound is formed by dimerisation of triplet nitrene.[59] In the presence of O_2, PhN^3 gives oxygen-containing photolysis products.[4,11,59]

The structure of diphenyltetraazadiene DPTA as an intermediate is not shown in Scheme 1 since there is no indisputable evidence for its participation in the formation of AB. Two questions should evidently be singled out—is the formation of a diphenyltetraazadiene structure generally feasible; and, if it formed during the photolysis of PhA, is its decomposition to a nitrogen molecule and two phenylnitrenes possible?

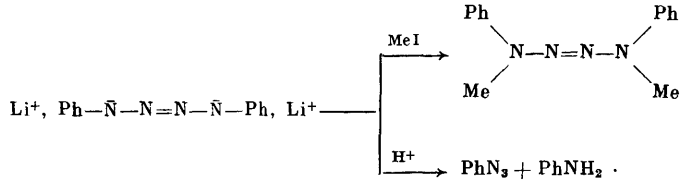
There is a positive answer to the first question. As has already been mentioned, the formation of DPTA and AB radical anions have been detected by mass spectrometry in the reaction between the PhN radical anion and PhA:[50]

$$PhN^{\cdot-} + PhN_3 \longrightarrow [Ph{-}N{=}N{-}N{=}N{-}Ph]^{\cdot-} + [Ph{-}N{=}N{-}Ph]^{\cdot+},$$

and the rate constant of this process ($k = 1 \times 10^{-12}$ cm^3 s^{-1}) proved to be almost equal to the rate constant of the gas-phase reaction for formation of AB in the reaction between PhN and PhA.[46]

Diaryltetraazadiene structures are generated under very mild conditions (20 °C) in exothermic reactions of aryl azides with transition metal complexes and are stabilised through formation of two metal—nitrogen σ-bonds with the N(1) and N(4) atoms. The reaction between a metal nitrene and azide at an intermediate stage has been suggested.[49]

The lithium salt of the DPTA dianion has some interesting properties. On treatment with methyl iodide it gives dimethyldiphenyltetrazine while proton solvents cause it to decompose to PhA and aniline:[69]



It follows from the data of X-ray diffraction analysis[69] that metal complexes with DPTA as the ligand are actually 2-tetrazene derivatives. For example, the following values of the bond lengths were for obtained for a palladium complex: 1.39 Å for N(1)—N(2); 1.26 Å for N(2)—N(3); and 1.37 Å for N(3)—N(4), which corresponds to two single and one double bond.

The formation of a fairly stable intermediate in reactions involving naphthylnitrenes is suggested by the data on the increase in yield in the dark of azo compounds when irradiated solutions are left to stand,[58] but there is no real evidence for a tetraazadiene structure. Hence, the second question—whether DPTA participates in the formation of AB—remains open.

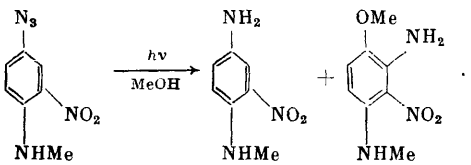
The structure of benzazirine that was widely discussed in earlier studies on the photochemistry of PhA is also not shown on the general scheme (Scheme 1) for interconversion of intermediates. The formation of condensed azirines during low-temperature photolysis of naphthyl azides was experimentally demonstrated from the appearance of bands in the region of 1700—1740 cm^{-1} in the IR

spectrum.[36] In similar studies of monocyclic aryl azides, the IR and UV spectroscopic data indicated the formation of DHA,[22,51,70] while UV and EPR spectroscopic data provided evidence for the formation of PhN^3.[13,17,19,51]

In order to resolve this contradiction, Leyva, et al.[51] suggested that the primary photolysis product is in fact PhN^3 and DHA is formed as a result of secondary photochemical reactions of nitrene. However, a recent examination of the results of low-temperature photolysis of PhA showed that this theory is only partly correct. In fact, on irradiation of PhA with light over a wide spectroscopic range ($\lambda > 210$ nm), including the region of PhN^3 absorption, the latter rapidly undergoes secondary reactions.[71] But photolysis with light at the region of the absorption minimum of PhN^3 (about 330 nm) also gave a mixture of DHA and PhN^3 in the ratio 1:4, whatever the concentration of PhA, matrix, or temperature. It was concluded that DHA, like PhN^3, is a primary photoproduct, namely at 12–45 K the proportion of "singlet" to "triplet" products formed at the same time is almost the inverse of that which occurs at 20 °C (we should recall that at 20 °C this proportion is equal to about 7:1).[27] An accurate knowledge of the composition of the photolysis products made it possible for Hayes and Sheridan[71] to record the IR spectrum of PhN^3 for the first time.

Thus, it is clear from the above that not a single method under any conditions has provided confirmation that benzazirine is formed during the photolysis of phenyl azide.

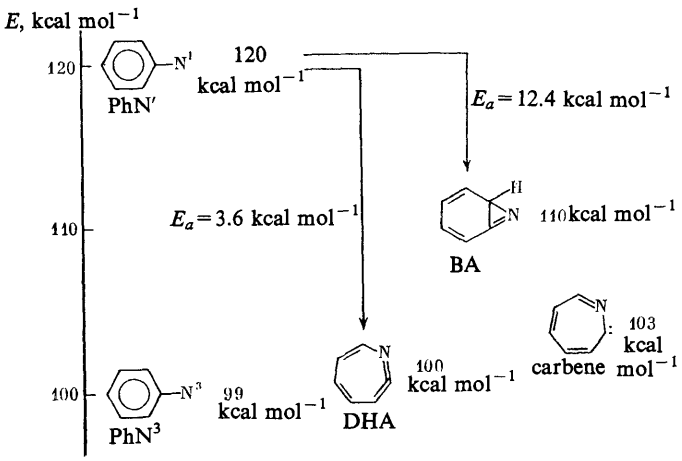
Indirect evidence for the existence of a benzazirine intermediate in the reactions of substituted PhA may possibly be provided by the results of a study by Nielsen and Buchardt,[72] in which during the photolysis of 3-nitro-4-methylamino-PhA migration of the nitrogen atom of the azide group to the *ortho* position of the benzene ring occurred and the corresponding isomeric anilines were isolated:



As was mentioned above, the most probable intermediate in this type of migration in a series of naphthyl azides is naphthazirine.[28,37] It should be noted that some of the findings of Nielsen and Buchardt[72] give rise to doubt. In the flash photolysis of PhA the authors did not succeed in detecting an intermediate with an absorption in the region above 300 nm, at variance with an earlier study[31] and more recent ones.[51,55,61]

Let us consider again the question of the tautomers of singlet PhA. After the unsuccessful attempts to find spectroscopic evidence for the formation of benzazirine, the only argument in favour of the existence of this intermediate was provided by the results of quantum-chemical calculations[34] which placed BA below DHA on the energy scale. Using this MNDO method[61] the potential energy surface for the interconversions of structures with the composition of PhN was calculated (Scheme 2).

Scheme 2



The calculated value of the singlet–triplet splitting (21 kcal mol^{-1}) is higher than the experimentally determined value of 4.3 kcal mol^{-1} for PhN, but Li, et al.[61] note that the MNDO method provides a reliable prediction of relative rather than absolute energy differences.

A more important result is that the calculated heat of formation of BA is 10 kcal mol^{-1} higher than that of DHA. Moreover, the energies of activation of the processes involving conversion of singlet PhN^1 to BA and DHA are equal to 12.4 and 3.6 kcal mol^{-1} respectively. Thus, calculations of both thermodynamic and kinetic criteria indicated the preference for a dehydroazepine structure as an intermediate, in complete agreement with the experimental results.

The reliability of this method was confirmed by calculations of the reaction route for 1-naphthylnitrene, for which it was found that, conversely (compared to PhA), naphthazirine is 10 kcal mol^{-1} more stable than the isomeric benzodehydroazepine and the activation barriers for their formation are equal to 3.1 and 13 kcal mol^{-1} respectively, which is also fully consistent with the experimental results.[36,37]

Li, et al.[61] subsequently considered the question of the possible structure of the intermediate "X" formed during interconversions of PhN^3 and DHA. It is generally assumed that the reaction occurs via PhN^1. In the opinion of the authors,[61] the intermediate conversion of DHA to a triplet carbene rather than PhN^1 is more probable. As an argument, use was made of the results of calculations in which it was found that the energy difference ΔE(carbene–DHA) = 3 kcal mol^{-1} was considerably less than the difference $\Delta E(PhN^1 - DHA)$ = 20 kcal mol^{-1}. The results of these calculations should evidently not be overrated. Starting from the experimentally determined value of the difference $\Delta E(PhN^1 - PhN^3)$ = 4.3 kcal mol^{-1}, $\Delta E(PhN^1 - DHA)$ should be less than 4.3 kcal mol^{-1}, i.e. singlet nitrene as well as triplet carbene could act as "X". We should note that even for the second excited singlet state of PhN the experimental difference $\Delta E(PhN^{*1} - PhN^3)$ = 8.8 kcal mol^{-1},[73] in other words, the calculated value for PhN^1 (21 kcal mol^{-1}) is considerably overestimated.

The quantum yield of dissociation of PhA under different conditions was determined by Budyka, et al.[74] It was shown that over a concentration range of $10^{-4} - 10^{-1}$ M the value of Φ_{-PhA} stays equal to less than one (0.4–0.5), which is in agreement with the study of Reiser and Marley[33] and at variance with the data of

Waddell, et al.[1-8] Also, in contrast to the latter[1-8] but in agreement with the studies of Schuster, et al.,[55,61] the polymer was predominant amongst the photolysis products of concentrated solutions and the yield of AB did not exceed 20%.

Table 1. Effect of conditions of photolysis of phenyl azide on the quantum yield of photodissociation (Φ) and the ratio of reaction products (in an inert medium unless shown otherwise).

Solvent	[PhA], M	T, K	Φ	Yield, %*				Refs.
				AB	aniline	insertion product	polymer	
Benzene	0.1	298	—	5	—	—	p	[24]
Acetic acid	0.1	298	—	—	—	21	—	[24]
Hexane	—	298	0.53	—	—	—	—	[33]
Benzene	0.01	293	—	50±3	5±2	<3	50±1	[27]
Cyclohexane	0.01	293	—	51±3	4±2	<3	48±7	[27]
Methanol	0.01	293	—	5±3	7±2	~80	0	[27]
Benzene, acetonitrile	—	303	—	i	i	—	p	[75]
Hexane	1×10^{-4}	293	—	t	t	t	p	[31]
Piperidine	—	293	—	—	—	35	—	[76]
Acetonitrile	1.3×10^{-4}	293	0.58(O_2)—	—	—	—	—	[7]
	0.125	293	2920(O_2)	—	—	—	—	[7]
	0.722	293	15 300	—	—	—	—	[7]
	1×10^{-4}	293	—	45	—	—	—	[55]
	4.4×10^{-3}	293	—	9	—	—	p	[55]
Diethylamine	—	273	—	0	0	80	—	[51]
	—	77	—	44**	28	0	—	[51]
Phenyl azide		293	—	—	—	—	15	[68]
Cyclohexane	5×10^{-3}	293	—	15	—	—	p	[61]
Acetonitrile	2×10^{-4}	293	0.5(O_2)	i	i	—	—	[74]
	0.1	293	—	20	i	—	p	[74]
	0.1	293	0.4(O_2)	13	i	—	p	[74]

*Based on PhA reacted; i = insignificant quantity; t = traces; p = predominant product; absence of quantitative data indicated by lines: **After keeping at 195 K.

Thus, we may summarise our discussion of the photochemical properties of phenyl azide. In Table 1 the available data on the quantum yields of photodissociation of PhA and the ratio of the reaction products under different conditions have been arranged in chronological order (by insertion product is meant both substituted 3*H*-azepines and anilines that are substituted in the benzene ring—both are formed in reactions of isomers of singlet PhN with nucleophiles). It is clear from Table 1 that the total results can be divided into two groups: the first is made up by the results of Waddell, et al., and the results of the remaining research workers are in the second group. Despite the spread and frequent absence of values of the quantum and chemical (preparative) yields, on the whole the results of the second group are consistent with each other and are markedly at variance with the results of the first group. Up to the present time no one apart from Waddell, et al. has succeeded in observing a value of $\Phi > 1$ in the photodissociation of aryl azides and the quantitative formation of azobenzene in the reactions of PhA.

V. Photochemical chain reactions of azides

We shall now consider the available data on other photochemical chain reactions involving organic azides.

In 1963 it was found in a study of the photolysis of methyl azide in the gas phase that the quantum yield for liberation of nitrogen—the main gaseous product—varied from 1.7 to 2.3 on changing the wavelength of incident light from 313 to 254 nm (30 °C, 300 mm Hg), but it did not depend on the light intensity, temperature, or pressure. Radical "traps" inhibited the process and the composition of the condensate corresponded to a polymer with the general formula $(MeN)_n$.[77]

It was suggested that the methylnitrene which is formed at the first stage then reacts with the initial azide:

$$MeN_3 \xrightarrow{h\nu} MeN + N_2,$$
$$MeN + MeN_3 \rightarrow (MeN)_2 + N_2.$$

The resulting compound, presumably azomethane, also reacts with nitrene and at a higher rate than the azide since, firstly, azomethane was not present in the final products and, secondly, the addition of azomethane to the reaction mixture reduced the quantum yield:

$$MeN + (MeN)_2 \rightarrow (MeN)_3.$$

However, these two reactions of nitrene could only explain values of Φ up to 1.5, so the reaction of thermally excited ("hot") nitrene with azide to form two nitrenes was also introduced:

$$MeN^* + MeN_3 \rightarrow 2MeN + N_2.$$

Confirmation of the formation of nitrene in an excited state, in the opinion of Currie and Darwent,[77] was the dependence of Φ on the wavelength of radiation and the considerable excess of energy of the absorbed quantum of light over the energy of dissociation of the N—N bond. A similar explanation—reactions of nitrene in a "hot" state—was introduced to interpret the effect of the wavelength of exciting light on the ratio of the photolysis products of 4-cyanophenyl azide.[67]

A somewhat different interpretation of the values of Φ greater than 1 in the gas-phase photolysis of methyl azide was later put forward.[48] It was suggested that nitrene reacts with azide to form azomethane and also an aminonitrene, which on reacting with azide gives the trimer, etc., subsequently producing the polymer:

$$MeN + MeN_3 \rightarrow MeNHCH_2N + N_2,$$
$$MeNHCH_2N + MeN_3 \rightarrow (MeN)_3 + N_2,$$
$$MeN + (MeN)_3 \rightarrow (MeN)_4 \ldots$$

In contrast to the gas-phase reaction, the quantum yield of photodissociation of methyl azide (and hydrazoic acid) in methanol solution increased with an increase in concentration and reached a maximum value of 2.1 at a concentration above 1 M.[78] The dependence of the molar absorption index of these compounds on concentration suggested that molecules of azides were associating with each other or with molecules of solvent. On the basis of kinetic analysis Koch[78] assumed that the azide does not decompose in a

monomolecular reaction to nitrene, but existing for a sufficient time in an excited state, reacts with another, unexcited molecule of azide, solvent or intermediates. It is interesting to note that the quantum yield for ethyl azide under similar conditions did not depend on the concentration of azide and was equal to unity.[78]

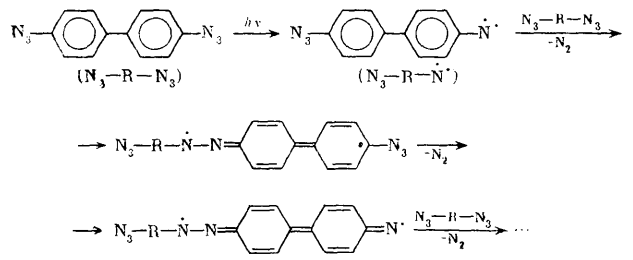
The thermolysis of PhA induced by chloromethyl radicals at 79.8 °C was autocatalytic in nature.[79] The sequence of stages of this reaction is similar to that proposed in the PACD reaction, if the radical nature of triplet PhN is assumed:

$$PhN_3+\dot{C}Cl_3 \rightarrow Ph-\dot{N}-N=N-CCl_3,$$
$$Ph-\dot{N}-N=N-CCl_3 \rightarrow Ph-\dot{N}-CCl_3+N_2.$$

Amongst the large number of nucleophilic substitution reactions known at present that are induced by electron transfer,[80] there are those that involve an azide. Thus, in the preparation of 4-nitrocumyl azide from the corresponding chloride and sodium azide it has been demonstrated that the substitution reaction is considerably accelerated when the reaction mixture is irradiated with light. The maximum quantum yield recorded was $\Phi \sim 6000$.[81] The dependence of Φ on the wavelength of incident light supported the conclusion that the first stage of the reaction is electron phototransfer within a charge-transfer complex between the cumyl chloride and azide ion followed by dissociation of the radical anion of the chloride and reaction with a second azide ion:

$$RCl+N_3^- \rightleftharpoons (RCl\cdot N_3^-),$$
$$(RCl\cdot N_3^-) \xrightarrow{h\nu} (RCl^{\cdot-}, N_3^{\cdot}),$$
$$RCl^{\cdot-} \rightarrow R^{\cdot}+Cl^-,$$
$$R^{\cdot}+N_3^- \rightarrow RN_3^{\cdot-},$$
$$RN_3^{\cdot-}+RCl \rightarrow RN_3+RCl^{\cdot-},$$
$$R=NO_2-C_6H_4-C(CH_3)_2- .$$

A polymer is formed in the photolysis of aromatic diazides in the crystalline stage. It has been suggested that the reaction may occur by a linear (nonbranching) chain mechanism, as, for example, that of diazidobiphenyl:[82]



Zelentsov, et al.[82] suggested that the conditions needed for this mechanism to occur are: firstly, a triplet state of the nitrene, which prevents the recombination of the adduct at the second stage of the reaction to an azo compound; secondly, a conjugation chain for intramolecular transfer of spin to the α-position of the second azide group; and thirdly, proximity of the nitrene to the azide group of the neighbouring molecule, which is determined by the packing of the diazide molecules in the crystal.

Theoretical calculation of the densest packing of the molecules of diazidobiphenyl in the crystal demonstrated the possibility for achieving a favourable molecular configuration. The fact that it is for this diazide (from the series of those studied), in which all three conditions are met, that the maximum yield of polymer occurred was considered to be experimental confirmation of a chain mechanism of decomposition.

In a study of the pyrene-sensitised photodissociation of 4-dimethylaminocarbonylphenyl azide in acetonitrile it was shown that the reaction is initiated by electron transfer from pyrene to azide with subsequent decomposition of the azide radical anion (Pyr = pyrene):[83]

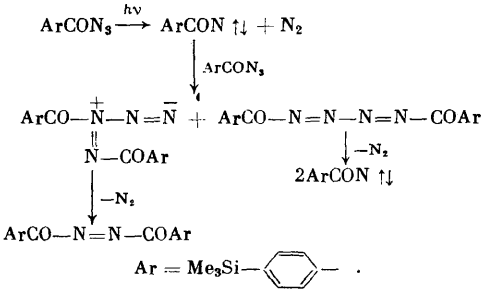
$$ArN_3 \xrightarrow{h\nu/Pyr} ArN_3^{\cdot-} \longrightarrow ArN^{\cdot-} + N_2,$$
$$Ar=Me_2NCO-C_6H_4- .$$

In order to account for the exclusive formation of an azo compound during the sensitised photolysis, Schuster, et al.[83] suggested that, in addition to dimerisation of nitrene, the nitrene radical anion may give rise to a chain reaction of azide decomposition.

A chain process initiated by 4-nitro-PhA radical anions was found in the electrochemical decomposition of this azide in the presence of weak methylene acids such as diethyl malonate.[84,85] Reaction resulted in the transfer of a diazo group from azide to ester to form aniline and diazoalkane, while the passage of not more 0.1 Coulomb mol^{-1} was sufficient for a quantitative yield of products:

$$ArN_3 + \bar{e} \rightleftarrows ArN_3^{\cdot-} \xrightarrow[-N_2]{SH} ArNH^-,$$
$$ArNH^-+H_2C(CO_2Et)_2 \rightleftharpoons ArNH_2+H\bar{C}(CO_2Et)_2,$$
$$ArN_3+H\bar{C}(CO_2Et)_2 \rightleftharpoons ArNH^-+N_2=C(CO_2Et)_2,$$
$$Ar = NO_2-C_6H_4- .$$

In 1989 the PACD reaction of an acyl azide—4-trimethylsilylbenzoyl azide—was reported. Abraham, et al.[86] found that the quantum yield of photodissociation of this azide in cyclohexane reached a value of $\Phi = 3-4$ at azide concentrations of 0.01–0.1 M; in dilute solution, as in the case of unsubstituted benzoyl azide, $\Phi < 1$ was obtained. With reference made to a study of Waddell, et al.,[5] the following reaction scheme was proposed:



In contrast to the earlier study,[5] the chain carrier was assumed to be singlet nitrene, although triplet is postulated as the ground state of nitrene (for a number of aroyl azides it was shown that singlet is the

ground state).[87,88] Isocyanate and cyclohexylamide, which were isolated as reaction products, are obtained from excited singlet azide and singlet nitrene. No products derived from triplet nitrene could be detected.

In support of their proposed reaction scheme, Abraham, et al.[86] refer to a study of Lwowski, et al.[89] in which photolysis of pure liquid ethyl azidoformate results in the isolation of an azo compound. However, it is shown by a special experiment in this study[89] that the reaction between thermally generated nitrene and azide does not result in the formation of an azo compound. It should be noted that in this case as well, there is no need to introduce this reaction in order to explain the values of $\Phi > 1$.

If it is assumed that the initiator of a chain process, if it exists, is triplet nitrene, it is possible that fluorinated PhA derivatives would be suitable substrates for the PACD reaction, since it has been demonstrated for them that singlet nitrene is not isomerised to DHA (or BA) but is quantitatively converted to the triplet state.[90] In studies of the chemical properties of fluorophenyl azides it was found that one of the main reaction products, and the predominant one in some cases, is the corresponding fluoroazobenzene.[91,92] However, there is no information about the quantum yields of photodissociation of these products.

---o0o---

Thus, the literature data on the photoinitiated autocatalytic chain decomposition reaction of azides are contradictory, and it is evidently premature to say for certain that such a reaction may occur.

It can be stated that the main detected primary products of the photolysis of phenyl azide are dehydroazepine and triplet nitrene in the ratio of about 7:1 at 20 °C and about 1:4 below 77 K. Aromatic azo compounds may be formed both by dimerisation of nitrene and from its reaction with azide.

With regard to the reaction routes during photolysis of phenyl azide, it would appear that a complete picture of the possible intermediates and the ways in which they are interconverted has been built up, and the discussion about the photochemical properties of this compound can be brought to a close. However, new questions have arisen with the development and research application of novel physicochemical methods.

Recently high-resolution pulsed laser photolysis was used to study the rotational and spin structure of the electronic transition in the spectrum that was attributed to phenylnitrene,[93] and it was concluded that the data obtained were difficult to correlate with what was expected for phenylnitrene. Although the results of studies in the gas phase cannot be completely transposed to reactions in condensed media, Cullin, et al.[93] consider that with this lack of confirmation of a nitrene structure for the intermediate, it will be necessary to make a careful check of all the previously obtained data.

In our view, the aromatic azide with the simplest structure has proved to be probably the most complex in terms of its properties.

References

1. W H Waddell, C Lee Go *J. Am. Chem. Soc.*, 1982, **104** 5804
2. N B Feilchenfeld, W H Waddell *Chem. Phys. Lett.*, 1983, **98** 190
3. W H Waddell, N B Feilchenfeld *J. Am. Chem. Soc.*, 1983, **105** 5499
4. C Lee Go, W H Waddell *J. Org. Chem.*, 1983, **48** 2897
5. C H Lee Go, W H Waddell *J. Am. Chem. Soc.*, 1984, **106** 715
6. N B Feilchenfeld, W H Waddell *Chem. Phys. Lett.*, 1984, **106** 297
7. J P Costantino, H W Richter, C H Lee Go, W H Waddell *J. Am. Chem. Soc.*, 1985, **107** 1744
8. R F Jenkins, W H Waddell, H W Richter *J. Am. Chem. Soc.*, 1987, **109** 1584
9. P A S Smith *Azides and Nitrenes, Reactivity and Utility* (Edited by E F V Scriven), Academic Press, Orlando, 1984, p. 95
10. L Eggert, M G Kuzmin, V L Ivanov *Z. Chem.*, 1990, **30** 9
11. E F V Scriven, K Turnbull *Chem. Rev.*, 1988, **88** 298
12. G Smolinsky, E Wasserman, W A Yager *J. Am. Chem. Soc.*, 1962, **84** 3220
13. E Wasserman, G Smolinsky, W A Yager *J. Am. Chem. Soc.*, 1964, **84** 3166
14. R M Moriarty, M Rahman, G J King *J. Am. Chem. Soc.*, 1966, **88** 842
15. J H Hall, J M Fargher, M R Gisler *J. Am. Chem. Soc.*, 1978, **100** 2029
16. A Reiser, V Fraser *Nature (London)*, 1965, **208** 682
17. A Reiser, G Bowes, R J Horne *Trans. Faraday Soc.*, 1966, **62** 3162
18. H Kashiwagi, S Iwata, T Yamaoka, S Nagakura *Bull. Chem. Soc. Jpn.*, 1973, **46** 417
19. S B Brichkin, V A Smirnov, M V Alfimov, et al. *J. Photochem.*, 1980, **12** 25
20. O L Chpman, J P Le Roux *J. Am. Chem. Soc.*, 1978, **100** 282
21. O L Chapman, R S Sheridan, J P Le Roux *J. Am. Chem. Soc.*, 1978, **100** 6245
22. O L Chapman, R S Sheridan, J P Le Roux *Recl. Trav. Chim. Pays-Bas*, 1979, **98** 334
23. V A Smirnov, S B Brichkin *Chem. Phys. Lett.*, 1982, **87** 548
24. W E Doering, R A Odum *Tetrahedron*, 1966, **22** 81
25. J S Splitter, M Calvin *Tetrahedron Lett.*, 1968, 1445
26. J S Swenton, T J Ikeler, B H Williams *J. Am. Chem. Soc.*, 1970, **92** 3103
27. A Reiser, L Leyshon *J. Am. Chem. Soc.*, 1971, **93** 4051
28. S E Hilton, E F R Scriven, H Suschitzky *J. Chem. Soc., Chem. Commun.*, 1974, 853
29. A Reiser, G C Terry, F W Willets *Nature (London)*, 1966, **211** 410
30. A Reiser, F W Willets, G C Terry, et al. *Trans. Faraday Soc.*, 1968, **64** 3265
31. B A DeGraff, D W Gillespie, R J Sundberg *J. Am. Chem. Soc.*, 1974, **96** 7491
32. R J Sundberg, S R Suter, M Brenner *J. Am. Chem. Soc.*, 1972, **94** 513
33. A Reiser, R Marley *Trans. Faraday Soc.*, 1968, **64** 1806
34. D D Shillady, C Trindle *Theor. Chim. Acta*, 1976, **43** 137
35. R A Abramovitch, B A Davis *Chem. Rev.*, 1964, **64** 149
36. I R Dunkin, P C P Thomson *J. Chem. Soc., Chem. Commun.*, 1980, 499
37. J Rigaudy, C Igier, J Barcelo *Tetrahedron Lett.*, 1975, 3845
38. P A S Smith *Nitrenes* (Edited by Y Lwowski), Wiley, New York, 1970, p. 99
39. E F V Scriven *Reactive Intermediates* (Edited by R A Abramovitch), Plenum Press, New York, 1982, p. 1

40. H Durr, H Kober *Top. Curr. Chem.*, 1976, **66** 89
41. L Horner, A Christmann, A Gross *Chem. Ber.*, 1963, **96** 399
42. P A S Smith, H Duonchis *J. Org. Chem.*, 1973, **38** 2958
43. R A Abramovitch, S R Challand, E F V Scriven *J. Am. Chem. Soc.*, 1972, **94** 1374
44. R A Abramovitch, S R Challand, E F V Scriven *J. Org. Chem.*, 1972, **37** 2705
45. B Iddon, O Meth-Cohn, E F V Scriven, et al. *Angew. Chem., Int. Ed. Engl.*, 1979, **18** 900
46. P A Lehman, R S Berry *J. Am. Chem. Soc.*, 1973, **95** 8614
47. W D Crow, C Wentrup *Tetrahedron Lett.*, 1967, 4379
48. A Reiser, H M Wagner *The Chemistry of the Azido Group* (Edited by S Patai), Interscience, New York, 1971, p. 441
49. P Overbosch, G van Koten, O Overbeek *J. Am. Chem. Soc.*, 1980, **102** 2091
50. R N McDonald, A K Chowdhury *J. Am. Chem. Soc.*, 1980, **102** 5118
51. E Leyva, M S Platz, G Persy, J Wirz *J. Am. Chem. Soc.*, 1986, **108** 3783
52. T V Liang, G B Schuster *J. Am. Chem. Soc.*, 1986, **108** 546
53. M W Geiger, M M Elliot, V D Karacostas, et al. *Photochem. Photobiol.*, 1984, **40** 545
54. A Reiser, L Leyshon *J. Am. Chem. Soc.*, 1970, **92** 7487
55. A K Shrock, G B Schuster *J. Am. Chem. Soc.*, 1984, **106** 5228
56. F D Lewis, W H Saunders, Jr. *J. Am. Chem. Soc.*, 1968, **90** 7033
57. L Leyshon, A Reiser *J. Chem. Soc., Faraday Trans. 2*, 1972, **68** 1918
58. A K Shrock, G B Schuster *J. Am. Chem. Soc.*, 1984, **106** 5234
59. T V Liang, G B Schuster *J. Am. Chem. Soc.*, 1987, **109** 7803
60. C J Shields, D R Chrisope, G B Schuster, et al. *J. Am. Chem. Soc.*, 1987, **109** 4723
61. Z-Y Li, J P Kirby, M W George, et al. *J. Am. Chem. Soc.*, 1988, **110** 8092
62. T Kobayashi, H Ohtani, K Suzuki, T Yamaoka *J. Phys. Chem.*, 1985, **89** 776
63. M Sumitani, S Nagakura, K Yoshihara *Bull. Chem. Soc. Jpn.*, 1976, **49** 2995
64. M Tsuda, S Oikawa, K Nagayama *Photogr. Sci. Eng.*, 1983, **27** 118
65. C Wentrup *Reactive Intermediates* (Edited by R A Abramovitch), Plenum Press, New York, 1980, Part 1, p. 263
66. R A Abramovitch, E P Kyba *The Chemistry of the Azido Group* (Edited by S Patai), Interscience, New York, 1971, p. 221
67. R A Odum, G Wolf *J. Chem. Soc., Chem. Commun.*, 1973, 360
68. E W Meijer, S Nijhuis, F C B M van Vroonhoven *J. Am. Chem. Soc.*, 1988, **110** 7209
69. S W Lee, G A Miller, Ch F Campana, et al. *J. Am. Chem. Soc.*, 1987, **109** 5050
70. T Donelly, I R Dunkin, D S D Norwood, et al. *J. Chem. Soc., Perkin Trans. 2*, 1985, 307
71. J S Hayes, R S Sheridan *J. Am. Chem. Soc.*, 1990, **112** 5879
72. P E Nielsen, O Buchardt *Photochem. Photobiol.*, 1982, **35** 317
73. P S Drzaic, J I Brauman *J. Am. Chem. Soc.*, 1984, **106** 3443
74. M F Budyka, M M Kantor, M V Alfimov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1992(3)
75. R A Abramovitch, S R Challand *J. Chem. Soc., Chem. Commun.*, 1972, 964
76. S E Carroll, B Nay, E F V Scriven, H Suschitzky *Tetrahedron Lett.*, 1977, 943
77. C L Currie, B De B Darwent *Can. J. Chem.*, 1963, **41** 1552
78. E Koch *Tetrahedron*, 1967, **23** 1747
79. J E Leffler, H H Gibson, Jr. *J. Am. Chem. Soc.*, 1968, **90** 4117
80. W R Bowman *Photoinduced Electron Transfer* (Edited by M A Fox, M Chanon) Elsevier, Amsterdam, 1988, Part C, p. 487
81. P A Wade, H A Morrison, N Kornblum *J. Org. Chem.*, 1987, **52** 3102
82. S V Zelentsov, A V Oleinik, L N Karyakina *Khim. Vys. Energ.*, 1986, **20** 339
83. C J Shields, D E Falvey, G B Schuster, et al. *J. Org. Chem.*, 1988, **53** 3501
84. D E Herbranson, M D Hawley *J. Electroanal. Chem.*, 1983, **144** 423
85. D E Herbranson, M D Hawley *J. Org. Chem.*, 1990, **55** 4297
86. W Abraham, S Stiegert, D Kreysig *J. Prakt. Chem.*, 1989, **331** 177
87. T Autrey, G B Schuster *J. Am. Chem. Soc.*, 1987, **109** 5814
88. I Woelfle, B Saverinein, T Autrey, G B Schuster *Photochem. Photobiol.*, 1988, **47** 497
89. W Lwowski, T W Mattingly, T J Maricich *Tetrahedron Lett.*, 1964, 1591
90. I R Dunkin, P C P Thomas *J. Chem. Soc., Chem. Commun.*, 1982, 1192
91. E Leyva, M J T Young, M S Platz *J. Am. Chem. Soc.*, 1986, **108** 8307
92. E Leyva, D Munoz, M S Platz *J. Org. Chem.*, 1989, **54** 5938
93. D W Cullin, L Yu, J M Williamson, et al. *J. Phys. Chem.*, 1990, **94** 3387

Translated from *Uspekhi Khimii* 61 75–101 (1992) U.D.C. 547.412

Iodoperfluoroalkanes

L E Deev, T I Nazarenko, K I Pashkevich, V G Ponomarev
Institute of Chemistry of the Bashkir Scientific Centre, Urals Branch of the Russian Academy of Sciences, Sverdlovsk
Perm Branch of the State Institute of Applied Chemistry

ABSTRACT. **In this review the methods for preparing iodoperfluoroalkanes and their chemical properties, namely, radical addition to the carbon–carbon multiple bonds of unsaturated compounds with functional groups, reactions with elements of groups IV–VI and their compounds, cleavage of single bonds by an R_f radical, oxidation of iodoperfluoroalkanes with degradation of the perfluoroalkyl chain or formation of iodonium derivatives, the formation of charge-transfer complexes, and α-halodefluorination reactions are examined. The uses of iodoperfluoroalkanes are described.**

The bibliography includes 285 references.

Contents

I. Introduction 40
II. Preparation of iodoperfluoroalkanes 40
III. Chemical properties of iodoperfluoroalkanes 44
IV. Use of iodoperfluoroalkanes and perfluorinated iodine-containing ethers 49
V. Conclusion 50

I. Introduction

The iodoperfluoroalkanes (IPFAs) CF_3I and C_2F_5I were first prepared at the end of the 1940s for use in the synthesis of organomercury compounds.[1] This marked the beginning of extensive research into perfluoroalkyl derivatives. The use of IPFAs in the syntheses of organic and organoelemental compounds demonstrated their potential as perfluoroalkylating agents[2–6] and reagents for telomerisation.[7] Separate applications for IPFAs in laser,[8–15] electronics,[16] and other fields of engineering[17–19] were progressively established, stimulating further research into preparative methods and a study of their reactivity. At the present time IPFAs are key products in a number of countries for the industrial synthesis of organofluorine compounds and for preparing the initial compounds in the production of drugs and surfactants and the components of artificial blood.[16]

Prominent amongst IPFAs are tertiary iodoperfluoroalkanes,[20,21] which have future potential as working solids for gas lasers.[11]

However, the monographs that are currently available on the chemistry of organofluorine compounds[6,7,16,22–24] do not give a sufficiently clear idea of the methods of synthesis, reactivity, or application of iodoperfluoroalkanes.

In this review an attempt is made to provide a correlated report on the preparative and synthetic methods for obtaining IPFAs and their chemical properties and applications.

With the exception of alkenes with functional groups, reactions of IPFAs with alkenes, which are described in sufficient detail in one monograph,[7] are not covered by the present review. We have made perfluoroalkylation reactions, which are of very considerable synthetic importance and involve extensive literature material, the subject of a separate review.

II. Preparation of iodoperfluoroalkanes

1. Exchange or addition of halogens

Iodoperfluoroalkanes, in particular CF_3I, were first obtained by fluorination of tetraiodomethane.[1] Because of the difficulty in obtaining periodides, this method has more historic significance than preparative value.

$$CI_4 \xrightarrow[20-100^\circ C]{IF_5} CF_3I. \quad 95\%$$

Some considerable time later 2-iodoperfluoro-2-methylpropane was successfully obtained by trifluoromethylation of CI_4 in a glow discharge:[25]

$$CI_4 + CF_3{-}CF_3 \xrightarrow[30\ mm\ Hg]{glow\ discharge} (CF_3)_3CI. \quad 55\%$$

$(CF_3)_3CI$ was synthesised in low yield from 2-bromo-perfluoro-2-methylpropane.[27]

$$(CF_3)_3CBr + NaI \xrightarrow[refluxing]{CH_3CN} (CF_3)_3CI. \quad 5.5\%$$

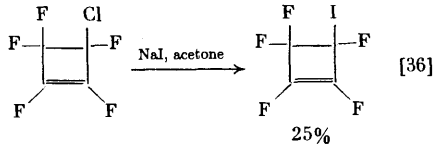
The replacement of iodine in diiodopolyfluoroalkanes is of somewhat greater importance. Usually the reaction consists of the formation of an α,β-diiodoperfluorocarbon by iodination of the corresponding perfluoroalkene followed by replacement of one of the iodine atoms by fluorine. For the substitution reaction use is made of iodine pentafluoride,[1] mixed halofluorides of pentavalent antimony or sulphur tetrafluoride,[28,29] electrochemical fluorination in anhydrous HF,[30,31] and fluorination with hydrogen fluoride in the presence of the catalysts $HF-H_2SO_4$, I_2-HNO_3, $I_2-SO_2Cl_2$ [32] or metal oxides.[33,34]

$$CF_2{=}CF_2 \xrightarrow{I_2} ICF_2CF_2I \longrightarrow \underset{75-100\%}{CF_3CF_2I}.$$

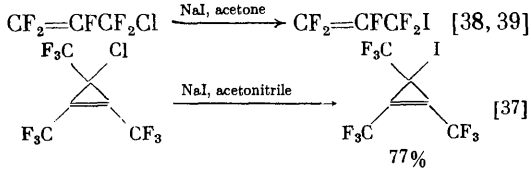
Iodotrifluoromethane labelled with ^{18}F isotope was obtained in 3% yield on treatment of tetrafluoromethane with a mixture of I_2 and $^{18}F_2$:[35]

$$CF_4 \xrightarrow{^{18}F_2+I_2} CF_2{}^{18}FI.$$

Replacement of chlorine at an allylic position by iodine in cyclic and aliphatic chloroperfluoroalkenes is achieved by treatment with sodium iodide in solution at room temperature. Replacement of fluorine on sp^2-hybridised carbon does not occur in this case.[36–39]



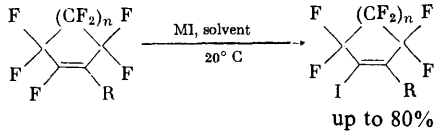
[36]



[38, 39]

[37]

At the same time substitution of a fluorine atom at a vinyl position mainly occurs for perfluorinated cycloalkenes.[40–42] This forms the basis of the preparation of iodoperfluorocycloalkenes by treatment of the respective perfluorocycloalkenes with potassium iodide[40] or sodium iodide[41–43] in a polar solvent. At an elevated temperature the formation of diiodoperfluorocycloalkenes along with the monosubstituted derivative is possible.[43]



,

n = 1, 2; R = CF_3, F; M = Na, K.

At the same time when a fluorine and chlorine atom occur on an sp^2-hybridised carbon it is the chlorine atom which is replaced,[44,56] which corresponds to the order of replacement at an allylic position.

$$(CF_3)_2C{=}CFCl \xrightarrow[\text{refluxing}]{\text{NaI, acetone}} (CF_3)_2C{=}CFI.$$

60%

On treatment of tetraiodoethylene with iodine pentafluoride, addition of fluorine to the double bond takes place together with the replacement of three iodine atoms leading to the formation of iodopentafluoroethane.[1] This method has no preparative value.

$$CI_2{=}CI_2 \xrightarrow[0-130^\circ C]{IF_5} CF_3{-}CF_2I.$$

26%

An interesting case of the formation of iodopentafluoroethane on treatment of iodotrifluoroethylene with an $F_3NO.BF_3$ complex at low temperatures has been reported in a patent.[46]

$$CF_2{=}CFI \xrightarrow[-196^\circ C]{F_3NO\cdot BF_3} CF_3CF_2I.$$

2. Preparation from derivatives of perfluorocarboxylic acids

The slow heating of anhydrous silver perfluoroalkanecarboxylates with a slight excess of iodine (the Borodin–Hunsdiecker reaction) affords the corresponding iodoperfluoroalkanes in high yield.[47,48] The reaction is versatile and can be used to synthesise not only aliphatic[47] but also cyclic[22] and perfluoroalkoxyl iodides[49] as well as diiodoperfluorocarbons (in the case of dibasic acids).[22] This method is important industrially—for the production of CF_3I, for example.

It is assumed[50] that the Borodin–Hunsdiecker reaction occurs via the formation of acyl hypoiodites.

$$R_fCOOAg \xrightarrow{I_2} [R_fCOOI + AgI] \longrightarrow R_fI + AgI + CO_2$$

$R_f{=}C_nF_{2n+1}$ [47], $CF_3OCF_2CF_2$ [49],

$I(CF_2)_n$, cyclo-C_8F_{11} [22].

Iodoperfluoroalkanes can also be obtained from salts of alkali metals[51] or mercury,[52] but in lower yield. The reaction is usually carried out in an aprotic polar solvent. When iodine is replaced by the more polar iodine monochloride in this reaction, the yield of IPFAs does not increase.[53] The two-stage nature of the process and the length of time needed for evaporation and drying of the intermediate salts have impeded the application of this method in industry.

Iodoperfluoroalkanes are also formed by the decomposition of perfluorocarboxylic acid derivatives. Thus, electrolysis of trifluoroacetyl hypoiodite[54] or the decomposition of trifluoroacetyl iodide at room temperature in the presence of hexamethyldistannane[55] gives iodotrifluoromethane in low yield.

$$CF_3COOI \xrightarrow{\text{electrolysis}} CF_3I \xleftarrow{(CH_3)_3Sn-Sn(CH_3)_3} CF_3COI.$$

A method for the synthesis of higher iodoperfluoroalkanes by reaction of the corresponding acids with iodine and benzoyl peroxide has been developed.[56–59] The reaction is radical in nature and takes place in a nonpolar solvent (dibromo- or dichloro-ethane, dibromopropane). The method of preparing IPFAs as described in a patent[56] has industrial value.

$$F(CF_2)_7COOH \xrightarrow[BrCH_2CH_2Br;\ 110^\circ C]{I_2 + (C_4H_9COO)_2} F(CF_2)_7I \quad .$$

60%

3. Preparation from perfluoroalkenes

Because of the ready availability of lower perfluoroalkenes, iodotrifluoromethane, and iodofluorinating agents at the present time, the synthesis of IPFAs from perfluoroalkenes has assumed increasing importance and has been developed in three areas: electrophilic iodofluorination, nucleophilic iodofluorination, and telomerisation of perfluoroalkenes with iodotrifluoromethane and iodopentafluoroethane.

Electrophilic iodofluorination. This was first reported in the case of tetrafluoroethylene (TFE) when a mixture of iodine and iodine pentafluoride was used.[60–62] The reaction takes place via the formation of a carbocation on addition of iodine to the alkene. The reaction is suitable for alkenes with different structures,[63,64] including

perfluoroisobutene[65,66] and perfluoromethylvinyl ether.[67] High yields of the products were obtained (Table 1).

$$R^1R^2C{=}CF_2 + [I{-}F] \xrightarrow{(IF_5+2I_2)} [R^1R^2C\overset{+}{C}F_2] \xrightarrow{F^-} R^1R^2ClCF_3.$$

Iodopentafluoroethane was obtained at 60–80 °C and atmospheric pressure in 90% yield. The conversion of tetrafluoroethylene was 40%.[68] The latter increases on introducing catalysts such as metals[73] or their salts[69–72] into the iodofluorinating mixture. Metal fluorides[69–71] are recognised as the most effective catalysts of the electrophilic iodofluorination of TFE. The methods reported in two Japanese patents[70,71] have been used in the industrial production of iodopentafluoroethane.

Table 1. Yields of products of the iodofluorination of $R^1R^2C{=}CF_2$

R^1	R^2	Yield, %	R^1	R^2	Yield, %
H	F	76*	F	CF_3O	94
Cl	F	95*	F	CF_3	69
F	F	99	F	F	90
F	CF_3	69	F	F	70

*Total yield of isomers is given.

Electrophilic iodofluorination of excess TFE with a mixture of iodine and iodine pentafluoride in the presence of antimony fluorides gives a mixture of telomeric IPFAs[74–77] with a small quantity of C_2F_6:

$$CF_2{=}CF_2 \xrightarrow[[SbF_5;\ SbF_3]]{I_2+IF_5} F(CF_2CF_2)_nI + ICF_2CF_2I + \text{cyclo-}C_4F_8 + C_2F_6,$$

$$n=1-8.$$

Iodoperfluoroalkane polyfluorides have been proposed for the electrophilic iodofluorination of hexafluoropropene (HFP).[78]

The principles of the electrophilic addition of interhalogen compounds have been reviewed.[79]

Nucleophilic iodofluorination. This was first put forward by several authors[80–82] in the 1960s and is achieved in aprotic polar solvents on heating. The reaction is initiated with the addition of a fluoride anion to perfluoroalkene. Thus, for example, 2-iodoperfluoropropane is obtained by reaction of HFP with iodine and potassium fluoride in acetonitrile at 100 °C in an autoclave.[80]

$$CF_3CF{=}CF_2 \xrightarrow[CH_3CN]{KF} CF_3{-}\overline{C}F{-}CF_3 \xrightarrow[CH_3CN]{I_2} \underset{60\%}{CF_3CFICF_3}.$$

Even perfluoro-2-butene,[80] which is extremely stable towards iodofluorination,[63] reacts under such conditions. The nucleophilic iodofluorination of perfluoroisobutene takes place the most readily,[82–84] giving 2-iodoperfluoro-2-methylpropane in high yield. In this case even bound iodine (from an organic compound) adds to the intermediate perfluoro-t-butylcarbanion.[85–87]

$$(CF_3)_2C{=}CF_2 \xrightarrow{CHI_3+KF} \underset{7\%}{(CF_3)_3CI}.$$

Iodoperfluorocyclobutane is formed in a nucleophilic iodofluorination reaction of perfluorocyclobutene.[80] Conjugated nucleophilic addition of (IF) to perfluoro(methyl vinyl ether) only occurs under severe conditions, giving 1-iodoperfluoro-1-methoxyethane in negligible yield.[67] Lur'e, et al.[67] attribute this to destabilisation of the intermediate $CF_3O\overline{C}FCF_3$ by the electron pair of the neighbouring oxygen. An industrial method for the iodofluorination of TFE using hydrogen fluoride and lead(II) oxide has been reported in a French patent.[88]

$$CF_2{=}CF_2 \xrightarrow[200^\circ C]{I_2,\ HF,\ PbO} \underset{90\%}{CF_3CF_2I}.$$

2-Iodoperfluoro-2-butene has been obtained in a similar manner from perfluoro-2-butyne.[89]

$$CF_3C{\equiv}CCF_3 \rightarrow CF_3CF{=}ClCF_3.$$

A modification of this reaction occurs in the preparation of iodoperfluoroalkoxyalkanes with a branched chain[90,91] by reaction of hexafluoroacetone with the respective alkene and I_2 in the presence of excess alkali metal fluoride in a solvent.[90–95]

$$(CF_3)_2C{=}O \xrightarrow{F^-} (CF_3)_2CF{-}O^- \xrightarrow{RCF=CF_2} (CF_3)_2CFOCF_2\bar{C}FR \xrightarrow{I_2} \rightarrow (CF_3)_2CFOCF_2CFIR.$$

R=F (17%), CF_3 (13%) [89].

The nucleophilic iodofluorination of perfluoroalkenes has been studied in greater detail in a review by Joung,[96] and the mechanism of the reaction between alkoxide anion and fluorine-containing alkenes in the presence of iodine is examined in a report by Evans, et al.[97]

Radical iodofluorination. Radical iodofluorination of perfluoroalkenes has not been used very extensively. Only the preparation of 2-iodoperfluoropropane from hexafluoropropane has been reported.[98]

$$CF_3CF{=}CF_2 \xrightarrow{F_2+I_2} \underset{60\%}{CF_3CFICF_3}.$$

With the methods for preparing iodoperfluoroalkanes and iodoperfluoroalkoxyalkanes examined above it is possible to obtain mainly compounds with a short carbon chain containing up to eight carbon atoms.

Radical addition. For the synthesis of higher IPFAs, radical addition of lower iodoperfluoroalkanes and iodoperfluoroalkoxyalkanes to perfluoroalkenes is normally used, frequently with

oligomerisation of the latter occurring at the same time. The process is usually carried out in solution under pressure in the presence of metal salts.[99–102]

Thus, IPFAs with 5–29 carbon atoms in the chain have been obtained by addition of CF_3I to TFE.[102] This method is important industrially. However, on exposure to radiation IPFAs are formed containing not more than 11 carbon atoms in the chain.[103] Higher IPFAs are also obtained by electrophilic iodofluorination of TFE[76] together with C_2F_5I (see above). These methods have future potential for the production of higher perfluorocarboxylic acids from the corresponding IPFAs.[104]

The addition of CF_3I to HFP is not regiospecific and occurs with a low conversion. The formation of specific products depends on the conditions. Thus, Deev, et al,[27] on conducting the reaction in a nickel tube at a temperature of up to 380 °C, succeeded in obtaining about 77% 2-iodoperfluoro-2-methylpropane.

$$CF_3I + CF_3CF{=}CF_2 \xrightarrow{h\nu} CF_3CFIC_2F_5 + (CF_3)_2CFCF_2I \quad [105]$$
$$80\% \qquad 20\%$$
$$CF_3I + CF_3CF{=}CF_2 \xrightarrow[320-380^\circ C]{[Ni]} CF_3CFIC_2F_5 + (CF_3)_2CFCF_2I + (CF_3)_3CI \quad [27]$$
$$9\% \qquad 6\% \qquad 77\%$$

It was possible to obtain trifluoromethyl-substituted IPFAs containing more than 33 carbon atoms from HFP and higher IPFAs by oligomerisation on exposure to radiation.[106] Branched perfluoroalkenes containing more than three carbon atoms on exposure to radiation with iodotrifluoromethane give products derived from the replacement of fluorine at vinyl and allyl positions together with addition products.[107]

$$CF_3I + (CF_3)_2CFCF{=}CF_2 \xrightarrow{h\nu}$$
$$\longrightarrow (CF_3)_2CFCFICF_2CF_3 \quad 22\%$$
$$\longrightarrow (CF_3)_2CFCF(CF_3)CF_2I \quad 5\%$$
$$\longrightarrow (CF_3)_2CFCI{=}CF_2 \quad 16\%$$
$$\longrightarrow (CF_3)_2C{=}CFCF_2I \quad 12\%$$
$$\longrightarrow (CF_3)_2CFCFICF_3 \quad 2\%$$

Oligomerisation of tetrafluoroethylene with C_2F_5I in the presence of antimony pentafluoride or organic peroxides under pressure and at an elevated temperature[108,109] gives IPFAs with an even number of carbon atoms in the chain.

$$C_2F_5I + nCF_2{=}CF_2 \xrightarrow[(CCl_2{=}CClCOO)_2]{65-75\ ^\circ C,\ 7-10\ atm} C_2F_5(CF_2CF_2)_nI \quad n=1-5,\ 95-97\%$$
$$C_2F_5I + nCF_2{=}CF_2 \xrightarrow[(C_6H_5COO)_2]{125^\circ C} C_2F_5(CF_2CF_2)_nI \quad n=5-7,\ 95\%$$

Both of the isomeric iodoperfluoropropanes undergo a similar reaction, forming IPFAs with 21–25 carbon atoms.[110,111] IPFAs with an isomeric structure containing from 5 to 23 carbon atoms are obtained by oligomerisation of $(CF_3)_2CFI$ with TFE in the presence of peroxides.[110,112,113] In the absence of catalysts IPFAs can be obtained under pressure.[114]

The aqueous-emulsion oligomerisation of TFE with $(CF_3)_2CFI$ or C_2F_5I at 15–30 °C in the presence of ammonium persulphate or emulsifying agents has been reported.[115]

$$(CF_3)_2CFI + nCF_2{=}CF_2 \xrightarrow[[NaHSO_4+C_8F_{17}COONH_4]]{[(NH_4)_2S_2O_8]} (CF_3)_2CF(CF_2CF_2)_nI$$
$$n=2-5,\ 63\%.$$

Thus, by varying the initial reactants and their ratio, using different catalysts and solvents, and changing the process conditions it is possible to obtain iodoperfluoroalkanes and iodoperfluoroalkoxyalkanes with quite a long carbon chain. Even though the use of a telomerisation process leads to the formation of a wide range of products that are difficult to separate, the production of iodoperfluoroalkanes with seven or more carbon atoms in the chain is actually based on this process.

4. Other methods for preparing iodoperfluoroalkanes

It was shown by Knunyants, et al.[26] that reaction between nitrosoperfluoroalkanes with iodine in an aprotic polar solvent leads to the formation of IPFAs in high yield.

$$R_fNO + I_2 \xrightarrow{50-70^\circ C} R_fI \quad 80-95\%$$
$$R_f{=}CF_3,\ C_3F_7,\ (CF_3)_3C.$$

Iodotrifluoromethane is formed by prolonged UV irradiation of methyl trifluoromethyl sulphide[116] and bis(trifluoromethyl) sulphide[117] in the presence of sources of iodine radicals.

$$CF_3SCF_3 \xrightarrow[h\nu]{n\text{-}C_3F_7I} CF_3I \xrightarrow[h\nu]{CH_3I} CF_3SCH_3$$
$$64\%\ [117] \qquad 30\%\ [116]$$

On treatment of perfluoropropane-2-sulphinic acid with iodine monochloride, 2-iodoperfluoropropane was formed in 33% yield.[118] The action of an alcoholic solution of iodine on perfluoroalkanesulphonyl chloride at an elevated temperature results in the replacement of the sulphonyl chloride group by iodine.[119]

$$R_fSO_2X \xrightarrow[R_f'=(CF_3)_2CF,\ X=H]{ICl} (CF_3)_2CFI$$
$$R_fSO_2X \xrightarrow[R_f=R_f'OCF_2CF(CF_3)OCF_2,\ X=Cl]{I_2} R_f'OCF_2CF(CF_3)OCF_2I.$$

Oxidation of the triiodomethyl ester of n-perfluoropropanesulphonic acid on exposure to UV radiation gives 1-iodoperfluoropropane through removal of iodine from the triiodomethyl group.[120]

$$n\text{-}C_3F_7SO_3CI_3 \xrightarrow{\text{UV irradiation, } O_2} n\text{-}C_3F_7I.$$

The progress made by different research workers[121,122] in the 1980s in studies on the chemistry of perfluoroalkenyl fluorosulphates led to the development of a preparative method for the synthesis of 1-iodoperfluoro-2-propene and other 1-iodoperfluoro-2-alkenes through replacement of the fluorosulphate group by iodine and made this class of compounds, which was previously little-studied but very promising in terms of synthesis, quite accessible.

$$R_fCF_2OSO_2F \xrightarrow{NaI,\ solvent} R_fCF_2I$$
$$R_f=CF_2=CF,\quad CCl_2=CCl,\quad (CF_3)_2CFCF=CF,\quad (CF_3)_3CCF=CF.$$

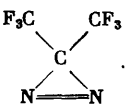
Iodoperfluoroalkanes are also formed by reaction of perfluoroalkyl-containing organoelemental compounds with iodine[123–129] or iodine monochloride.[130] Thus, reaction of iodine with $(CF_3)(CH_3)_2Bi$ or iodine monochloride with $(CF_3)_3Bi$ [123] gives iodotrifluoromethane, while reaction of iodine with bis-(perfluoroisopropyl)mercury gives 2-iodoperfluoropropane.[124] The replacement of halogens in haloperfluorocycloalkenes by iodine in the presence of ethylmagnesium bromide constitutes a variant of this method.[45]

Mixed alkylpolyfluoroalkylsilanes[125] and organolithium compounds behave in a similar manner. The latter are obtained at quite low temperatures.[126,129] It has been shown that the reaction is nucleophilic in nature towards iodine.[126]

$$(R_f)_n - M - R_m + I_2 \xrightarrow[\text{acetonitrile}]{DMF\ or} R_fI.$$

Small quantities of 2-iodoperfluoro-2-methylpropane are obtained from perfluoro-t-butyl chloroformate and potassium iodide or bis(trifluoromethyl)diazirine and iodotrifluoromethane.[26]

$$(CF_3)_3COCOCl \xrightarrow[\text{yield 30\%}]{KI,\ 180-200\ ^\circ C} (CF_3)_3Cl \xleftarrow[\text{yield 10–12\%}]{CF_3I,\ 150-200\ ^\circ C}$$



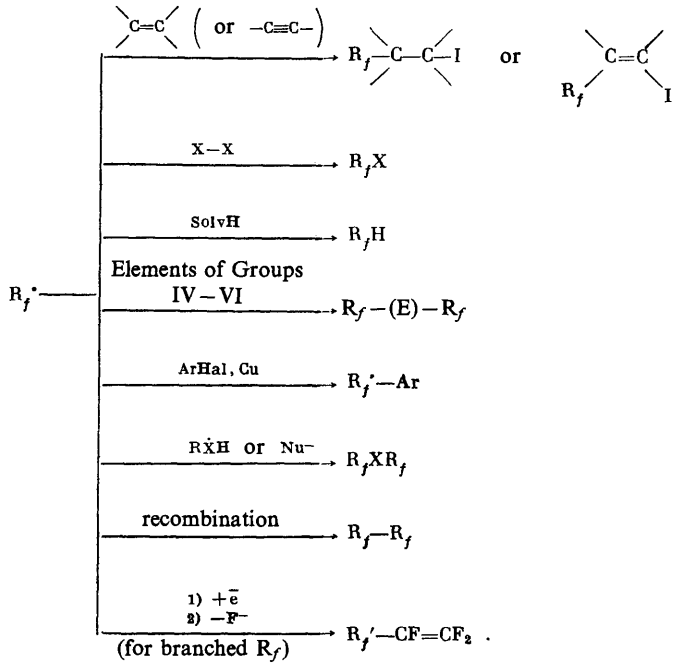
Thus, it is possible to approach the synthesis of IPFAs in different ways, but only some of the methods examined can be used in industry. Amongst these are the reaction of perfluorocarboxylates of Group I metals with iodine, the catalytic electrophilic iodofluorination of perfluoroalkenes, fluorination of diiodoperfluoroalkanes, and the oligomerisation of TFE and HFP with iodotrifluoromethane, iodopentafluoroethane, and iodoperfluoropropanes. The reaction between polyfluoroalkyl fluorosulphates and sodium iodide also appears to have considerable potential.

III. Chemical properties of iodoperfluoroalkanes

The energy of the C–I bond in iodoperfluoroalkanes is low, and they readily undergo homolytic dissociation to form $R_f^{\cdot}$ and $I^{\cdot}$ radicals on thermal or photochemical excitation. They yield an $R_f^{\cdot}$ radical from the action of radical initiators (RIs) or $R_f^{\cdot}$ and I^- on capture of an electron from an electron donor [optical electron detector (OED)] although in far from every case is it possible strictly to distinguish these reactions.

$$R_f^{\cdot} + I^- \leftarrow R_fI^{\cdot-} \xleftarrow{OED} R_fI \xrightarrow{RI} R_f^{\cdot}.$$

The resulting perfluoroalkyl radicals $R_f^{\cdot}$ are highly reactive and are stabilised through addition to carbon–carbon multiple bonds, homolytic cleavage of the bonds of molecules of substrate or solvent, and as a result of perfluoroalkylation of aromatic compounds, nucleophiles, and certain elements, and to a lesser degree by recombination or reduction to a perfluorocarbanion followed by ejection of F^- and formation of an alkene:



On the whole the above scheme almost completely governs the chemical properties and general trend for the synthetic use of IPFAs, which are characterised exclusively by radical or radical anion processes rather than by ionic reactions as proposed in early studies.[22,84,131] Beyond the scope of our review is a small group of reactions, also partly radical in nature, related to the oxidative conversions of iodine itself in an IPFA molecule, the oxidative degradation of $R_f^{\cdot}$, the formation of donor-acceptor complexes, and the halodefluorination of the CF_2I group, which are also examined in the present review.

Through lack of sufficient space we shall not examine the radical addition reactions of IPFAs to multiple bonds, as analysed in a monograph,[7] except for those reactions with unsaturated compounds that contain in addition to the multiple bond other functional groups. Reactions that are initiated by one-electron transfer have also been excluded.

1. Addition to unsaturated functional compounds

Radical reaction of iodoperfluoroalkanes with alkenes containing functional groups occurs exclusively as an addition to the C=C bond without affecting the functional groups[132,133] whereas radical-ion reactions can also occur on the functional groups. As a rule the reactions take place on treatment with conventional radical initiators such as azo compounds,[134,135] and hydrocarbon[136] and fluorinated[137] peroxides. In certain cases initiation is achieved photochemically, with the reaction carried out in a solvent.[132]

Thus, CF_3I adds to methyl vinyl ketone at its C=C bond with an anti-Markownikoff orientation.[138]

$$CF_3I + CH_2{=}CHCOCH_3 \xrightarrow{h\nu} CF_3CH_2CHICOCH_3.$$

The radical reaction of other iodoperfluoroalkanes[133–135,139–153] and iodoperfluoroethers[154,155] with unsaturated alcohols,[133–135,139–144] alkoxy alcohols,[134,147–152] and diols[153] occurs in a similar manner. Most frequently the reactions are carried out in the presence of azobis(isobutyronitrile) (ABN) at its decomposition temperature (70–85 °C),[134,135] while peroxides[136] or UV irradiation with heating[155] are used less often.

$$CH_2{=}CH{-}R{-}CH_2OH + R_fI \xrightarrow{\text{[initiator]}} R_fCH_2CHI{-}R{-}CH_2OH,$$

$R_f = C_3F_7,\ C_4F_9,\ (CF_3)_2CF,\ (CF_3)_2CFO(CF_2)_8;$

$R = -CH_2OCH_2\underset{|}{C}HOH,\ -CH_2OCH_2\underset{|}{C}HCH_3,\ -CH_2OCH_2-,$
$-(CH_2)_9-$ [133–135, 147–154].

Unsaturated carboxylic acids,[137,156–158] their amides,[159] and nitriles and esters[137,138,158,160–164] behave in a similar manner.

$$R_fI + CH_2{=}CH(CH_2)_nC(O)X \xrightarrow[ABN]{70-80^\circ C} R_fCH_2CHI(CH_2)_nC(O)X,$$

X=OH: $R_f = CF_3,\ C_3F_7,\ C_4F_9,\ C_6F_{13},\ C_7F_{15}$,

n=0–4 [137, 156–158];

$X=NH_2$: $R_f = C_7F_{15}$, n=8 [159];

X = OR: $R_f = (CF_3)_2CFO(CF_2)_m$,
where m = 2, 5, 6, n = 8 — 18 [160, 162, 163, 165];

$R_f = (CF_3)_2CF,\ CF_3(CF_2)_m$,

where m = 1 — 7, n = 1, 2 [162, 163].

$$R_fI + CH_2{=}CH(CH_2)_nCN \xrightarrow{\text{[initiator]}} R_fCH_2CHI(CH_2)_nCN,$$
$R_f = CF_3$, n=0 [138]; $R_f = C_3F_7$, n=1, 2 [158, 163].

Carboxylic acids with two or three CH_2 groups between the carboxyl group and the double bond constitute an exception. After addition of R_fI to the double bond these acids undergo lactonisation through intramolecular nucleophilic dehydroiodination. The process is assisted by *gem*-substitution.[137]

$$R_fI + CH_2{=}CHCH_2\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{-}COOH \xrightarrow{\text{[initiator]}} R_f{-}CH_2{-}CHICH_2\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{-}COOH \xrightarrow{-HI}$$

$$\longrightarrow R_f{-}CH_2{-}\underset{H_3C\ CH_3}{\overset{O}{\underset{|}{\overset{|}{C}}}}{=}O \quad .$$

With initial esterfication of the carboxyl group it is possible to obtain esters of unsaturated carboxylic acids with perfluoroalkyl substituents from these acids.[137]

$$CH_2{=}CHCH_2\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{-}COOR \xrightarrow[2)\ -HI]{1)\ C_6F_{13}I,\ [ABN]} C_6F_{13}CH{=}CHCH_2\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{-}COOR.$$

There is no information available on the addition of IPFAs to unsaturated functional compounds with a trifluorovinyl group.

The products of the addition of IPFAs to unsaturated compounds as listed above have considerable industrial value since they are the starting compounds for the synthesis of organofluorine surfactant and textile-auxiliary materials (see, for example, several studies).[133–136,147–163,166–168]

The radical addition of IPFAs to vinyl and allyl esters of carboxylic acids occurs in a similar manner.[161,166–170] All of the members of the homologous series of iodoperfluoroalkanes up to n = 14 undergo a reaction with vinyl acetate.[166,170] The reaction provides a preparative method for the synthesis of higher homologues of carboxylate esters with a terminal polyfluoroalkyl group and an iodine atom at the β-position relative to the R_f substituent.[168,171]

$$C_3F_7I + CH_2{=}CH(CH_2)_nOCOCH_3 \xrightarrow[70^\circ C]{\text{[ABN]}} C_3F_7CH_2CHI(CH_2)_nOCOCH_3,$$
n=3–9.

The characteristics of the reaction between vinyl and allyl acetates and IPFAs in the presence of peroxides have been reviewed in a monograph.[7] Iodoperfluoro(isopropyl alkyl ethers)[160,162] react with vinyl acetates to form monomers for the synthesis of fluorine-containing polymers with unique properties.

$$(CF_3)_2CFO(CF_2)_{1-20}I + CH_2{=}CH(CH_2)_{0-8}OCOCH_3 \xrightarrow{\text{[initiator]}}$$
$$\longrightarrow (CF_3)_2CFO(CF_2)_{1-20}CH_2CHI(CH_2)_{0-8}OCOCH_3.$$

The addition of nonbranched IPFAs to unsaturated carbocyclic acids occurs stereospecifically (up to 97% *exo* isomer is formed), whereas branched IPFAs form *endo* and *exo* isomers in a ratio of about 1 : 1.[171]

Radical addition of IPFAs to amines containing a double bond in the carbon chain[147] and perfluorovinyl sulphur pentafluoride[172] also results in saturation of the C=C bond.

$$CF_3CF_2CFISF_5 \xleftarrow[R_f = CF_3]{CF_2{=}CFSF_5,\ h\nu} R_fI \longrightarrow$$

$$\xrightarrow[\text{[ABH]};R_f = C_7F_{15}]{CH_2{=}CHCH_2NHC_2H_5} C_7F_{15}CH_2CHICH_2NHC_2H_5.$$

The radical reaction of iodoperfluoroalkanes with acetylenic compounds containing other functional groups,[164] including silicon[173] and germanium[174] atoms, generally occur in a similar manner with these groups remaining unaffected. A characteristic of these reactions is the inability of the resulting perfluoroalkyl-substituted alkenes to react further with IPFAs, apparently because of the inductive effect of R_f, which renders the double bond inert. For example, the addition of 1-iodoperfluoropropane to diethyl propargylmalonate[164] stops when the monoadduct is formed.

$$\underset{|}{\overset{CH_2C{\equiv}CH}{C_2H_5OCOCHCOC_2H_5}} \xrightarrow{C_3F_7I} \underset{|}{\overset{CH_2CI{=}CHC_3F_7}{C_2H_5OCOCHCOC_2H_5}}.$$

Radical addition of IPFAs to functionally substituted olefins and acetylenes is a convenient method of preparing polyfluoroalkyl-substituted compounds.

2. Stabilisation of $R_f^{\cdot}$ radicals by addition to elements of Groups IV–VI and their derivatives

Apart from the addition to unsaturated carbon–carbon bonds, a set of radical reactions with elements of Groups IV–VI (S, Se, P, As) and their compounds, occurring as a result of the unfilled state of the outer electron shells of these elements, is also characteristic of IPFAs. Thus, the reaction of iodoperfluoroalkanes with sulphur at 250 °C gives a mixture of di- and tri-sulphides,[175,176] while at 300 °C a mixture of mono-, di-, and tri-sulphides is formed. The reaction of branched IPFAs with sulphur occurs in a similar manner.[177]

$$R_fI \xrightarrow{250-300^\circ C} R_f^{\cdot} + I^{\cdot},$$
$$R_f^{\cdot} + S \rightarrow R_fS^{\cdot},$$
$$R_fS^{\cdot} + R_fS^{\cdot} \rightarrow R_fSSR_f + R_fSS^{\cdot} + R_f^{\cdot},$$
$$R_fS^{\cdot} + S \rightarrow R_fSS^{\cdot},$$
$$R_fSSR_f + R_fSS^{\cdot} \rightarrow R_fSSSR_f + R_fS^{\cdot},$$
$$R_fSS^{\cdot} + S \rightarrow R_fSSS^{\cdot},$$
$$R_fSSS^{\cdot} + R_fSR_f \rightarrow R_fSSSR_f + R_fS^{\cdot},$$
$$R_fS^{\cdot} + R_f^{\cdot} \rightarrow R_fSR_f.$$

At the same time, when IPFAs were reacted with HgS,[177] only 22% bis(perfluoroisopropyl) disulphide was formed, with 74% conversion of 2-iodoperfluoropropane leading to the formation of 2,3-perfluorodimethylbutane through recombination of perfluoroisopropyl radicals.

Under more severe conditions perfluorinated iodine-containing ethers react with sulphur to give mainly disulphides.[178]

$$2(CF_3)_2CFOCF_2CF_2I \xrightarrow{S;\ 450^\circ C} [(CF_3)_2CFOCF_2CF_2S]_2.$$

Reactions of IPFAs with selenium can be carried out in continuous flow systems,[179] with diselenides mainly being formed in good yield.

$$CF_3I + Se \xrightarrow[40-160\ s]{300-350\ ^\circ C} CF_3—Se—Se—CF_3.$$
79%

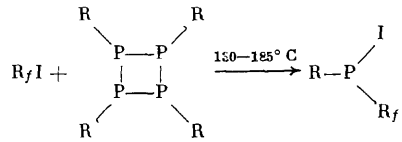
A characteristic of reactions of IPFAs with sulphur and selenium is the participation of the resulting $I^{\cdot}$ radicals solely in chain termination.

In reactions of IPFAs with phosphorus and arsenic[180–185] different types of phosphines and arsines are obtained depending on the structure of the perfluoroalkyl radicals. For the reaction of iodotrifluoromethane the formation of all three possible iodotrifluoromethylphosphines, apparently through the participation of iodine atoms along with $R_f^{\cdot}$ in chain termination, has been detected.[181,182]

$$CF_3I + P \xrightarrow[pressure]{220\ ^\circ C;\ 48\ h} (CF_3)_3P + (CF_3)_2PI + CF_3PI_2.$$

The formation of tris(perfluoroalkyl)phosphines and tris(perfluoroalkyl) arsines does not occur in the case of longer perfluoroalkyl radicals (C_2-C_{10}).[183–185]

Asymmetric iodophosphines have been obtained in reactions of IPFAs with tetrakis(alkyl or perfluoroalkyl)cyclotetraphosphines.[186–188]



$R=CF_3,\ C_3F_7,\ (CF_3)_2CF,\ C_2H_5;\quad R_f=C_2F_5,\ (CF_3)_2CF.$

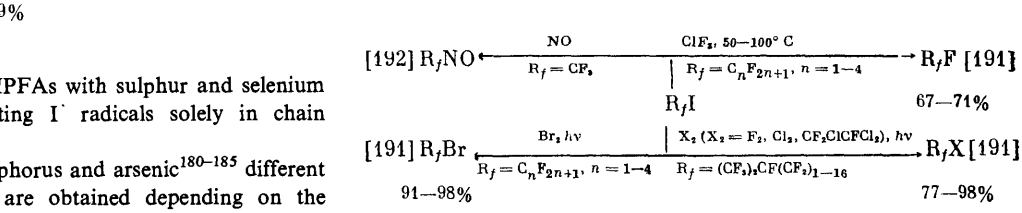
It has been established kinetically that on changing from n-C_3F_7I to $(CF_3)_2CFI$ the rate constant and energy of activation of the reaction are reduced [*sic*. The latter is presumably increased, (Ed. of Translation)], namely, the reactivity of the iodoperfluoroalkanes decreases as the degree of chain branching increases, because of both the increasing electronegativity of the fluoroalkyl group and steric hindrance.

A general reaction of nonbranched iodoperfluoroalkanes is their addition to silicon difluoride.[189]

$$R_fI + SiF_2 \rightarrow R_fSiIF_2,$$
$R_f=CF_3,\ C_2F_5,\ C_3F_7.$

3. Stabilisation of $R_f^{\cdot}$ radicals through cleavage of single bonds

In addition to radical reactions involving the addition to carbon–carbon multiple bonds, IPFAs exhibit a wide range of reactions with stabilisation of $R_f^{\cdot}$ through cleavage of the single bonds of organic and inorganic molecules and the subsequent formation of products that are more stable under the conditions of radical decomposition than the initial IPFAs. During radical initiation the iodine atom of IPFAs is readily replaced by more electronegative halogens or groups,[190–194] resulting in the formation of more stable polyfluoroalkyl-containing compounds. In this case the primary radical source can be a halogen molecule,[192,193] if the energy of its homolytic dissociation is lower than that of the IPFA.



On the other hand, in the radical reaction of IPFAs with cyanogen, in which it is possible to obtain nitriles of the corresponding perfluoroalkylcarboxylic acids in quantitative yield, the IPFAs act as a radical source.[194] The radical nature of the reaction is confirmed by the presence of a small quantity of product derived from the coupling of polyfluoroalkyl radicals:

$$R_fI + (CN)_2 \xrightarrow[pressure]{350^\circ C} R_fCN + R_f—R_f.$$
trace amounts

On reacting with hydrogen, IPFAs are converted to monohydroperfluoroalkanes.[195] The involvement of hydrocarbon iodoalkanes in radical reactions is also possible. Thus, 1,1,1-trifluoroethane and 1,1-difluoroethylene are formed from iodomethane. The latter is formed as a result of stabilisation of the excited state of 1,1,1-trifluoroethane through elimination of HF.[198,199]

$$CF_3I + CH_3I \xrightarrow{h\nu} CF_3CH_3^* + I_2 \xrightarrow[-HF]{} CF_2{=}CH_2.$$

Stabilisation of an $R_f^{\cdot}$ radical may also be achieved by the removal of a proton from a C–H bond of alcohols,[152] alkanes, cycloalkanes,[200–202] and alkylsilanes.[203]

$$CF_3H \xleftarrow[h\nu;\ 100^\circ C]{(CH_3)_3SiSi(CH_3)_3} CF_3I \xrightarrow[C_3H_8 \text{ or cycloalkane}]{h\nu} CF_3H.$$

Reactions of IPFAs by a radical mechanism depend in many respects on the process conditions and are principally governed by initiation (thermal, photochemical, or using initiators). The addition of IPFAs to multiple bonds and elements of Groups IV–VI as well as reactions with cleavage of X–X bonds (X = CN, Hal) occur most frequently by this mechanism. By varying the methods of generating radicals and the length and branching of the hydrocarbon chain of IPFAs it is possible to influence the reaction route, achieving the formation of given products. A characteristic of all these processes is that other functional groups present in the molecule, such as a nitrile group as well as the perfluoroalkyl-substituted double bond formed from alkynes, are stable towards IPFAs during reaction.

A radical mechanism is in doubt for certain cases of these reactions, since in addition to energetic excitation of the molecules there is the theoretical possibility of electron transfer, and this in turn can alter the process mechanism.[204]

4. Oxidation of iodoperfluoroalkanes

The oxidation of IPFAs is one of the few reactions which, depending on the conditions and nature of the oxidising agent, occurs either on the iodine atom or on the perfluoroalkyl group leading to its degradation.

Oxidation of IPFAs on the iodine atom. This gives perfluoroalkyl compounds of polyvalent iodine and takes place with all of the bonds being preserved in the molecule. Of reactions of this type, prominence should be given to oxidative halogenation. This reaction was first carried out using chlorine trifluoride,[205,206] and then subsequently with fluorine diluted with nitrogen[207] and with xenon difluoride.[208] Depending on the reagent, oxidative fluorination occurs with the formation mainly of perfluoro-alkyliodine tetrafluorides and perfluoroalkyliodine difluorides. A similar reaction may be carried out when other oxidising agents such as chlorine nitrate or perchlorate[210–212] and trifluoroperacetic acid[209] are used. The ratio of the iodine oxidation products depends on the reaction conditions.

R_fI —

- $\xrightarrow[T<0^\circ C]{ClF_3}$ $R_fIF_4 + R_fIF_2$ ($R_f = C_nF_{2n+1}$), trace amounts; $n = 2-22$ [205, 206]; (when $R_f = CF_3$ yield of R_fIF_4 100%)
- $\xrightarrow[-78^\circ C]{F_2/N_2,\ CCl_3F}$ R_fIF_2 ($R_f = CF_3$ [207])
- $\xrightarrow[20^\circ C]{XeF_2}$ R_fIF_2 ($R_f = C_3F_7$ (60%) [208])
- $\xrightarrow[\text{pressure}]{ClONO_2}$ $R_fI(NO_2)_2$ ($R_f = CF_3$ [210])
- $\xrightarrow[-78\text{—}-20^\circ C]{ClONO_2,\ CCl_3F}$ $R_fICl(NO_2)$ + $R_fI(NO_2)_2$ ($R_f = CF_3$ [211])
- $\xrightarrow{ClOClO_3}$ $R_fI(OClO_3)_2$ ($R_f = (CF_3)_2CF$ [212])
- $\xrightarrow[(CF_3CO)_2O,\ CF_3COOH]{80\%\ H_2O_2}$ $R_fI(OCOCF_3)_2$ ($R_f = C_3F_7$ (65%) [209]).

The resulting perfluoroalkyliodine difluorides and tetrafluorides are sensitive to hydrolysis. The stability of the tetrafluorides at 20 °C increases in the series

$$CF_3 < (CF_3)_2CF < C_6F_5 \ [206].$$

Perfluoroalkyliodine dinitrates and diperchlorates are obtained in low yield, probably because of their low stability at room temperature compared to the corresponding polyfluorides. The decomposition of perfluoroalkyliodine dinitrates may evidently occur according to the following scheme:[210,211]

$$10CF_3I(NO_3)_2 \rightarrow 5CF_3I + 5COF_2 + 10N_2O_5 + I_2 + IF_5 + I_2O_5.$$

Starting from perfluoroalkyliodine difluorides and acetates, L M Yagupol'skii, et al.[6,209,213] developed a preparative method for the previously inaccessible arylperfluoroalkyliodonium salts, which are convenient reagents for the preparative perfluoroalkylation of

different nucleophiles, which determines the considerable synthetic value of these compounds.

$$R_fIF_2 + BF_3 \longrightarrow R_f\overset{+}{I}FBF_4^- \xrightarrow{C_6H_5CH_3} CH_3C_6H_4\overset{+}{I}R_fBF_4^-;$$
87% (R_f=C_3F_7)
83% (R_f=C_6F_{13})

$$CH_3C_6H_4\overset{+}{I}R_fX^- + MNu \rightarrow R_fNu \quad [6]$$

M=Na, K; Nu=PhS, PhSe, NO_2, SCN, SeCN.

Oxidation with degradation of the perfluoroalkyl chain. Photochemical oxidation of perfluoroalkanes with oxygen occurs quite rapidly and is accompanied by stepwise degradation and the formation of carbonyl fluoride. When the oxidation is carried out in a quartz vessel, silicon tetrafluoride is also found amongst the reaction products. It is thought that decomposition of the perfluoroalkyl residue occurs via the formation of a perfluoroalkoxy radical. The latter, by eliminating COF_2, forms a new perfluoroalkyl radical which contains one less CF_2 group and which undergoes further oxidation.[22,214]

$$C_3F_7I \xrightarrow{h\nu} C_3F_7^{\cdot} + I^{\cdot} \xrightarrow{O_2} C_3F_7OO^{\cdot} \xrightarrow{C_3F_7I} C_3F_7OOI + C_3F_7^{\cdot} \xrightarrow{O_2} \text{etc.}$$

$$C_3F_7OOI + C_3F_7^{\cdot} \xrightarrow{C_3F_7I} C_3F_7O^{\cdot} + IO^{\cdot} \longrightarrow C_2F_5^{\cdot} + COF_2$$

$$C_2F_5^{\cdot} + COF_2 + I^{\cdot} \longleftarrow C_3F_7OI + C_3F_7^{\cdot}$$

$C_2F_5^{\cdot}$ + O_2 → etc.; $C_2F_5^{\cdot}$ + O_2 → etc.

In the presence of water or mixtures of water and chlorine and bromine, which is better, the radicals formed during oxidation undergo side reactions, giving perfluoroalkylcarboxylic acids. Thus, a mixture of acids is obtained on photochemical oxidation of 1-iodoperfluoropropane with oxygen in the presence of moist bromine.[22]

$$C_3F_7I \xrightarrow[h\nu]{O_2,\ Br_2,\ H_2O} \underset{45\%}{C_2F_5COOH} + \underset{23\%}{CF_3COOH}.$$

On treatment with other oxidising agents, such as oleum, degradation of the carbon skeleton does not usually occur, and polyfluorocarboxylic acid fluoride and a small quantity of perfluoroalkyl fluorosulphate are formed. Both products contain one less CF_2 group compared to the initial IPFAs.[215]

$$R_fCF_2I \xrightarrow[130-200\ ^\circ C,\ 1-20\ h]{\text{oleum}} \underset{88\%}{R_fCOF} + \underset{1.8\%}{R_fCOOH} + \underset{2.7\%}{R_fCF_2OSO_2F}.$$

When iodoperfluoroisopropoxyalkanes were oxidised with oleum, the product derived from the replacement of the fluorine atom of the fluorosulphate group in the by-product fluorosulphate by a second fluorosulphate group was identified together with the normal acid fluoride:[216]

$$(CF_3)_2CFO(CF_2)_6I \xrightarrow[140^\circ C]{SO_3} \begin{cases} \longrightarrow (CF_3)_2CFO(CF_2)_5COF \\ \longrightarrow (CF_3)_2CFO(CF_2)_6OSO_2OSO_2F. \end{cases}$$

The temperature of the process can be reduced by the addition of chlorine and zinc sulphates to oleum.[217] A number of methods for the oxidation of IPFAs to perfluorocarboxylic acid fluorides are currently available. It may be assumed that the process for preparing acid fluorides by oxidation of IPFAs (provided that iodine is returned to the process cycle) can compete successfully with the traditional method for preparing them—electrochemical fluorination in anhydrous hydrogen fluoride. Complex equipment design, high energy consumption, and low yields of acid fluorides because of degradation of the carbon skeleton of the initial molecule are characteristic of the latter.[16]

5. Formation of charge-transfer complexes

The polarisation of the C–I bond in IPFAs, which is the reverse of that in CH_3I, gives rise to their ability to form molecular complexes (1 : 1) with electron-donating solvents in which the iodine acts as the acceptor.[218–225] This is supported experimentally by the shift of absorption bands that are characteristic of IPFAs in the UV spectra[218,219] and by changes of the chemical shifts in the ^{19}F NMR spectra.[219]

$$R_f\overset{\curvearrowleft}{I} + :B \longrightarrow R_fI-B$$

R_f=CF_3, C_2F_5, C_3F_7, $(CF_3)_2CF$, $(CF_3)_3C$;
B:=$C_6H_5NR_2$, C_5H_5N, $(CH_3)_3N$, C_2H_5OH, $(C_2H_5)_2O$.

In the complexes the C–I bond in IPFAs changes its nature and becomes similar to the corresponding bond in hydrocarbon iodoalkanes. The reactivity of the complexes differs slightly from that of IPFAs. Thus, $(CF_3)_2CI$ in a solution of diethyl ether reacts with diethylamine to form the corresponding enamine:[84]

$$-\overset{|}{N}: + I-C(CF_3)_3 \longrightarrow \left[-\overset{|}{N}^{\delta+}\cdots I^{\delta-}\cdots C^{\delta-}(CF_3)_3\right] \longrightarrow$$

$$\longrightarrow -\overset{|}{N}^{+}-I + {}^{-}C(CF_3)_3 \xrightarrow[-F^-]{} CF_2=C(CF_3)_2 + \left[-\overset{|}{N}-I\right]^+F^- \xrightarrow[-HF]{(C_2H_5)_2NH}$$

$$\rightarrow (CF_3)_2C=CFN(C_2H_5)_2.$$

It should be noted that the greatest shifts of the absorption bands occur in the UV spectra of a mixture of 2-iodoperfluoro-2-methylpropane with diethyl ether and ethanol.

6. Reaction between iodoperfluoroalkanes and aluminium halides

Iodotrifluoromethane readily reacts with aluminium halides, forming a mixture of substitution products.[226] Eapen, et al.[227] found that its higher homologues and iodoperfluoroalkoxyalkanes also undergo such a reaction in the presence of a 1.5- to 3-fold excess of $AlCl_3$ or $AlBr_3$.

$$R_fCF_2I \xrightarrow[75-120\ ^\circ C,\ 24-74\ h]{AlX_3} \underset{55-56\%}{R_fCX_3}$$

R_f=C_3F_7, C_8F_{17}, $C_{10}F_{21}$; X=Cl, Br.

It follows from the experimental results that the formation of trichloro derivatives occurs via the intermediate formation of R_fCCl_2I. The latter can be isolated at a lower temperature with a

yield of about 15%. In our opinion, cleavage of the stronger C–F bond occurs in this case because the formation of AlF_3 is thermodynamically more favourable compared to AlX_3 (X = Cl, Br). The reaction with branched iodoperfluoroalkoxyalkanes is complicated by dechlorofluorination and more extensive substitution of fluorine atoms, probably because of the close proximity of the electron-donating oxygen atom.

$$(CF_3)_2CFOCF_2CF_2I \xrightarrow[60\ h]{AlCl_3,\ 100-105\ ^\circ C} \begin{cases} \longrightarrow (CF_3)_2CFOCF_2CCl_3 \quad 26\% \\ \longrightarrow (CF_3)_2CFOCF{=}CCl_2 \quad 19\% \\ \longrightarrow (CF_3)_2CFOCCl{=}CCl_2 \quad 19\% \\ \longrightarrow (CF_3)_2CFOCCl_2CCl_3\ . \quad 2\% \end{cases}$$

IV. Use of iodoperfluoroalkanes and perfluorinated iodine-containing ethers

Iodoperfluoroalkanes and perfluorinated iodine-containing ethers have found extensive use in chemical technology and in different areas of science and engineering—in laser technology, etching of dielectrics, separation of carbon isotopes, and as intermediates in the synthesis of surfactants, textile-auxiliary materials, and biologically active compounds.

1. Use of IPFAs in chemical technology and engineering

In 1971 the use of iodopentafluoroethane on a support was proposed as a source of radicals for the initiation of polymerisation processes.[228,229] Highly fluorinated oils were subsequently obtained by polymerisation of tetrafluoroethylene[230] and other perfluoroalkenes[231] in the presence of C_2F_5I. It should be noted that IPFAs can be used in polymerisation processes not only for initiation but also for modification of the polymers obtained.[323]

Long-chain branched IPFAs with the general formula $(CF_3)_2CF(CF_2CF_2)_nI$ (n = 6–16) are used as components of self-lubricating compositions (at a level of 5–30%).[233,234]

Starting in 1979 there has been an increase in the number of publications on the use of IPFAs in photodissociation iodine lasers (FIL). Laser generation from the transition of an excited iodine atom (obtained by pulsed photolysis of CF_3I) to an unexcited state was first achieved in 1964.[8]

For the last 20 years the processes that occur during pulsed photolysis of CF_3I and after it and the parameters of a CF_3I laser have been thoroughly investigated. In order to improve the energetic characteristics of a FIL and to simplify its use, including the ability to use an active medium repeatedly, the use of homologues of iodotrifluoromethane—n-C_3F_7I, n-$C_5F_{11}I$, n-$C_6F_{13}I$ and their isomers and also $C_2F_5CFICF_3$ and $(CF_3)_3CI$—has been proposed.[9–11,235–238] Amongst these compounds there is considerable interest in 2-iodoperfluoro-2-methylpropane because, in contrast to other IPFAs, the $(CF_3)_3C^{\cdot}$ radical formed during its photochemical decomposition mainly gives the initial compound on account of its structural characteristics and high stability in recombination processes, thus preventing the formation of molecular iodine and making it theoretically possible to produce a frequency FIL.[11]

The use of IPFAs in laser technology is not restricted solely to FILs. The use of a mixture of CF_3I with hydrogen-containing components such as iodomethane, hydrogen bromide, and fluorine and hydrogen has been proposed for obtaining an HF-laser emission.[13–15,198] Studies have been conducted on the production of a laser based on molecular iodine by excitation of a mixture of CF_3I and argon with an electron beam.[239]

The coincidence of the absorption spectrum of iodotrifluoromethane containing a small quantity of $^{13}CF_3I$ with the wavelength of a CO_2 laser forms the basis of the use of iodotrifluoromethane in the separation of carbon isotopes by multiphoton dissociation of CF_3I at –80 °C in the field of a CO_2 laser.[17] The efficiency of this method is very high (enrichment coefficient 600); in future it is likely to evolve as the principal method for ^{13}C isotope enrichment.

2. Surfactants based on iodoperfluoroalkanes

At the beginning of the 1960s Brace[156,159] and then Litt and Blöchl[93,240] established that starting from 1-iodo-1,1,2,2-tetrahydroperfluoroalkanes or iodoperfluoroalkoxyalkanes it is possible to obtain compounds that can produce a marked change in the surface tension of solutions and which are considerably superior to known surfactants. Research in this field has been considerably extended.[168,178,195,241–250] Current methods for the synthesis of surfactants based on IPFAs are exhibited in the scheme given in a monograph.[16] This scheme can be supplemented by the following:

$$C_3F_7I \begin{cases} \longrightarrow C_3F_7CH_2CHI(CH_2)_nOCH_2OCOCH_3 \longrightarrow C_3F_7CH_2CHI(CH_2)_nOCH_2OH \\ \qquad\qquad\qquad\

1-iodoperfluoroheptane.[147,252,253] 1-Iodoperfluorooctane is used in the synthesis of antisoiling agents for fabrics.[149–152,156] A more extensive group of iodoperfluoroalkanes R_fI (R_f = C_4-C_{16} perfluoroalkyl) is used in the synthesis of ammonium polyhydroxyalkylselenates and their derivatives, which impart oil and water resistance to textile fibres.[150] Members of the homolytic series of IPFAs with the number of C atoms $\leqslant 4$ are used less frequently for this purpose.[133,135,254–256]

Iodoperfluoroalkoxyalkanes are the starting materials for the preparation[162,163,257] of esters that are used in the synthesis of the corresponding acids and their complexes with chromium hypochlorite. The latter are efficient oil-repellent agents.

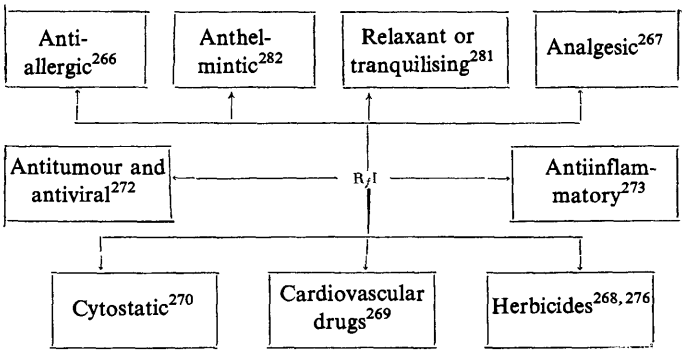
IPFAs and iodoperfluoroalkoxyalkanes have been used to synthesise novel monomers and polymers,[134,153,154,258,259] such as fluorine-containing polyurethanes,[153,260] with dust- and soil-resistant properties. The monomers obtained using IPFAs with the number of carbon atoms ranging from 1 to 10 have proved promising for the synthesis of novel polymer materials having the properties of rubbers,[261] vulcanised rubber,[262] and other vulcanised materials,[263] as well as vulcanising agents.[139]

By using 1-iodoperfluoropropane in the synthesis of fluorine-containing benzoxazoles, the authors of one patent[264] discovered novel anticorrosive lubricant additives.

4. Biologically active compounds

The use of IPFAs in the synthesis of biologically active compounds has assumed a prominent position. Reaction of CF_3I and certain of its homologues with organic substrates gives cyclic, aromatic, and heterocyclic perfluoroalkylated compounds that have diverse forms of biological activity (Scheme 1).[265–282] Iodotrifluoromethane is used most frequently in the syntheses of biologically active compounds because the compounds prepared from it have the greatest activity and also because of the high stability of CF_3I. As a consequence of the latter, the trifluoromethylation reactions, which are usually carried out at a temperature not lower than 110 °C, are not accompanied by side reactions due to the degradation of the perfluoroalkyl substituent. This is a considerable advantage in the synthesis of pharmacological compounds.

Scheme 1. Spectrum of biological effect of perfluoroalkyl-containing compounds obtained by perfluoroalkylation of aromatic and heteroaromatic substrates.



Research into novel alkylating agents for the preparation of biologically active fluorine-containing compounds has recently been undertaken. Halodifluoroacetic acids and their derivatives have been used in particular for this purpose. Thus, Delyagina, et al.[283] pointed out their ability to undergo nucleophilic substitution, while in subsequent syntheses with methyl iododifluoroacetate it was shown that they are characterised by addition and substitution reactions that are normal for IPFAs, including the alkylation of aromatic and heterocyclic compounds.[284] As a result of these studies it was possible to introduce the CH_3OOCCF_2 group into complex organic molecules, considerably extending the synthetic possibilities of the resulting compounds.

5. Other areas of application

In addition to the traditional areas of application, IPFAs and iodoperfluoroalkoxyalkanes are used as intermediates in the synthesis of various materials with useful properties,[16] including the production of dyes.[262] Iodoperfluoroalkanes are used as sources of fluorine for etching glass surfaces in order to improve their stability towards water and aqueous solutions.[18] An assessment of the possibility of using CF_3I in radiation dosimetry has been carried out.[19] In certain cases IPFAs are convenient solvents in IR spectroscopy.[285]

V. Conclusion

The presence of the highly fluorinated R_f residue in IPFAs gives rise to a basic difference between them and their hydrocarbon analogues, involving a withdrawal of electron density for the C–I bond. This almost completely deprives the molecule of the ability to participate in nucleophilic substitution reactions. Radical and radical-ion reactions are typical. Nevertheless, IPFAs, like their nonfluorinated analogues, are convenient alkylating agents, and by using simple methods they enable fluorine-containing substituents to be introduced into complex organic molecules without causing them to degrade, thus establishing their main use in organic synthesis.

The independent practical value of IPFAs results from their use in areas of modern technology such as mechanical engineering, laser technology, isotope separation, etc.

IPFAs (in particular CF_3I and n-C_3F_7I) have disadvantages in terms of their practical application because of their relatively high costs, since at the present time no technologies for synthesising them have been developed that can compete with the Borodin–Hunsdiecker method. Therefore, the development of alternative and oxygen-containing iodoperfluoroalkanes based on available products is a useful and promising trend.

We do not claim that the bibliography presented in this review is comprehensive in its coverage. However, the main directions of research into the preparative methods as well as the reactivity of iodoperfluoroalkanes are fully reflected in it. We hope that the contents of this review will be useful not only to researchers working in the field of the organic chemistry of fluorine but also to a wider circle of synthetic chemists.

References

1. A A Banks, H J Emeleus, R N Haszeldine *J. Chem. Soc.*, 1948, 2188
2. P L Coe, N E Milner *J. Fluorine Chem.*, 1972, **2** 167
3. N V Kondratenko, L G Yurchenko, G I Matyushecheva *Ukr. Khim. Zh., (Russ. Ed.)*, 1981, **47** 871
4. Japanese Appl. 54-22371; *Ref. Zh. Khim.*, 1980, 60383

5. Y Kobayahsi *J. Chem. Soc., Perkin Trans. 1*, 1980, 2755
6. L M Yagupol'skii *Aromaticheskie i Geterotsiklicheskie Soedineniya s Ftorsoderzhashchimi Zamestitelyami* (Aromatic and Heterocyclic Compounds with Fluorine-containing Substituents), Naukova Dumka, Kiev, 1988, p. 320
7. A I Rakhimov *Khimiya i Tekhnologiya Ftororganicheskikh Soedinenii* (The Chemistry and Technology of Organofluorine Compounds), Khimiya, Moscow, 1986, p. 271
8. J V V Kasper, G C Pimentel *Appl. Phys. Lett.*, 1964, **5** 231
9. G A Skorobogatov, V E Khomenko *Vestn. Leningr. Univ.*, 1970, **2** 170
10. G A Skorobogatov, V G Seleznev *Zh. Tekh. Fiz.*, 1975, **45** 2454
11. A S Kozlov, A M Pravilov *Khim. Vys. Energ.*, 1981, **15** 514
12. L K Gavrilina, V A Katulin, N N Korzhavina, et al. *Kvantovaya Elektronika* (Quantum Electronics), 1979, **6** 1495
13. M J Berry *Chem. Phys. Lett.*, 1972, **15** 269
14. R D Coombe, G C Pimentel *J. Chem. Phys.*, 1973, **59** 535
15. A N Oraevskii *Khim. Vys. Energ.*, 1974, **8** 3
16. N Isikawa (Editor) *Recent Developments in the Technology of Fluorine Compounds* (Translated into Russian), Mir, Moscow, 1984, p. 591
17. S Bittenson, P L Houston *J. Chem. Phys.*, 1977, **67** 4819
18. US P. 3 314 772
19. S M Seltzer, M J Berger *Int. J. Appl. Radiat. Isotop.*, 1982, **33** 1189
20. A Probst, K Raab, K Ulm, K von Werner *J. Fluorine Chem.*, 1987, **37** 223
21. S I Pletnev, S M Igumnov, I N Rozhkov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2057
22. R E Banks *Fluorocarbons and their Derivatives*, Oldbourne Press, London, 1964, p. 161
23. W A Sheppard, C M Sharts *The Organic Chemistry of Fluorine* (Translated into Russian), Mir, Moscow, 1972, p. 480
24. A M Lovelace, D A Rausch, W Postelnek *Fluorine-containing Aliphatic Compounds* (Translated into Russian), Izd. Inostr. Lit., 1961, p. 345
25. US P. 3 992 424
26. B L Dyatkin, A A Gevorkyan, I L Knunyants *Izv. Akad. Nauk SSSR*, Ser. Khim., 1965, 1873
27. L E Deev, T I Nazarenko, K I Pashkevich *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 402
28. US P. 3 351 671
29. US P. 3 072 730
30. French P. 2 343 824
31. BRD P. 2 610 148
32. H Millauer *Angew. Chem.*, 1973, **85** 988
33. US P. 3 133 125
34. French P. 96 082
35. N Colebourne, R Wolfgang *J. Chem. Phys.*, 1963, **38** 2782
36. US P. 3 682 876
37. M W Grayson, D M Lemal *J. Am. Chem. Soc.*, 1976, **98** 1278
38. K Stanley, D W McBride *Can. J. Chem.*, 1975, **53** 2537
39. Y Amimoto *7th European Symposium on Fluorine Chemistry*, Venice, 1980, p. 40
40. K V Dvornikova, V E Platonov, L N Pushkina, et al. *Zh. Org. Khim.*, 1972, **8** 1042
41. G Camaggi, F Gozzo *Tezisy Dokladov Mezhdunarodnogo Simpoziuma po Khimii Ftora* (Abstracts of Reports at the International Symposium on Fluorine Chemistry), Nauka, Moscow, 1969, p. 49
42. G Camaggi, F Gozzo *J Chem. Soc., C*, 1971, 925
43. G Camaggi *J. Chem. Soc., C*, 1971, 2382
44. S A Postovoi, Yu V Zeifman, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 2826
45. G Hagele, G Bauer *Z. Naturforsch.*, 1979, **34** 1252
46. US P. 3 346 652; *Chem. Abs.*, 1968, 21500g
47. A L Henne, W G Finnegan *J. Am. Chem. Soc.*, 1950, **72** 3806
48. H J Emelaus, R N Haszeldine *J. Chem. Soc.*, 1949, 2948
49. A V Tumanova, V A Gubanov, I M Dolgopol'skii *Zh. Obshch. Khim.*, 1965, **35** 587
50. A L Henne, W F Zimmer *J. Am. Chem. Soc.*, 1951, **73** 1362
51. D Paskovich, P Gaspar, G S Hammond *J. Org. Chem.*, 1967, **32** 833
52. H-R Feist, D Naumann *J. Fluorine Chem.*, 1980, **16** 571
53. T I Nazarenko, L E Deev, K I Pashkevich *Tezisy Dokladov Vsesoyuznoi Konferentsii po Khimii Ftora* (Abstracts of Reports at the All-Union Conference on Fluorine Chemistry), Moscow, 1986, p. 171
54. G Petit, J Bessiere *J. Elektroanal. Chem.*, 1970, **25** 317
55. W R Cullen, G E Styan *Can. J. Chem.*, 1966, **44** 1225
56. US P. 3 716 592
57. US P. 3 666 820
58. L S Sildert *J. Am. Oil Chem. Soc.*, 1969, **46** 615
59. US P. 3 531 535; *Chem. Abs.*, 1971, 88243p
60. US P. 2 614 131
61. [This reference is missing from the Russian original (Ed. of Translation)]
62. R D Chambers, W K R Musgrave, J Savory *J. Chem. Soc.*, 1961, 3779
63. P Sartori, A J Lehnen *Chem. Ber.*, 1971, **104** 2813
64. H C Fielding *Organofluorine Chemicals and their Industrial Applications*, Chichester, London, 1979, p. 250
65. J A Young, T M Reed *J. Org. Chem.*, 1967, **32** 1682
66. T Takeuti *Yuki Gosei Kagaku Kyokaishi*, 1970, **32** 580
67. E P Lur'e, I L Knunyants, B L Dyatkin *Zh. Org. Khim.*, 1971, **7** 1835
68. US P. 340 621
69. BRD P. 2 033 755
70. Japanese P. 49-41402; *Ref. Zh. Khim.*, 1975, 15N23
71. Japanese P. 49-41401; *Ref. Zh. Khim.*, 1975, 15N22
72. Japanese P. 56-2054; *Ref. Zh. Khim.*, 1982, 4N19
73. US P. 3 933 931
74. B.P. 998 235
75. Swiss P. 477 385
76. Swiss P. 486 402
77. US P. 3 283 020
78. G Oates, J M Winfield *J. Chem. Soc., Dalton Trans.*, 1974, 119
79. *Uspekhi Khimii Ftora* (Progress in Fluorine Chemistry), Khimiya, Leningrad, Vols. III, IV, 1970, p. 448
80. C G Krespan *J. Org. Chem.*, 1962, **27** 1813
81. US P. 3 052 732
82. I L Knunyants, S T Kocharyan, E M Rokhlin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 1910
83. E P Mochalina, B L Dyatkin, I V Galakhov, I L Knunyants *Dokl. Akad. Nauk SSSR*, 1966, **169**(6) 1346
84. C-Y Chen, H-K Jiang, B-Q Chen, M-L Liang *Sci. Sinica.*, 1966, **15** 498
85. N I Delyagina, E I Mysov *Dokl. Akad. Nauk SSSR*, 1974, **217** 836
86. N I Delyagina, B L Dyatkin *Tetrahedron*, 1974, **30** 4031

87. S A Postovoi, L T Lantseva, Yu V Zeifman, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 2531
88. French P. 1 540 866
89. R D Chambers, S Partington *7th International Symposium on Fluorine Chemistry*, 1973
90. US P. 3 501 534
91. US P. 3 542 859
92. US P. 3 409 512
93. US P. 3 453 333
94. US P. 3 558 721
95. US P. 3 758 538
96. J A Joung *Fluorine Chem. Rev.*, 1967, **1** 359
97. F Evans, M Litt, F Avonda *IVth International Symposium on Fluorine Chemistry*, Munich, 1968, p. 66
98. French P. 148 092
99. Swiss P. 484 207
100. Swiss P. 498 163
101. Swiss P. 518 247
102. Swiss P. 535 729
103. D S Ashton, J M Tedder *J. Chem. Soc., Faraday Trans. 1*, 1974, **70** 299
104. K Ukikashi, T Utino *Kagaku Kogaku*, 1978, **42**(6) 330; *Ref. Zh. Khim.*, 1978, 23N73
105. R Gregoru, R N Haszeldine *J. Chem. Soc., C*, 1971, 1216
106. Japanese P. 20 282; *Ref. Zh. Khim.*, 1969, 17N35
107. R N Haszeldine, I D Mir *J. Chem. Soc., Perkin Trans. 1*, 1976, 1170
108. BRD P. 1 915 395
109. L O Moore *Can. J. Chem.*, 1971, **49** 666
110. Japanese P. 56-8013
111. Japanese P. 48-42852
112. Japanese P. 20 283
113. US P. 3 525 758
114. US P. 3 345 424
115. BRD P. 2 235 885
116. R N Haszeldine, B Hewitson, A E Tipping *J. Chem. Soc., Perkin Trans. 1*, 1974, 1706
117. R N Haszeldine, R B Rigby *J. Chem. Soc., Perkin Trans. 1*, 1972, 1506
118. O A Radchenko, A N Il'chenko *Tezisy Dokladov III Vsesoyuznoi Konferentsii po Khimii Ftororganicheskikh Soedinenii* (Abstracts of Reports at the IIIrd All-Union Conference on the Chemistry of the Organofluorine Compounds), Odessa, 1978, p. 153
119. Japanese P. 57-159805
120. R N Haszeldine, R B Rigby, A E Tipping *J. Chem. Soc., Perkin Trans. 1*, 1973, 676
121. C G Krespan, D C England *J. Am. Chem. Soc.*, 1981, **103** 5598; R E Banks, J M Birchall, R N Haszeldine, W J Nicholson *J. Fluorine Chem.*, 1982, **20** 133
122. V F Cherstkov, S R Sterlin, L S German, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 220; V P Cherstkov, S R Sterlin, I L Knunyants *J. Fluorine Chem.*, 1985, **29** 2
123. T N Bell, B J Pullman, B O West *Aust. J. Chem.*, 1963, **16** 636; D Naumann, W Tyrra *J. Organomet. Chem.*, 1987, **334** 323
124. W T Miller, M B Freedman *J. Am. Chem. Soc.*, 1963, **85** 180
125. H C Clark, J T Kwon, D Whyman *Can. J. Chem.*, 1963, **41** 2628
126. B L Dyatkin, S R Sterlin, B I Martynov, I L Knunyants *Tetrahedron Lett.*, 1971, 345
127. B L Dyatkin, B I Martynov, I L Knunyants *J. Organomet. Chem.*, 1973, **57** 423
128. J L Adcock, E B Renk *J. Org. Chem.*, 1979, **44**(19) 3431
129. P Dodman, J C Tatlow *J. Fluorine Chem.*, 1976, **8** 263
130. D Naumann, R Walter *9th International Symposium on Fluorine Chemistry*, Avignon, 1979, p. 43
131. J Banks, H J Emeleus, R N Haszeldine *J. Chem. Soc.*, 1951, **1** 60
132. A P Pascual, M E Wolff *J. Med. Chem.*, 1971, **14** 164
133. US P. 3 285 975
134. US P. 3 794 623
135. US P. 3 786 089
136. US P. 3 384 627
137. N O Brace *J. Org. Chem.*, 1964, **29** 1247
138. H C Low, J M Tedder *Int. J. Chem. Kinet.*, 1978, **10** 325
139. US P. 4 243 770
140. G Haufe, M Muhlstadt *Z. Chem.*, 1979, **19** 170
141. H G Meunir, P J Abell *J. Phys. Chem.*, 1967, **71** 1430
142. A El Soueni, J M Tedder, J C Walton *J. Fluorine Chem.*, 1981, **17** 51
143. N O Brace, J E Van Elswyk *J. Org. C* ·., 1976, **41** 766
144. N O Brace *J. Org. Chem.*, 1966, **31** 28'
145. N O Brace *J. Org. Chem.*, 1973, **38** 316
146. P Piccardi, M Modena *J. Chem. Soc. C*, '59
147. Belgian P. 730 819
148. US P. 3 625 929
149. US P. 3 734 687
150. US P. 3 622 590
151. US P. 3 872 058
152. US P. 4 080 507
153. US P. 3 759 874
154. US P. 3 388 078
155. US P. 3 781 370
156. US P. 3 231 604
157. US P. 3 274 081
158. N O Brace *J. Org. Chem.*, 1971, **36** 1904
159. US P. 3 257 407
160. US P. 3 575 890
161. French P. 1 570 174
162. US P. 3 641 083
163. US P. 3 674 800
164. N O Brace *J. Org. Chem.*, 1975, **40** 851
165. US P. 3 514 487
166. US P. 3 277 039
167. US P. 3 282 095
168. T Kuwamura, H Takahashi *J. Chem. Soc. Jpn., Chem. and Chem. Ind.*, 1974, 1731
169. A I Rakhimov, V I Kaluga *Zh. Org. Khim.*, 1980, **16** 223
170. US P. 3 378 609
171. N O Brace *J. Org. Chem.*, 1979, **44** 1964
172. R E Banks, M G Barlow *J. Chem. Soc., Perkin Trans. 1*, 1974, 126
173. O G Yarosh, M G Voronkov *Tezisy Dokladov III Vsesoyuznoi Konferentsii po Khimii Ftororganicheskikh Soedinenii* (Abstracts of Reports at the IIIrd All-Union Conference on the Chemistry of Organofluorine Compounds), Odessa, 1978, p. 115
174. M G Voronkov, R G Mirskov, A L Kuznetsov *Zh. Org. Khim.*, 1979, **49** 720
175. G V D Tiers *J. Org. Chem.*, 1961, **26** 3515
176. M Hauptschein, A V Grosse *J. Am. Chem. Soc.*, 1951, **73** 5461

177. R D Chambers, W K R Musgrave, J Savory *J. Chem. Soc.*, 1962, 1993
178. US P 3 821 290
179. L S Koshcheeva, A N Lavrent'ev *Zh. Obshch. Khim.*, 1974, **44** 2108
180. K G Sharp, J Schwager *Inorg. Chem.*, 1976, **15** 1697
181. H-G Von Horn *Chem.-Ztg.*, 1971, **95** 742
182. L F Doty, R G Cavell *Inorg. Chem.*, 1974, **13** 2722
183. H G Ang, M E Redwood, B O West *Aust. J. Chem.*, 1972, **25** 493
184. BRD P. 2 110 769
185. J W Thompson, J D Witt, J R Durig *Inorg. Chem.*, 1973, **12** 2124
186. I G Maslennikov, A N Lavrent'ev, V I Shibaev, E G Sochilin *Zh. Obshch. Khim.*, 1976, **46** 1904
187. A N Lavrent'ev, I G Maslennikov, E G Sochilin *Zh. Obshch. Khim.*, 1975, **45** 1702
188. USSR P. 423 788; *Byull. Izobret.*, 1974, (14) 81; *Ref. Zh. Khim.*, 1976, 2N19
189. G S Kenneth *7th International Symposium on Fluorine Chemistry*, California, 1973, p. 1
190. E N Okafo, E Whittle *Int. J. Chem. Kinet.*, 1973, **5** 1047
191. R N Haszeldine *J. Chem. Soc.*, 1953, 3761
192. O P Studzinskii, A V El'tsov *Zh. Vses. Khim. Obshch. im D I Mendeleeva*, 1974, **19** 376
193. G Pearson, J Songstad *J. Am. Chem. Soc.*, 1967, **89** 1827
194. US P. 3 234 267
195. US P. 3 697 564
196. L V Gurvich, G V Karachentsev, V N Kondrat'ev, et al. *Energii Razryva Khimicheskikh Svyazei. Potentsial Ionizatsii i Srodstvo k Elektronu* (Dissociation Energies of Chemical Bonds. Ionisation Potential and Electron Affinity), Nauka, Moscow, 1974, p. 351
197. G J Shack, K O Christe *J. Fluorine Chem.*, 1980, **16** 63
198. M J Berry, G C Pimentel *J. Chem. Phys.*, 1968, **49** 5190
199. E Cuellar, J H Parker *J. Chem. Phys.*, 1974, **61** 422
200. M H Arican, E Potter *J. Chem. Soc., Faraday Trans. 1*, 1973, 1811
201. D A Whytock, J D Clarke *J. Chem. Soc., Faraday Trans. 1*, 1974, 411
202. J A McCleverty *J. Organomet. Chem.*, 1976, **119** 261
203. W J Bevan, R N Haszeldine *J. Chem. Soc., Dalton Trans.*, 1975 620
204. O Yu Okhlobystin *Perenos Elektrona v Organicheskikh Reaktsiyakh* (Electron Transfer in Organic Reactions), Izv. Rostov. Univ., Rostov, 1974, p. 122
205. US P. 3 377 390
206. O R Chambers, G Oates, J M Winfield *J. Chem. Soc., Chem. Commun.*, 1972, **14** 839
207. J Baumanns, L Deneken *J. Fluorine Chem.*, 1974, **3** 323
208. I I Maletina, V V Orda, L M Yagupol'skii, et al. *Zh. Org. Khim.*, 1976, **12** 1371
209. V V Lyalin, V V Orda, L A Alekseeva, L M Yagupol'skii *Zh. Org. Khim.*, 1970, **6** 329
210. K O Christe, C J Schach, R D Wilson *Inorg. Chem.*, 1974, **13** 2811
211. D Nauman, H H Heinsen, E Lehmann *J. Fluorine Chem.*, 1976, **8** 243
212. C J Schack *7th International Symposium on Fluorine Chemistry*, California, 1973, p. 25
213. L M Yagupol'skii, A A Mironova, I I Maletina, V V Orda *Zh. Org. Khim.*, 1980, **16** 232
214. R N Haszeldine *J. Chem. Soc.*, 1955, 2151
215. US P. 3 351 644
216. US P. 3 706 773
217. BRD P. 2 207 177
218. R N Haszeldine *J. Chem. Soc.*, 1953, 2662
219. Q Chen, Z-Y Yang *J. Fluorine Chem.*, 1987, **37** 171
220. V I Shibaev, L S Koshcheeva *Zh. Obshch. Khim.*, 1977, **47** 2601
221. N F Cheetham, A D E Pullin *Aust. J. Chem.*, 1971, **24** 479
222. N F Cheetham, A D E Pullin *J. Chem. Soc., Chem. Commun.*, 1965, 418
223. N F Cheetham, I J McNaught, A D Pullin *Aust. J. Chem.*, 1974, **27** 987
224. N F Cheetham, A D E Pullin *J. Chem. Soc., Chem. Commun.*, 1967, 233
225. D W Larsen, A L Allred *J. Phys. Chem.*, 1965, **69** 2400
226. P Piccardi, M Modena, G C Serboli, M Ragazzini *J. Chem. Soc., C*, 1970, 949
227. K C Eapen, K I Eisentraut, M T Ryan, C Tamborski *J. Fluorine Chem.*, 1986, **31** 405
228. US P. 3 594 358
229. B. P. 1 257 161
230. W S Mungall, C L Martin, G C Borgeson *Macromolecules*, 1975, **8** 934
231. M Tatemoto *9th International Symposium on Fluorine Chemistry*, Avignon, 1979, p. 67
232. US P. 3 838 110
233. US P. 3 531 432
234. US P. 3 575 875
235. K Hohla, K L Kompa *Z. Naturforsch., A*, 1972, **27** 938
236. M J Berry *J. Chem. Phys.*, 1973, **59** 6229
237. S Kimel, S Speiser *Chem. Rev.*, 1977, **77** 437
238. E B Gordon, A I Nadkhin, S A Sotnichenko, I A Boriev *Chem. Phys. Lett.*, 1982, **86** 209
239. A K Hays, J M Hoffman, G C Tisone *Chem. Phys. Lett.*, 1976, **39** 353
240. US P. 3 535 393
241. US P. 3 663 590
242. T Kuwamura, M Ohshima, E Kameyama *J. Chem. Soc. Jpn., Chem. and Chem. Ind.*, 1974, 545
243. US P. 3 937 724
244. US P. 4 283 533
245. A Sekya, N Ishikawa *Chem. Lett.*, 1977, 81
246. P Moreau, G Dalverny *J. Fluorine Chem.*, 1975, **5** 265
247. US P. 3 255 228
248. US P. 343 802
249. R N Haszeldine, B Hewitson, B Higginbottom, et al. *J. Chem. Soc., Chem. Commun.*, 1972, 249
250. French P. 2 305 421
251. Japanese P. 25 361; *Ref. Zh. Khim.*, 1978, 3N154
252. US P. 3 937 724
253. US P. 3 810 939
254. French P. 2 301 511
255. T Hayashi, R Aihara, et al. *Kagaku Kogaku*, 1978, **42** 330
256. US P. 3 625 929
257. F Mares, B C Oxenrider *J. Fluorine Chem.*, 1976, **8** 373
258. P L Coe, N E Milner *J. Organomet. Chem.*, 1974, **70** 147
259. B. P. 1 294 661
260. US P. 3 759 874

261. M C Henry, C G Griffiths, E C Stump *Fluorine Chem. Rev.*, 1967, 1
262. G Wolfrum *Organofluorine Chemistry and Industrial Applications*, Chichester, London, 1979, p. 208
263. US P. 3 880 949
264. US P. 4 120 863
265. US P. 3 947 408
266. US P. 3 859 442
267. US P. 3 821 289
268. Japanese P. 54-22371; *Ref. Zh. Khim.*, 1980, 6O383
269. US P. 3 850945
270. D Cech, G Herrmann, R Staske, et al. *J. Prakt. Chem.*, 1979, **321** 488
271. Japanese P. 50-11891; *Ref. Zh. Khim.*, 1976, 9N138
272. F Lin, Y-S Gao *J. Med. Chem.*, 1983, **26** 598
273. US P. 3 907 897
274. E J Soloski, G J Moore, C Tamborski *J. Fluorine Chem.*, 1976, **8** 295
275. J R Griffith, J G O'Rear *Synthesis*, 1974, 493
276. Japanese P. 57-1638; *Ref. Zh. Khim.*, 1983, 15N165
277. B. P. 1 355 682
278. R A Firestone *J. Med. Chem.*, 1982, **25** 539
279. US P. 4 371 541
280. US P. 3 867 435
281. [This reference is missing from the Russian original (Ed. of Translation)]
282. US P. 4 001 406
283. N I Delyagina, Yu V Zeifman, L S German, I L Knunyants *Tezisy Dokladov Vsesoyuznoi Konferentsii po Khimii Ftora* (Abstracts of Reports at the All-Union Conference on Fluorine Chemistry), Moscow, 1986, p. 10
284. T Taguchi, O Kitagawa, J Kobayashi *6th Regular Meeting of Soviet-Japanese Fluorine Chemists. Symposium on Fluorine Chemistry in Novosibirsk*, 1989, Vol. 1
285. D N Glew, N S Rath *Can. J. Chem.*, 1971, **49** 837

Translated from *Uspekhi Khimii* **61** 102–123 (1992) U.D.C. 667.28;773.79

Organic dyes for constant memory optical discs

T N Gerasimova, V V Shelkovnikov
Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk

ABSTRACT. **Literature data on the use of organic dyes in constant memory optical discs and information recording by semiconductor laser irradiation in the 780–830 nm range are summarised and systematised. Questions on the suitability of the properties of different classes or organic dyes for the main requirements of optical information-recording media have been considered. Future trends in the development of the field of organic dyes for the laser recording of discrete information have been defined.**

Bibliography includes 232 references.

Contents

I. Introduction 55
II. Optical disc recording layers based on organic compounds 55
III. Dyes for optical discs with absorbance in the near-infrared region of the spectrum 57
IV. Conclusion 63

I. Introduction

Optical information disc drives have a number of advantages over magnetic discs (higher recording density, possible contact-free reading, storage life of recorded information, etc.) and have been increasingly used abroad over recent years. They are mainly used in the external memories (EM) of computers. The recording of information on an optical disc is achieved by a focused laser beam, which deposits a particular trace on the surface of an active layer. The recorded information can be read by the same laser at lower power by measuring changes in the characteristics of the reflected beam.[1–5]

Memory recordings may be assigned to one of three categories with respect to the type of the recording/reading regime and the properties of the support: 1) permanent external memory devices with single recording and multiple reading (DRAW or WORM) and reversing facilities. The present review is concerned with the use of organic dyes with the DRAW type of optical discs.

The optical disc consists of a profiled support on to which an active layer <1 μm in thickness is deposited. The reaction of the laser beam on the light-sensitive layer may involve different mechanisms. The ablation process has been most extensively used. In this process the energy of the laser pulses with a duration of $\leqslant 1$ μsec is converted into heat energy causing an increase in temperature of up to 1000 °C or more at the point of exposure, leading to melting of the film, and the material is therefore unsuitable since it vapourises or decomposes. As a result of this process pits $\lesssim 1$ μm in diameter are formed. The information is read by a laser beam of energy less than the threshold value by measuring the difference in the reflectivity from the pit and the background surface. A quantitative characteristic of the recording is the signal/noise ratio at the point of recording (CNR, carrier-noise ratio).[6–9]

The recording LWR-(laser write and read) medium of the optical disc may have a mono-, bi- or tri-layer structure. A metal monolayer transferred on to the support by vacuum evaporation as a thin (ca. 30 nm) film is the most extensively used structure. The recording leads to a decrease in the reflection from the surface of the pits relative to the background. In the bi-layer (antireflex) structure the metal film is covered by a layer of organic dye $\leqslant 100$ nm in thickness. This leads to a decrease in the reflection from the surface of the recording layer of up to ca. 5% and to an increase in its sensitivity. In the pits obtained by ablation the reflectivity increases by up to ca. 90%. In the tri-layer structure the absorbing layer is separated from the metallic mirror by a transparent dielectric which leads to an increase in the efficiency with which the laser beam energy is utilised, i.e. to a further increase in the sensitivity of the material.[8,10] An increase in the number of layers of accurately controlled thickness naturally creates complications in the preparation and also leads to an increase in the price of the optical disc. The recording medium is a key component of the optical disc and should provide higher sensitivity to laser irradiation (ca. 10^{-2} J cm^{-2}), high recording resolution ($\geqslant 1000$ lin mm^{-1}), adequate recording contrast (CNR > 50 dB) a real time recording with immediate reading, and also an adequate storage period for the recording ($\geqslant 10$ years).[8–12]

Gas lasers were used in the initial stage of development of the optical discs of computer memories. Since the beginning of the eighties solid body diode lasers were most widespread and had a number of advantages such as low cost, small dimensions, long storage period, in-use stability, and the possibility of rapid change-over. Present-day optical memory systems are based on the use of GaAlAs semiconductor lasers with emission in the 780–850 nm range.[13–15]

II. Optical disc recording layers based on organic compounds

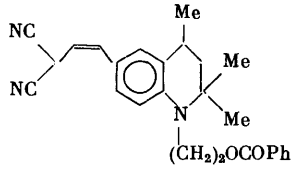
Systematic screening of metals and chalcogenides to identify optimal materials for photothermal recording showed that tellurium and its alloys possess the best characteristics,[5] although it is difficult to produce optical discs based on these materials, since tellurium readily undergoes oxidative degradation in a moist atmosphere.[14] This finding created interest in LWR-media based on organic dyes, since on account of their high stability and low toxicity they are more marketable than Te-containing layers.[11]

Carlson was first to propose the use of organic materials for laser recording in 1969.[16] Recording with a helium-neon laser beam on to a film containing a triarylmethane dye in nitrocellulose was achieved at the expense of the decolourisation of the dye. Two new

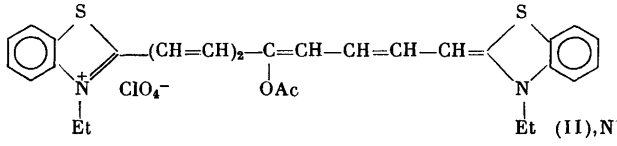
laser recording processes in an organic dye were subsequently proposed. In the first process a bi-layer structure of a polymeric dye was used. In the presence of argon-laser irradiation the dye diffused into the polymeric substrate, thereby causing a change in the spectral characteristics of the layer. 1,4-Diaminoanthraquinone and a series of polymethine dyes (PMD) on a polyethyleneterephthalate film 50 μm in thickness were used as the recording system.[17]

The second process which later became extensively used involved recording with a laser beam through ablation on a film of an organic dye deposited by vacuum evaporation on to a reflecting surface (an aluminium layer 30 nm in thickness on a glass support).[18] With a layer of fluorescein 58 nm in thickness 90% of the incident light was absorbed. The recorded information was ready by means of the difference in the reflectivities from the surface of the pits formed during the recording from the dye layer. This material was superior to the mono-layer structures based on metals in regard to sensitivity and contrasting.[18]

A defect in this system is the possibility of crystallisation of the dye in the sprayed state leading to a decrease in the CNR value.[18] Law et al. were able to surmount this process,[19] by proposing that the dye dissolved in a polymeric matrix should be used as the absorbing layer. A polyvinylacetate film 59 nm in thickness and containing 20% (by mass) of dye (I) when transferred on to a reflecting layer of aluminium provided a higher degree of sensitivity and contrast during recording with a helium-cadmium laser than layers based on tellurium. Similar bi-layer structures based on organic dyes sensitive in the visible range of the spectrum were later described in several reports.[20,21]



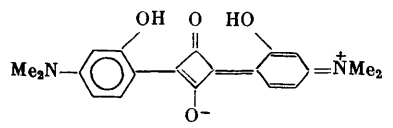
The first report on a DIP-system (dye in polymer) sensitive to irradiation in the near-infrared region of the spectrum appeared in 1981.[13] A film 105 nm in thickness containing 20% PMD (II) in polyvinylacetate transferred on to an aluminiumised glass support exhibited 3.5-fold higher sensitivity than a 15 nm tellurium monolayer during recording with a laser beam with λ_{gen} = 835 nm.



(II), NK-1748

The absorption spectra of dye (II) in the film and in methanol are presented in Fig. 1.

In the same year publications appeared on the use of vanadylphthalocyanine[22] and squarylium dye (III) [23] absorbing in the near-infrared region for laser recording.



In order to use the organic dye as a reflecting type of recording medium in a mono-layer structure, it was essential that the film formulated from the dye had adequately high reflectivity. Data confirming that this was the case were obtained for the first time in 1983.[24] It was shown that a film of a naphthaquinone dye 50 nm in thickness transferred by vacuum deposition on to a polymethylmethacrylate (PMMA) support and absorbing more than 40% of the incident light at a reflectivity of >20% provides adequate sensitivity towards irradiation of the diode laser and good recording characteristics (CNR > 50 dB at a pulse power of ≤5.5 mW).

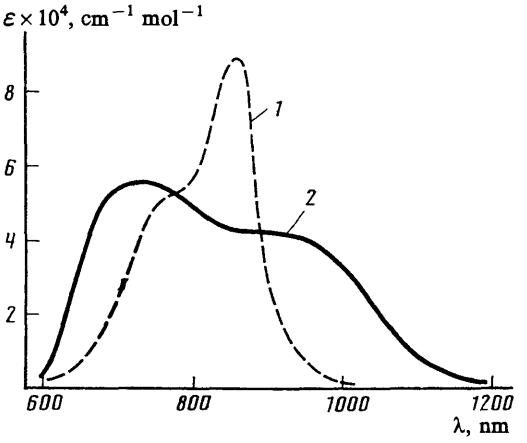
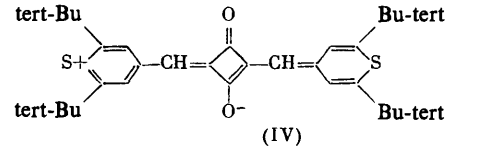
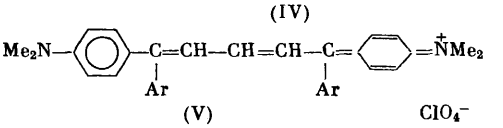


Figure 1. Absorption spectra of dye (II) in methanol (*1*) and in a poly(vinyl acetate) (*2*).

Even higher CNR values were found by certain authors with mono-layer structures obtained by spin-coating of solutions of dyes (IV) and (V) on to profiled PMMA and glass discs.



(IV)



(V) ClO_4^-

As already mentioned above the formation of pits in the LMR type of recording media is largely a photothermal process in which incident light energy is converted into heat more efficiently the more effective is the light absorption and the subsequent oscillatory relaxation of the dye molecules. By studying the mechanism of this process in the DIP-layers as described in earlier reports,[6,23,26,27] and by comparison with layers based on tellurium and other metals, it was possible to determine the optimal characteristics of the recording media and the recordings on them. The laser beam power was 5–10 mW when the diameter of the latter was 1 μm, the threshold energy of the recording was 0.1–0.2 nJ/bit, the energy essential for

the total opening of the pit and to obtain a satisfactory CNR (50–60 dB) was 0.5–1.0 nJ/bit, the optimal thickness of the layer was 60–120 nm, and the recording time was 50–100 nsec. In order to attain these values, the recording material should possess a high extinction coefficient (ca. 10^5 M^{-1} cm^{-1}) at the recording wavelength, low thermal conductivity (5×10^4 cal sec^{-1} deg^{-1}) and thermal capacity, and also a sufficiently low melting point and vaporisation temperature (100–250 °C).

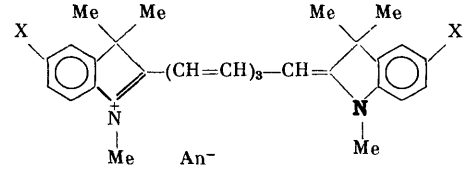
Chemical and photochemical stability under the disc storage conditions and also resistance to the action of the reading beam are important properties determining the suitability of organic dyes as active media in optical memory discs.[15] Testing of the recording layers involves maintenance at an elevated temperature (35–70 °C) in a moist atmosphere (90–95% relative humidity), illumination with visible light at ⩾50000 lux, and continuous reading over a prolonged period.

The characteristics of the DIP-layer are dependent not only on the absorbing dye but also on the properties of the polymer. Determination of the threshold energy of the recording on DIP-layers of dye (I) with different polymers (polyvinylacetate, polyvinylbutyral, PMMA, polycarbonate, etc.) showed that the viscosity and vitrification temperature of the latter do not affect the sensitivity of the recording material.[28] Nevertheless the pit size and hence the quality of the recording is dependent on the viscosity, due to the arisal of a reverse inflow of the pit after the recording.[7] A series of review articles have already been published in which the main criteria determining the selection of components (dyes and polymers) for such materials, their ratios, and the optimal physical and chemical properties of the polymer supports have been formulated.[9,11,15] These questions have been discussed in detail in the review by Pearson.[29] The further advancement in organic recording media for optical memories based on semiconductor lasers is mainly associated with the intensive development of studies of the synthesis of thermally and photochemically stable organic dyes exhibiting intense absorption in the near-infrared spectral range and the testing of these compounds in recording systems. The present state of the art and the potential for advancements in the field of infrared dyes for optical discs are described below.

III. Dyes for optical discs with absorbance in the near-infrared region of the spectrum

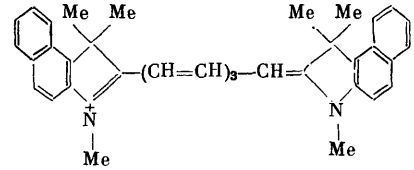
1. Polymethine dyes

Polymethine dyes have been most extensively used in laser recording, since the PMD films possess sufficiently high reflectivity (up to 40%) which provides a high degree of recording contrast.[11,14] Symmetrical polymethine dyes containing indolenine, quinoline, benzthiazole, benzoxazole residues etc. as terminal groups are most often used. Absorption in the region of semiconductor laser generation is achieved in the presence of a chain of seven or more methine groups† in the dye molecule, and therefore 1,1'3,3,3',3-hexamethylindotricarbocyaniniodide [dye NK-125 (VI),[38–41] its perchlorate,[42–44] the 4- and 5-chlorosubstituted dyes (VI) [45,46] including dye NK-2882 (VII),[47–49] 1,1,3,3,3',3-hexamethyl-4,4',5,5'-dibenzo-2,2'-indotricarbocyaninperchlorate (dye NK-2014, VIII)],[38,50–59] and 3,3'-dimethylthiatricarbocyaniniodide[60–63] are most often described in the patent literature as dyes for optical discs.



(VI), NK-125 : X = H, An = I^-

(VII), NK-2883 : X = Cl, An = ClO_4^-



(VIII), NK-2024, $\lambda_{max\ abs}$ = 782 nm

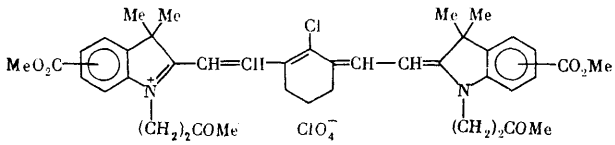
Heterocyclic nitrogen atoms in molecules of such dyes may in addition to the methyl group contain alkyl or substituted alkyl groups (Et, Pr, Bu, C_2H_4OH, etc.),[30–35,37,53,64,65] whereas the aromatic rings contain electron acceptor or electron donor substituents.[31–36] These spectra contain intense absorption bands in the 740–780 nm range. At a given polymethine chain length the benz[c,d]indole derivatives are the most deeply coloured.[66]

The polymethine colour may be deepened by increase in the length of the outer polymethine chain of the dye. In the symmetrical polycyanines an increase in length by one vinylene group leads to the displacement of the absorption maximum by 90–100 nm to longer wavelengths.[67] Thus the first dye in the polymethine series used to record information with the semiconductor laser was tetracarbocyanine(II).[13] However it is known that an increase in the number of vinyl groups to 4 or more leads to a sharp fall in the extinction and to the leveling of the absorption curve as a result of *trans-cis*-isomerisation in the polymethine chain.[68] In this case the thermal and photochemical stability of the dye also falls significantly.[69]

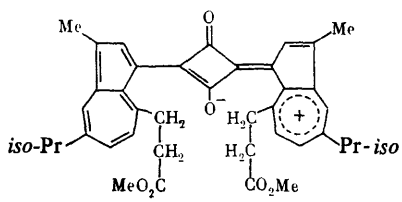
One approach by means of which a bathochromic effect may be obtained and at the same time the stability of the polymethine dye molecule is increased involves the cyclisation of part of the chromophore by bridging groups which rigidly fix the separate units of the polymethine chain.[69] There are a number of patents describing the use in optical discs of indo- and thiatri(penta)carbocyanines containing a di- or trimethylene bridge in the outer polymethine chain.[70–80] Thus a film of dye (IX) 75 nm in thickness transferred by spin-coating on to a glass support has a reflectivity of 37% and provides adequate sensitivity to semiconductor laser irradiation at 830 nm and high CNP values. The recording was stable when maintained at 50 °C in a moist atmosphere (after 150 h the CNP value decreases by 3% or more) and was stable to illumination with a 500 W daylight lamp (after 100 h the decrease in

† The use of dicarbocyanines with a maximum absorption up to 700 nm for recording with the semiconductor laser has been described.[30–37]

CNP was ⩽4% or less).[72] Hydrated aromatic or heteroaromatic rings may serve as the bridge.[11,81,82]



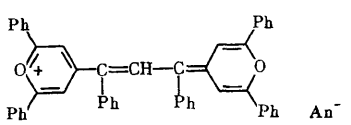
Polymethine dyes containing a squaric acid or a croconic acid fragment between the heterocyclic residues is widely used in laser recording materials.[12,14,26,83–85] Synthetic routes for squarylium dyes with absorbance in the near-infrared range of the spectrum have been described.[86] Their absorption maxima are displaced relative to the spectra of the corresponding symmetrical polymethine dyes with linear polymethine chains by 20–60 nm to longer wavelengths. The largest number of patents describe the type (X) squarylium dyes containing azulene rings[87–89] or their aza-analogues[90] as terminal groups. Active layers based on



(X), $\lambda_{max\ abs}$ = 773 nm

diazulyltri- and diazulylpentamethincyanines, which contain identically or differently substituted azulene rings, have been described.[91,92] Their absorption spectra are similar to those of polymethine dye derivatives of indolysine[93] which are also used in optical discs.[94] Replacement of hydrogen atoms in the azulene rings by alkyl groups leads to a bathochromic shift of the longwave band in the electronic spectrum and to an increase in the solubility in organic media.[89,92]

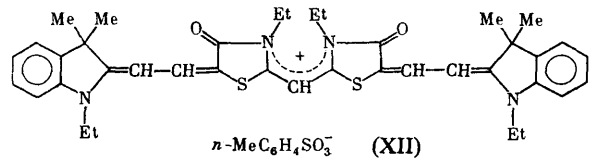
Intense absorption in the near-infrared region of the spectrum when the polymethine chain length is comparatively short may be achieved by replacement of the nitrogenous heterocycles in the polymethine dye molecules by pyrylium or thio- or selenopyrylium residues. Pyrylo- and thiopyrylocyanines containing three or five methine groups exhibit intense absorption in the 680–880 nm range and are suitable for recording information with the laser.[60,95–98] A film of dye (XI) 100 nm in thickness showed high sensitivity and good recording quality at 790 nm (stability to visible light at 54 000 lux for 50 h).[95]



(XI)

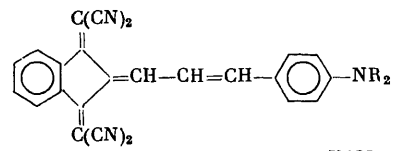
Good results have been obtained with type (IV) squarylium dyes containing pyrylium or thiopyrylium rings.[11,14,26,99] The presence of tert-butyl groups in the dye molecule increases it solubility in organic media and facilitates the formation of active layers by the spin-coating technique.[26]

There are relatively little data on the use of hemi- and mercocyanines for optical recording. Derivatives of indolenine, oxoindolysine, and pyrylium salts and their heteroanalogues,[12,100–107] assymmetrical polymethine dyes containing the azulene ring,[108–110] and also three- and four-nuclear polymethine dyes containing branched or linear chromosphores have been described.[11,112] Thus recording



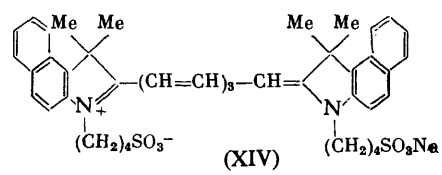
at 790 nm on a film of dye (XII) deposited on to a PMMA support by spin-coating gave a highly contrasted image stable to visible light.[111]

The identification of recording media for optical discs among the deeply coloured neutral polymethine dyes type (XIII), the dicyanomethyleneindan residue or its sulphur analogue serving as the acceptor group would appear to be a promising approach.[12,113,114]



(XIII)

Essentially the only method for the formation of thin polymethine dye films on formatted substrates of the optical discs is the spin-coating of their solutions in organic solvents,‡ dichloroethane and methyl ethyl ketone being most often used. Aqueous or aqueous-alcoholic solutions are used only for type (XIV) dyes, the latter molecules

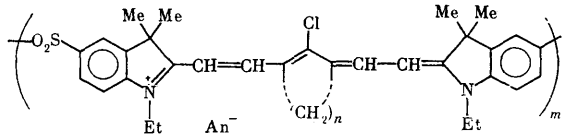


containing alkylsulphonate groups in positions 1 and 1′.[75,115]

The low solubility of polymethine dye salts in organic solvents and their tendency to crystallise are factors which hinder the production of homogeneous amorphous films which are stable and which have a suitable absorption coefficient in the semiconductor laser generation range. The most widely used method providing a means of surmounting this obstacle involves the creation of DIP-films. Nitrocellulose is most frequently used for this purpose,[55,57–59,97,102,104,106] and there are references in the literature on the use of polyvinylbutyral, PMMA and a number of other polymers and copolymers.[39,40,51,56,76,83,88] The preparation of

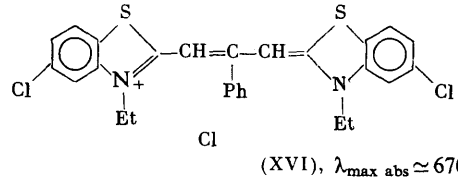
‡ Vacuum deposition may be used only for the squarylium type of polymethine dyes.[12,84]

recording layers based on type (XV) polymeric dyes has been described.[116,117] A positive effect is apparently achieved on deposition of a layer containing a mixture of two dyes.[44,118,119]

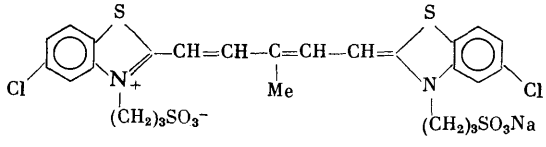


(XV) n=2, 3

Langmuir–Blodgett technology is a novel and extremely promising means of deposition of recording layers on to the reflecting supports.[120] Layers based on *J*-aggregates§ of dyes (XVI) and (XVII) exhibiting absorption in different spectral regions and obtained by this method have been described.[121]



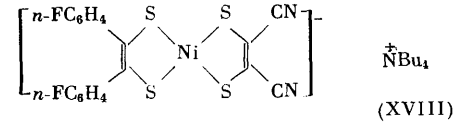
(XVI), $\lambda_{max\ abs} \simeq 670$ nm



(XVII), $\lambda_{max\ abs} \simeq 800$ nm

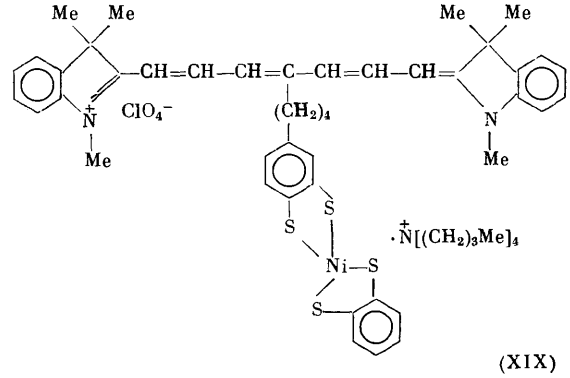
The structure of the layer containing these dyes in the Langmuir–Blodgett films and the change in its spectral characteristics by the action of a diode laser at 780 nm and xenon flash-lamps are presented in Fig. 2. The authors propose that an eight-fold spectral thickening of information is possible in the 400–800 nm range when the layer thickness of each dye is 10 monolayers, and at a total LWR-layer thickness of 250 nm and a *J*-aggregate absorption band width in the order of 50 nm.

Poor light stability is known to be a feature of polymethine dyes. There is relatively little information on the mechanism of discoloration of these dyes, although it has been proposed that an oxidative mechanism is responsible for this process.[122] In this regard recording layers based on polymethine dyes usually include singlet oxygen at a level equivalent to 10–50% of the mass of the dye. Derivatives of aliphatic and aromatic amines,[52,63,85,123] nickel acetylacetonate,[76] or titanium acetylacetonate[65] and also other transition metal complexes are used as stabilisers. Aliphatic or aromatic azomethines,[58,59,124] and derivatives of *o*-phenylenediamine, *o*-oxy- or *o*-aminothiophenol etc.,[49,55,547] may serve as organic ligands in these layers. The most widely used compounds are dithiobenzyl nickel and its substituted analogues,[61] and dithienes (dithiolates) of nickel and other transition metals.[41,42,48,53,54,98,100,125–127] Anionic salts of nickel dithienes possessing high sensitivity to atmospheric oxygen are particularly effective stabilisers.[128] There are patent data indicating that the introduction of 15% quencher (XVIII) into a recording layer based on polymethine dyes reduced the extent of its degradation by 75–80% on exposure to visible light.[125,126]



(XVIII)

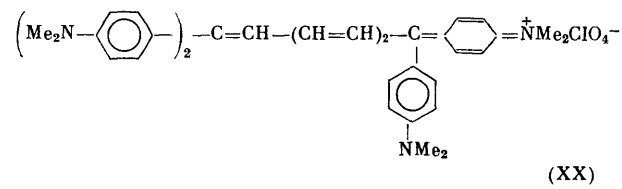
The light stability of the active layer and the repeated information reading may be significantly increased, when nickel salts of polycyanines containing alkylsulphonate or alkylcarboxylate groups at the heterocyclic nitrogen atoms are used in the LWR-layers,[129–131] and also when polymethine dyes containing nickel dithiolate fragments in the molecules are used.[132] Thus degradation of dye (XIX) in the presence of light is five-fold lower and stability to reading is ten-fold higher than those in the case of dye (VI).[132]



(XIX)

2. Dyes in the di(tri)arylmethane and triarylamine series

Triphenylmethane dyes with intense absorption in the visible range were some of the first dyes to be tested in recording layers of optical discs.[16,18] Examples of their use in computer external memories based on semiconductor lasers later appeared.[12,139] Absorption in the infrared range is achieved by introduction of chains of two or more vinylene groups into their molecules,[133–139] and in a number of cases by incorporation into the rings.[12,139] A similar effect is obtained, when the benzene rings are replaced by heteroaromatic residues,[140] and also when a squaric acid residue is introduced into the chain.[141] Type (XX) arylmethane dyes containing dialkylamino groups in *para*-positions of the aromatic rings have been most extensively used.[133–138,141]

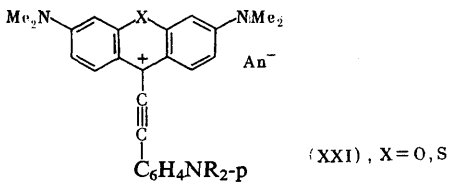


(XX)

It has been shown that the binding of two phenyl rings in the triphenylmethane dye molecule by means of a heteroatom containing unshared electron pairs leads to a deepening of the colour.[122,142]

§ *J*-Aggregation, aggregation of the dye molecules leading to the displacement of absorption to longer wavelengths.

The opposite effect was obtained by Japanese chemists on introduction of an acetylene group between the central carbon atom and the *p*-dialkylaminophenyl residue in the type (XXI) dye molecule.[143] Films of such dyes in polymer supports show adequate stability and are appropriate for laser recording.[144,145]



(XXI), X = O, S

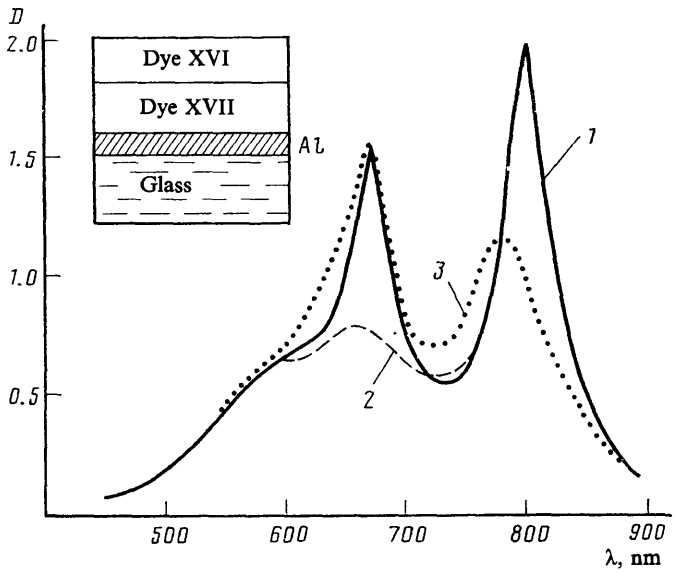
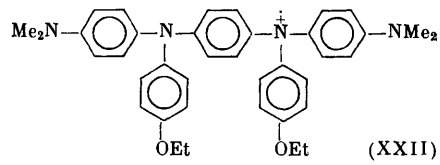


Figure 2. Absorption spectra of a Langmuir–Blodgett film containing layers of dyes (XVI) and (XVII) before irradiation (*1*), after irradiation with a xenon flash-lamp (*2*) and after irradiation with a diode laser at 780 nm (*3*).

Cationic arylmethane dyes have been tested in both mono-layer and bi-layer structures of LWR-materials. They may be deposited on to profiled supports by spin-coating of solutions in dichloroethane, methyl ethyl ketone, dimethylformamide, or some other organic solvent. Polymer additives (PMMA, nitrocellulose) or crown-ethers are used to form the film.[133,134] By using these additives a wider range of solvents will be suitable for this purpose.[138] Although the triarylmethane dyes share the common property of reduced light fastness,[122] there are patent data which describe the creation of films based on type (XX) dyes which have adequate resistance to the action of visible light[135] and to prolonged heating in a moist atmosphere.[139] The light fastness may be improved by introduction of nickel dithiolates into the recording layer.[137]

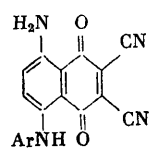
Triarylaminylic salts (the electronic spectra of which contain broad absorption bands in the near-infrared range) have also been proposed as dyes for optical discs.[142,146,147] Despite the cation-radical nature of these compounds and their thermal instability in solution there are patents describing the preparation of dye (XXII) in a film for the laser recording of a contrasted image stable to prolonged irradiation from a daylight lamp.[147] However, this type of dye is most often used in a mixture with a polymethine dye as a singlet oxygen quencher.[37,54,80]



(XXII)

3. Quinone and quinonimine derivatives

Calculation of the electronic absorption spectra of aminosubstituted naphtho- and anthraquinones shows that the longwave absorption band results from the $\pi-\pi^*$-transition involving the transfer of electron density from the benzene to the quinoid ring.[142,148] Consequently this band may be displaced to the near-infrared region as a result of the introduction of donor groups into positions 5 and 8 or acceptor substituents into positions 2 and 3 of the 1,4-naphthoquinone molecule. In accordance with this observation in 1983 it was shown that 2,3-dicyano-5-arylamino-8-amino-1,4-naphthoquinone (XXII) derivatives absorb in the 760–800 nm range and may be used in optical discs as the reflecting type of recording medium in the monolayer structure.[24,149,150] The synthesis of type (XXIII) dyes has been described in detail.[151]

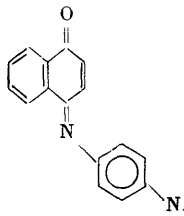


(XXIII)

In later years many patents have appeared on the use in laser recording of type (XXIII) dyes with different substituents (Alk, Hal, OR, NHR, NHAr, etc.) in the aryl residue.[12,14,152–162] The structure of the dye has a specific effect on the absorption range, and on the sensitivity and stability of the active layer. The best results were obtained with *p*-alkoxy-substituted compounds.[14,157,158,160] Other authors have shown that introduction of the methoxy group into the *para*-position of the N-aryl residue increases the stability of the recording from several months to ca. 10 years.[158]

The neutrality of the naphthoquinone dyes confers good solubility in organic media and high stability. Films of such dyes may therefore be formed on the supports by spin-coating and vacuum deposition.[151–162] At a thickness of 60–200 nm they have adequately high reflectivity ($\gtrsim$30%) and it is therefore possible to use them in monolayer structures without a metallic reflecting layer. Recording by GaAlAs-laser irradiation at 830 nm and an impulse strength of 4–10 mW provides a CNR value of more than 50 dB.[152,153,162]

In recent years the search for new naphthoquinone dyes for optical discs has advanced in several directions. One of these directions involves the use of the 1,4-naphthoquinone-4-imine (XXIV) structure containing the *para*-dialkylaminophenyl group in the nitrogen atom.[163]



(XXIV), $\lambda_{max\ abs} \simeq 580$ nm

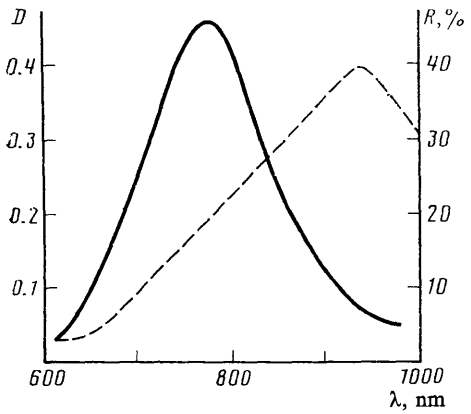
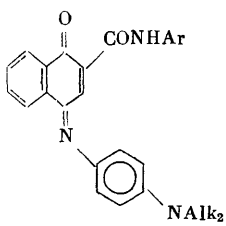


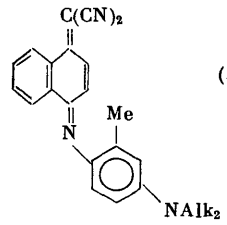
Figure 3. Absorption spectra and the reflection of a layer of dye (XXVI) in PMMA 60 nm in thickness.

Introduction of acceptor substituents into the quinoid moiety of the type (XXIV) dye molecule leads to the appearance of an intense absorption band with a charge-transfer in the near-infrared range which confers sensitivity to semiconductor laser irradiation.[163] Data in Japanese patents confirm that indoaniline dyes (XXV) may be used in mono- and bi-layer structures for laser recording at 780 nm.[164,165]



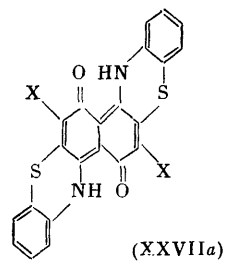
(XXV), $\lambda_{max\ abs} \geqslant 720$ nm

Displacement of the longwave absorption band into the infra-red range may be attained also as a result of the replacement of the oxygen atom in structure (XXIV) by the dicyanomethylene group. Synthesis of type (XXVI) dyes has been described.[166,167] Their films transferred on to a polymeric support have a broad absorption band in the 600–1000 nm range in the electronic spectrum and adequate reflectivity (Fig. 3) which provides excellent recording characteristics at 830 nm at a laser pulse power of 4 mW.[166–168]

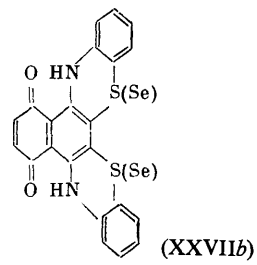


(XXVI), $\lambda_{max\ abs} \approx 760$ nm

Another approach for obtaining the quinoid type of infrared-absorbing dyes is the creation of structures (XXVII*a*, *b*) based on the 1,4- and 1,5-naphthoquinone molecules and containing azine heterocycles.



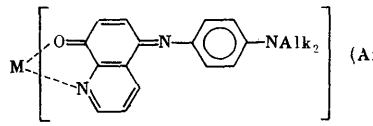
(XXVII*a*)



(XXVII*b*)

Compounds of this type have been obtained by interaction of a 6-X-substituted 2,3-dichloronaphthazarine with a salt of *o*-aminothio(seleno)phenol. Spectral studies showed that they exist in the quinoid form and that the introduction of *peri*-located phenylamino groups into the azine rings leads to a bathochromic shift of the longwave absorption band by 50–100 nm.[148,150,169,170] The 1,5-bis(phenothiazin)quinone (XXVII*a*) absorbs in a region of longer wavelengths in comparsion with 1,4-naphthoquinone (XXVII*b*).[170] An additional bathochromic shift is found for the disulphoxide, compound (XXVII*b*), owing to an increase in the electronegativity of the azine ring.[170] Bis(phenothiazine)quinone films 20–110 nm in thickness transferred to polymeric supports by vacuum deposition have been tested as a recording medium for use at 780 nm in mono-layer structures and were found to exhibit adequate thermostability.[169,171,172]

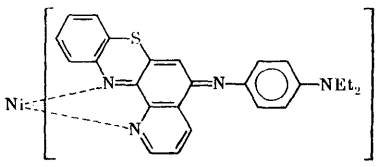
The stability of recording layers based on naphthoquinone dyes may be significantly increased by complex formation with cobalt salts.[158] This observation marked the beginning of a series of studies on the molecular "design" of infrared-absorbing dyes by creating transition metal complexes based on 1,4-naphthoquinone or 1,4-naphthoquinone-4-imine derivatives.[173–176] Complex formation leads to the appearance of an intense band with a charge-transfer in the near-infrared range. Its longwave shift relative to the absorption band attributable to the $\pi-\pi^*$-transition in the ligand molecule is 140–170 nm for type (XXVIII) structures.[175]



M=Ni, Co, Cu

(XXVIII), $\lambda_{max\ abs}$ ca. 770 nm

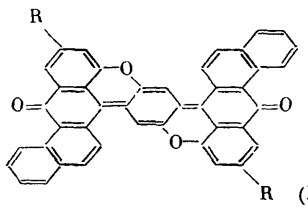
An even greater bathochromic effect is obtained during complex formation of pyrido-[2,3-a]phenothiazine dyes. For example when complex (XXIX) is obtained from the corresponding ligand, the longwave absorption band is displaced by 184 nm, and there is a 4,9-fold increase in the molar coefficient of extinction.[177,178] The complex of physical and chemical properties of type (XXVIII) and (XXIX) dyes determine their potential in the field of optical disc recording.



(XXIX), $\lambda_{max\ abs} = 838$ nm

There are relatively little data on the use of anthraquinone dyes in memories based on diode lasers. The patent and scientific literature describe anthraquinone derivatives containing the amino- and arylamino groups in *peri*-positions,[179,180] including the groups incorporated into azine rings.[150,169,181,182] The spectral properties of lasers based on these derivatives and also the characteristics of laser recording in such layers are similar to the readings obtained for analogous naphthoquinone derivatives.

In recent years patent data have appeared on the LWR-layers based on vat dyes, anthrapyridone derivatives,[183] and the (XXX) type of polycarbocycles.[184] Films from these compounds



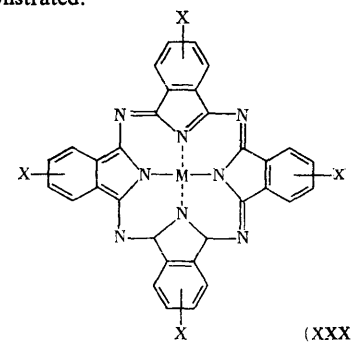
(XXX), $\lambda_{max\ abs} = 770$ nm

may be formed by vacuum deposition and by spin-coating, and they are highly resistant to heating in a moist atmosphere.

4. Phthalocyanines and other metallic complex dyes

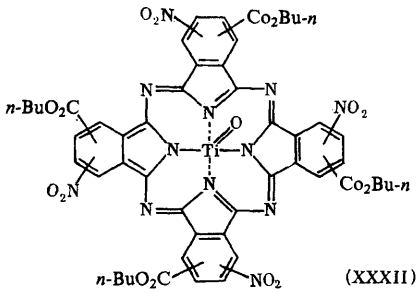
The phthalocyanines or tetrabenzotetraazaporphines are structurally similar to natural pigments based on the porphine-16-centric aromatic system. The spectra of metallised phthalocyanines contain narrow and very intense absorption bands in the 650–750 nm range. This class of dyes typically possesses extremely high thermal- and light-stability,[122,142] resulting in the use of phthalocyanines in optical disc information recording in the early stages in the development of this field.[14]

The use of phthalocyanines (XXXI) of both transition (manganese,[185,186] nickel,[187,188] iron,[188] titanium,[189,190]) and nontransition metals (magnesium,[191] zinc,[188] lead,[187,188,192] aluminium,[193,194] tin,[188,195] and silicon elements[196]) in optical discs has already been patented. The titanium, aluminium, tin, and silicon derivatives contain in the complex forming element an oxygen or halogen atom, Alk, Alko, Alk_3SiO-groups, etc. Materials based on copper[187,188,197–199] and vanadium[187,188,198,200–206] phthalocyanines have been most widely used. The possibility of laser recording on films of metal complexes of phthalocyanine thioanalogues has been demonstrated.[207,208]



(XXXI)

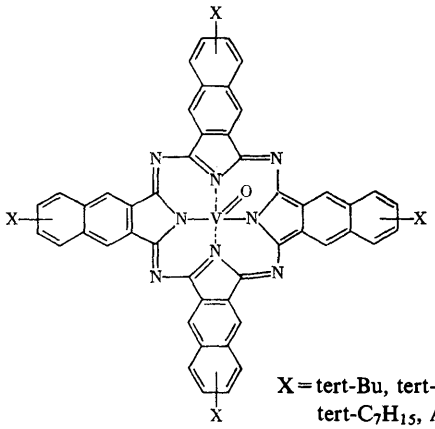
SSP molecular orbital calculations of phthalocyanine dye molecules show that excitation leads to the displacement of electron density from the centre of the molecule to its perimeter and consequently a decrease in the electronegativity of the complex forming group and the introduction of electron acceptor substituents into the benzene rings should lead to a bathochromic displacement of the longwave absorption band.[122] Accordingly in the electronic spectra of films based on titanylphthalocyanines (XXXII) containing strong electron acceptors in the aromatic nuclei



(XXXII), $\lambda_{max\ abs} = 805$ nm

absorption in the infrared range is found which provides high sensitivity to semiconductor laser irradiation and a recording with good contrast (CNR $\geqslant$ 51 dB).[189,190]

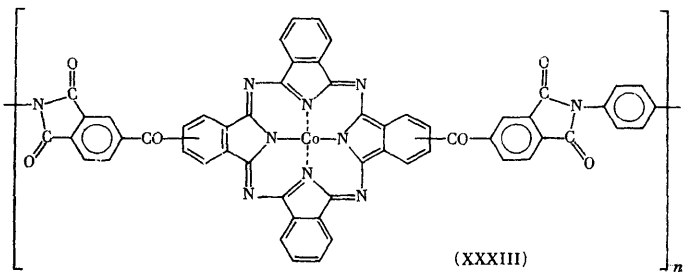
Naphthalocyanine dyes have been widely used in optical disc recording.[209–217] The extension of the conjugated system owing to linear annelation of benzene rings to form 2,3-naphthocyanine causes a bathochromic displacement of the absorbance by 80–100 nm, moving it nearer to the diode laser generation range (ca. 800 nm).[142] The same elements as those in the type (XXXI) phthalocyanines may serve as complex forming groups. Lasers based on vanadyl-naphthocyanine are most widely used.[218,220]



X = tert-Bu, tert-Am tert-C_7H_{15}, AlkS, N = NR and others

On account of their high thermal stability the phthalocyanine dyes may be deposited on supports by vacuum deposition.[185,191,195,208] Nevertheless despite the low solubility of the phthalocyanines in organic media, the spin-coating technology is becoming increasingly used.[186,189,190,194,202,209,214,216] Solubility can be increased by introduction into the dye molecule of alkyl or alkoxy groups containing three or more carbon atoms or silicon-containing residues containing long-chain alkyl groups or several halogen atoms.[186,187,194,202,204,211,214,216–219] Good recording characteristics were obtained on layers containing mixtures of phthalocyanines with polymethine dyes[43,199] and 2,3-dicyano-5-amino-8-arylamino-1,4-naphthoquinones.[221,222]

DIP-layers based on phthalocyanine dyes have been used much less frequently than those based on polymethine dyes. Nitrocellulose and polystyrene, etc. have been used as polymeric supports.[186,211,218] Excellent laser recording readings have been obtained on layers of polymeric dye (XXXIII).[223]

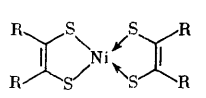


(XXXIII)

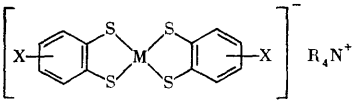
Films of metallic complexes of phthalocyanines possess relatively high reflectance in the near-infrared range and therefore may be used within both bi-layer recording materials incorporating a metallic reflecting layer (Sn,[203] Re,[224] Al[205,215,218]) and monolayer structures.[189,190,202,206] Thus a naphthalocyanine layer containing the complex-forming group $Ge(OSiEt_3)_2$ 90 nm in thickness has a reflectivity of 50% at 825 nm and provides a CNR value equal to 50 dB at a recording beam pulse power of 5.3 mW.[213]

A characteristic feature of the phthalocyanines is their high thermal and light stability.[122] The recording layers based on these compounds do not require the use of stabilisers, although a positive effect has been observed when they are supplemented with triarylaminyl salts[199,214] and titanium acetylacetonate.[200] The high operating features of the LWR-layers based on the phthalocyanine dyes and also on the inexhaustible flow of patent literature indicate that, together with the polymethine and naphthoquinone dyes, they are undoubtedly of interest in regard to the technology of the optical memory discs.

In addition to the phthalocyanines and metal-containing quinone derivatives (see previous section), metal (Ni, Cu, Co, Fe, etc.) complexes with *o*-oxynitrosonaphthalenes, aromatic azomethines, and other organic ligands have been reported as being active media for optical recording.[225,226] The extensive use of dithiolate complexes of metals and recording layers based on polymethine dyes and other dyes as singlet oxygen quenchers has already been described. Their use as supports in photothermal recording has also been described.[227–230] A large amount of data concerns both the neutral (XXXIV) [227–229] and also the anionic (XXXV) type[230,231] of nickel complexes.



(XXXIV)



(XXXV)

The metal dithiolates have low solubility in organic media which is a serious defect of these dyes, since only the spin-coating technique may be used to transfer them on to supports. Solubility may be increased by introducing into the ligand molecule alkyl groups with seven or more carbon atoms, several Me-groups, or halogen atoms[227,228,230,231] and also by creating dye-polymer compositions.[281,231] Since the metal dithiolate films have low reflectivity they may be used only in bi-layer structures with a metal reflecting layer (Al, Au).[227,228,232]

IV. Conclusion

Thus in the past decade a new direction has appeared in the field of non-silver photography, discrete laser recording on organic dyes for use in optical systems with a large capacity memory. A study of organic recording media has revealed a number of advantages over lasers based on tellurium and its alloys, i.e. high resistance to the action of atmospheric oxygen and moisture, lower toxicity, relatively low melting points conferring higher sensitivity, low thermal conductivity with the consequent attainment of a higher recording density, a comparatively inexpensive technology for disc preparation, and the possibility of altering the optical and thermomechanical properties of the recording medium by modification of the structure of the organic dye.

From the experience gained to date from the experimental study of the electronic structure of dyes and with the aid of quantum chemical calculations it is possible to conduct a targetted synthesis of dyes suitable for use in optical discs during recording with semiconductor lasers at a wavelength of 780–830 nm. The polymethine dyes, metallic complexes of phthalocyanines and naphthoquinone dyes are most promising. The growing market abroad in DRAW optical discs and the introduction of the flexible type of carrier for optical recording on organic dyes ("digital paper") are undoubtedly powerful stimulants for the further development of studies in the field of organic dyes and photothermal materials based on these compounds.

The authors wish to thank L V Ektova for assistance in compiling the literature.

References

1. G Maklaud *Elektronika*, 1988, (10) 29
2. G Maklaud *Elektronika*, 1989, (18) 43
3. A L Mikaelyan *Radiotekhnika i Elektronika*, 1989, **34** 673
4. *Kompyuter Press. Obozrenie Zarubezhnoi Pressy* (Computer Press. Review of the Foreign Press), 1990, Collection 5, 3

5. I A Akimov, V A Barachevskii, Yu P Gushcho, et al. *Perspektrivy i Vozmozhnosti Neserebryanoi Fotografii* (Perspectives and Possibilities in Non-Silver Photography), A L Kartuzhanskii (Editor), Khimiya, Leningrad, 1988, p. 160
6. J J Wrobel, A B Marchant, D G Howe *Appl. Phys. Lett.*, 1982, **40** 928
7. G E Johnson, K Y Law *Proc. SPIE*, 1983, **420** 336
8. V B Jipson, K Y Ahn *Solid State Technol.*, 1984, 141
9. M D Croucher, M A Hopper *Chem. Technol.*, 1987, 426
10. R A Bartolini *J. Vac. Sci. Technol.*, 1981, **18** 70
11. J E Kuder *J. Imag. Technol.*, 1986, **12** 140
12. M Umehara, M Abe, H Oba *J. Synth. Org. Chem. Jpn.*, 1985, **43** 334
13. K Y Law, P S Vincett *Appl. Phys. Lett.*, 1981, **39** 718
14. H Nakazumi *J. Soc. Dyes Colour*, 1988, **104** 121
15. J J Wrobel *Solid State Technol.*, 1989, 103
16. C O Carlson, H L Bernstein, E Stone, US P. 3 465 352 (1969)
17. V Novotny, L Alexandru *J. Appl. Polym. Sci.*, 1979, **24** 1321
18. A E Bell, F W Spong *IEEE J. Quant. Electron.*, 1978, **14** 487
19. K T Law, P S Vincett, R O Loutfy, et al. *Appl. Phys. Lett.*, 1980, **36** 884
20. T W Smith *J. Vac. Sci. Technol.*, 1981, **18** 100
21. D G Howe, J J Wrobel *J. Vac. Sci. Technol.*, 1981, **18** 92
22. P Kivits, K de Bont, J van d Veen *J. Appl. Phys.*, 1981, **A26** 101
23. V B Jipson, C R Jones *J. Vac. Sci. Technol.*, 1981, **18** 105
24. N Itoh, S Esho, K Nakagawa, et al. *Proc. SPIE*, 1983, **420** 332
25. D J Gravensteijn, C Steenbergen, J van d Veen *Proc. SPIE*, 1983, **420** 327
26. D J Gravensteijn, J van d Veen *Philips Tech. Rev.*, 1983, 84 **41** 325
27. H Oba, M Abe, M Umehara, et al. *Appl. Optics*, 1986, **25** 4023
28. K Y Law, G E Johnson *J. Appl. Phys.*, 1982, **54** 4799
29. J M Pearson *Adv. Chem. Ser.*, 1988, **218** 331
30. Japanese Appl. 63/99 991; *Chem. Abs.*, 1988, **109** 160 753
31. Japanese Appl. 01/40 384; *Chem. Abs.*, 1989, **111** 68 045
32. Japanese Appl. 01/40 385; *Chem. Abs.*, 1989, **111** 68 053
33. Japanese Appl. 01/40 386; *Chem. Abs.*, 1989, **111** 68 054
34. Japanese Appl. 01/40 383; *Chem. Abs.*, 1989, **111** 48 248
35. Japanese Appl. 01/40 381; *Chem. Abs.*, 1989, **111** 68 043
36. FRG Appl. 3 826 697; *Chem. Abs.*, 1989, **111** 79 904
37. Japanese Appl. 01/40 390; *Chem. Abs.*, 1989, **111** 48 259
38. M Sumitani *Kagaku Kogyo*, 1986, **37** 379; *Chem. Abs.*, 1987, **106** 25 034
39. Japanese Appl. 63/236 689; *Chem. Abs.*, 1989, **110** 145 147
40. Japanese Appl. 63/13 787; *Chem. Abs.*, 1988, **108** 229 797
41. International Appl. 85/04 372; *Chem. Abs.*, 1986, **104** 120 116
42. UK P. 2 165 658; *Chem. Abs.*, 1986, **105** 181 610
43. Japanese Appl. 63/189 291; *Chem. Abs.*, 1989, **110** 145 138
44. Japanese Appl. 63/189 292; *Chem. Abs.*, 1989, **110** 145 139
45. Japanese Appl. 62/11 682; *Chem. Abs.*, 1987, **107** 68 322
46. US P. 4 737 444; *Chem. Abs.*, 1988, **109** 201 596
47. Japanese Appl. 61/90 342; *Chem. Abs.*, 1986, **105** 181 630
48. Japanese Appl. 62/223 166; *Chem. Abs.*, 1988, **108** 214 058
49. Japanese Appl. 63/19 293; *Chem. Abs.*, 1988, **109** 119 813
50. Japanese Appl. 62/30 089; *Chem. Abs.*, 1987, **107** 68 133
51. Japanese Appl. 01/36 487; *Chem. Abs.*, 1989, **111** 87 570
52. Japanese Appl. 59/213 039; *Chem. Abs.*, 1985, **102** 141 009
53. Japanese Appl. 61/74 891; *Chem. Abs.*, 1986, **105** 181 618
54. FRG Appl. 3 724 981; *Chem. Abs.*, 1988, **109** 119 775
55. Japanese Appl. 60/36 190; *Chem. Abs.*, 1985, **103** 79 562
56. Japanese Appl. 01/38 287; *Chem. Abs.*, 1989, **111** 48 267
57. Japanese Appl. 60/35 054; *Chem. Abs.*, 1985, **103** 96 458
58. Japanese Appl. 60/44 389; *Chem. Abs.*, 1985, **103** 45 885
59. Japanese Appl. 60/44 390; *Chem. Abs.*, 1985, **103** 96 463
60. Japanese Appl. 61/277 943; *Chem. Abs.*, 1987, **106** 205 323
61. Japanese Appl. 59/55 794; *Chem. Abs.*, 1985, **102** 70 319
62. FRG Appl. 3 521 915; *Chem. Abs.*, 1986, **105** 143 647
63. FRG Appl. 3 636 959; *Chem. Abs.*, 1987, **107** 124 708
64. Japanese Appl. 01/45 473; *Chem. Abs.*, 1989, **111** 79 906
65. Japanese Appl. 59/198 193; *Chem. Abs.*, 1985, **102** 158 177
66. FRG Appl. 3608 214; *Chem. Abs.*, 1987, **107** 238 577
67. A D Kaukovskii *Stroenie i Tsvet Polimetinovykh Krasitelei* (Structure and Colour of the Polymethine Dyes), Nauk Dumka, Kiev, 1989, 231 pp
68. A I Tolmachev, Yu L Slominskii, M A Kudinova *Usp. Nauchoi Fotografii*, 1984, **22** 12
69. A I Tolmachev *Teubner-Texte zur Physik*, 1987, **13** 115
70. Japanese Appl. 62/41 088; *Chem. Abs.*, 1987, **107** 144 973
71. Japanese Appl. 62/41 088; *Chem. Abs.*, 1987, **107** 187 628
72. Japanese Appl. 62/74 690; *Chem. Abs.*, 1987, **107** 187 592
73. Japanese Appl. 62/82 080; *Chem. Abs.*, 1987, **107** 208 960
74. FRG Appl. 3 704 601; *Chem. Abs.*, 1988, **109** 30 232
75. Japanese Appl. 62/103 192; *Chem. Abs.*, 1987, **107** 246 784
76. Japanese Appl. 63/33 477; *Chem. Abs.*, 1988, **109** 101 973
77. Japanese Appl. 62/103 190; *Chem. Abs.*, 1987, **107** 208 968
78. FRG Appl. 3 819 688; *Chem. Abs.*, 1989, **111** 68 030
79. Japanese Appl. 59/150 795; *Chem. Abs.*, 1985, **102** 70 330
80. Japanese Appl. 62/30 088; *Chem. Abs.*, 1987, **107** 124 698
81. Japanese Appl. 62/207 686; *Chem. Abs.*, 1988, **109** 201 583
82. Japanese Appl. 60/78 787; *Chem. Abs.*, 1985, **103** 113 408
83. Japanese Appl. 58/112 792; *Chem. Abs.*, 1984, **101** 15 116
84. Japanese Appl. 58/217 391; *Chem. Abs.*, 1985, **102** 36 847
85. UK P. 2155 811; *Chem. Abs.*, 1986, **104** 234 361
86. N Kuramoto, K Natsukawa, K Asao *Dyes and Pigm.*, 1989, **11** 21
87. Japanese Appl. 62/135 388; *Chem. Abs.*, 1987, **107** 226 075
88. Japanese Appl. 61/239 990; *Chem. Abs.*, 1987, **106** 224 575
89. Japanese Appl. 01/71 792; *Chem. Abs.*, 1989, **111** 123 961
90. Japanese Appl. 63/102 990; *Chem. Abs.*, 1989, **110** 48 540
91. Japanese Appl. 63/247 086; *Chem. Abs.*, 1989, **111** 87 517
92. Europ. Appl. 310 080; *Chem. Abs.*, 1989, **111** 196 757
93. F N Stepanow, N A Aldanowa *Angew. Chem.*, 1959, **71** 125
94. Japanese Appl. 01/49 684; *Chem. Abs.*, 1989, **111** 205 602
95. Japanese Appl. 60/254 039; *Chem. Abs.*, 1986, **104** 216 631
96. Japanese Appl. 61/144 392; *Chem. Abs.*, 1987, **106** 41 708
97. Japanese Appl. 58/181 689; *Chem. Abs.*, 1984, **101** 219 921
98. Japanese Appl. 60/73 892; *Chem. Abs.*, 1985, **103** 79 586
99. Netherlands Appl. 83/00 155; *Chem. Abs.*, 1985, **102** 70 326
100. Japanese Appl. 60/83 892; *Chem. Abs.*, 1985, **103** 96 480
101. Europ. Appl. 224 261; *Chem. Abs.*, 1988, **108** 177 270
102. US P. 4 446 223; *Chem. Abs.*, 1984, **101** 63 593
103. Japanese Appl. 63/185 682; *Chem. Abs.*, 1989, **110** 105 179
104. Japanese Appl. 58/181 688; *Chem. Abs.*, 1984, **101** 201 654
105. Japanese Appl. 61/143 191; *Chem. Abs.*, 1987, **106** 41 690
106. US P. 4 584 258; *Chem. Abs.*, 1986, **105** 181 607
107. H Nakazumi, S Watanabe, S Kado, et al. *Chem. Lett.*, 1989, 1039
108. Japanese Appl. 62/138 459; *Chem. Abs.*, 1987, **107** 226 072
109. Japanese Appl. 01/30 791; *Chem. Abs.*, 1989, **111** 105 909
110. Japanese Appl. 61/108 584; *Chem. Abs.*, 1987, **106** 11 288
111. Japanese Appl. 60/179 292; *Chem. Abs.*, 1986, **104** 159 687

112. Europ. Appl. 295 144; *Chem. Abs.*, 1989, **111** 48 215
113. Japanese Appl. 63/75 065; *Chem. Abs.*, 1989, **110** 66 963
114. Japanese Appl. 62/295 963; *Chem. Abs.*, 1988, **109** 139 251
115. Japanese Appl. 60/103 532; *Chem. Abs.*, 1985, **103** 113 420
116. Europ. Appl. 194 747; *Chem. Abs.*, 1987, **106** 186 601
117. International Appl. 86/05 504; *Chem. Abs.*, 1987, **106** 111 438
118. Japanese Appl. 01/40 387; *Chem. Abs.*, 1989, **111** 68 055
119. Japanese Appl. 63/74 690; *Chem. Abs.*, 1989, **110** 67 033
120. Japanese Appl. 62/85 991; *Chem. Abs.*, 1987, **107** 187 612
121. Japanese Appl. 62/167 088; *Chem. Abs.*, 1987, **107** 246 796
122. P Gordon, P Gregory *Organic Chemistry of Dyes* (Translated into Russian), Mir, Moscow, 1987, 344 pp
123. Japanese Appl. 63/144 090; *Chem. Abs.*, 1987, **110** 85 736
124. Japanese Appl. 60/47 069; *Chem. Abs.*, 1985, **103** 96 462
125. Japanese Appl. 63/288 785; *Chem. Abs.*, 1989, **111** 87 548
126. Japanese Appl. 63/288 786; *Chem. Abs.*, 1989, **111** 87 549
127. Japanese Appl. 63/209 890; *Chem. Abs.*, 1989, **111** 31 420
128. G N Schrauzer, V P Mayweg *J. Am. Chem. Soc.*, 1965, **87** 1483
129. Japanese Appl. 60/124 289; *Chem. Abs.*, 1986, **104** 13 111
130. Japanese Appl. 61/16 891; *Chem. Abs.*, 1986, **105** 200 577
131. Japanese Appl. 61/16 894; *Chem. Abs.*, 1986, **105** 200 578
132. Japanese Appl. 61/72 586; *Chem. Abs.*, 1987, **106** 58 998
133. Japanese Appl. 58/219 090; *Chem. Abs.*, 1984, **101** 81 728
134. US P. 4 547 444; *Chem. Abs.*, 1986, **104** 139 380
135. Japanese Appl. 60/252 344; *Chem. Abs.*, 1986, **105** 15 349
136. Japanese Appl. 60/189 494; *Chem. Abs.*, 1986, **104** 139 391
137. Japanese Appl. 63/74 689; *Chem. Abs.*, 1989, **110** 105 088
138. Japanese Appl. 63/209 886; *Chem. Abs.*, 1989, **110** 163 684
139. FRG Appl. 3 537 539; *Chem. Abs.*, 1987, **106** 11 255
140. Japanese Appl. 61/32 793; *Chem. Abs.*, 1986, **105** 105 858
141. Japanese Appl. 62/187 087; *Chem. Abs.*, 1988, **108** 66 058
142. T V Artamonova, et al. *Izv. Vuzov. Khim. Khim. Tekhnol.*, 1989, **32** 5
143. S Nakatsuji, N Okamoto, K Nakashima, et al. *Chem. Lett.*, 1986, 329
144. Japanese Appl. 62/246 790; *Chem. Abs.*, 1988, **109** 14 870
145. Japanese Appl. 01/08 094; *Chem. Abs.*, 1989, **111** 15 463
146. Japanese Appl. 60/259 498; *Chem. Abs.*, 1986, **105** 15 353
147. Japanese Appl. 63/299 989; *Chem. Abs.*, 1989, **111** 48 242
148. K Takagi, M Matsuoka, et al. *J. Soc. Dyes and Colour*, 1985, **101** 140
149. S H Kim, M Marsuoka, T Kitao *Chem. Lett.*, 1985, 1351
150. Japanese Appl. 58/224 793; *Chem. Abs.*, 1984, **101** 219 925
151. K Takagi, M Matsuoka, Y Kubo, et al. *Dyes and Pigm.*, 1985, **6** 75
152. Japanese Appl. 60/132 794; *Chem. Abs.*, 1986, **104** 26 839
153. Japanese Appl. 61/290 092; *Chem. Abs.*, 1987, **107** 49 698
154. Japanese Appl. 01/22 592; *Chem. Abs.*, 1989, **111** 15 460
155. Japanese Appl. 01/22 593; *Chem. Abs.*, 1989, **111** 87 554
156. Japanese Appl. 59/48 187; *Chem. Abs.*, 1985, **102** 15 221
157. Japanese Appl. 59/199 291; *Chem. Abs.*, 1985, **102** 158 182
158. Japanese Appl. 60/149 490; *Chem. Abs.*, 1986, **104** 99 584
159. Japanese Appl. 60/150 241; *Chem. Abs.*, 1986, **104** 13 126
160. Japanese Appl. 60/190 388; *Chem. Abs.*, 1986, **104** 120 130
161. Japanese Appl. 62/288 088; *Chem. Abs.*, 1988, **109** 119 847
162. Japanese Appl. 63/104 888; *Chem. Abs.*, 1988, **109** 240 788
163. S H Kim, M Matsuoka, et al. *J. Soc. Dyes and Colour*, 1989, **105** 212
164. Japanese Appl. 62/181 381; *Chem. Abs.*, 1988, **108** 122 066
165. Japanese Appl. 62/231 795; *Chem. Abs.*, 1988, **109** 64 433
166. Y Kubo, F Mori, K Yoshida *Chem. Lett.*, 1987, 1761
167. Y Kubo, F Mori, et al. *J. Chem. Soc., Perkin Trans. 1*, 1988, 2439
168. Japanese Appl. 63/223 068; *Chem. Abs.*, 1989, **110** 67 026
169. M Matsuoka, S H Kim, T Kitao *J. Chem. Soc., Chem. Commun.*, 1985, 1195
170. M Matsuoka, S H Kim, et al. *J. Soc. Dyes and Colour*, 1986, **102** 134
171. Japanese Appl. 60/150 243; *Chem. Abs.*, 1985, **104** 13 125
172. Japanese Appl. 60/152 566; *Chem. Abs.*, 1986,. **104** 111 367
173. K Yoshida, M Ishiguro, Y Kubo *Chem. Lett.*, 1987, 2057
174. Japanese Appl. 63/227 569; *Chem. Abs.*, 1989, **111** 68 027
175. Y Kubo, K Sasaki, K Yoshida *Chem. Lett.*, 1987, 1563
176. Europ. Appl. 310 027; *Chem. Abs.*, 1989, **111** 205 570
177. Y Kubo, H Kataoka, K Yoshida *J. Chem. Soc., Chem. Commun.*, 1988, 1457
178. Y Kubo, H Kataoka, et al. *J. Chem. Soc., Perkin Trans. Part 1*, 1990, 585
179. Japanese Appl. 62/21 584; *Chem. Abs.*, 1987, **107** 87 297
180. Japanese Appl. 63/203 391; *Chem. Abs.*, 1989, **110** 145 144
181. Japanese Appl. 61/244 588; *Chem. Abs.*, 1987, **107** 49 663
182. Japanese Appl. 61/273 987; *Chem. Abs.*, 1987, **107** 49 692
183. Japanese Appl. 63/81 092; *Chem. Abs.*, 1988, **109** 160 749
184. Japanese Appl. 63/297 385; *Chem. Abs.*, 1989, **110** 203 045
185. Japanese Appl. 61/162 385; *Chem. Abs.*, 1987, **106** 186 587
186. Japanese Appl. 59/67 093; *Chem. Abs.*, 1985, **102** 176 583
187. Japanese Appl. 62/222 893; *Chem. Abs.*, 1988, **108** 159 073
188. Japanese Appl. 63/91 290; *Chem. Abs.*, 1988, **109** 140 766
189. Japanese Appl. 63/149 188; *Chem. Abs.*, 1989, **110** 105 174
190. Japanese Appl. 63/149 189; *Chem. Abs.*, 1989, **110** 105 175
191. Japanese Appl. 63/60 796; *Chem. Abs.*, 1988, **109** 160 581
192. International Appl. 87/01 076; *Chem. Abs.*, 1987, **107** 106 435
193. Japanese Appl. 61/197 281; *Chem. Abs.*, 1987, **106** 224 566
194. Japanese Appl. 01/04 390; *Chem. Abs.*, 1989, **111** 144 218
195. Japanese Appl. 58/56 892; *Chem. Abs.*, 1984, **101** 31 239
196. Japanese Appl. 62/233 288; *Chem. Abs.*, 1988, **109** 46 308
197. Japanese Appl. 61/197 280; *Chem. Abs.*, 1987, **106** 224 565
198. Europ. Appl. 279 426; *Chem. Abs.*, 1989, **110** 48 560
199. Japanese Appl. 63/306 091; *Chem. Abs.*, 1989, **111** 87 536
200. Japanese Appl. 60/124 292; *Chem. Abs.*, 1986, **104** 59 453
201. Japanese Appl. 61/246 091; *Chem. Abs.*, 1987, **106** 224 577
202. Japanese Appl. 62/146 682; *Chem. Abs.*, 1988, **108** 19 543
203. FRG Appl. 3 446 418; *Chem. Abs.*, 1987, **106** 11 261
204. Japanese Appl. 01/14 087; *Chem. Abs.*, 1989, **111** 144 219
205. Japanese Appl. 62/146 683; *Chem. Abs.*, 1988, **108** 29 547
206. Japanese Appl. 63/312 888; *Chem. Abs.*, 1989, **110** 222 744
207. Japanese Appl. 01/130 979; *Chem. Abs.*, 1989, **111** 222 226
208. Japanese Appl. 01/130 980; *Chem. Abs.*, 1989, **111** 222 227
209. Europ. Appl. 279 501; *Chem. Abs.*, 1989, **110** 77 514
210. Europ. Appl. 254 553; *Chem. Abs.*, 1989, **110** 48 533
211. Japanese Appl. 63/274 591; *Chem. Abs.*, 1989, **111** 87 541
212. Europ. Appl. 296 876; *Chem. Abs.*, 1989, **111** 105 880
213. Japanese Appl. 63/233 886; *Chem. Abs.*, 1989, **110** 163 677
214. Japanese Appl. 63/312 892; *Chem. Abs.*, 1989, **111** 48 225
215. FRG Appl. 3 622 590; *Chem. Abs.*, 1987, **107** 106 417
216. Japanese Appl. 01/93 396; *Chem. Abs.*, 1989, **111** 205 623
217. Japanese Appl. 01/136 786; *Chem. Abs.*, 1989, **111** 222 230
218. US P. 4 492 750; *Chem. Abs.*, 1985, **102** 158 202
219. Japanese Appl. 61/268 487; *Chem. Abs.*, 1987, **107** 124 687
220. Japanese Appl. 01/61 290; *Chem. Abs.*, 1989, **111** 144 230

221. Japanese Appl. 60/161 193; *Chem. Abs.*, 1986, **104** 59 478
222. Japanese Appl. 60/161 194; *Chem. Abs.*, 1986, **104** 59 479
223. Japanese Appl. 59/73 994; *Chem. Abs.*, 1985, **102** 195 254
224. Japanese Appl. 58/62 093; *Chem. Abs.*, 1984, **101** 31 269
225. Japanese Appl. 62/278 096; *Chem. Abs.*, 1988, **109** 139 254
226. Japanese Appl. 63/309 496; *Chem. Abs.*, 1989, **111** 87 538
227. FRG Appl. 3 505 751; *Chem. Abs.*, 1987, **106** 224 563
228. Res. Discl., 1982, **216** 117; *Chem. Abs.*, 1982, **97** 47 075
229. H Shozaki, H Nakazumi, Y Nakado, et al. *Chem. Lett.*, 1987, 2393
230. Japanese Appl. 63/299 991; *Chem. Abs.*, 1989, **111** 144 205
231. Japanese Appl. 82/11 090; *Chem. Abs.*, 1982, **97** 101 746
232. Netherlands Appl. 79/08 829; *Chem. Abs.*, 1981, **95** 159 942

Translated from *Uspekhi Khimii* **61** 124–138 (1992)

U.D.C. 542.973

Tin–antimony oxide catalysts: preparation conditions and properties

R A Lemberanskii, I B Annenkova, Z A Bakhshieva
Azizbekov Azerbaidzhan Industrial University, Baku

ABSTRACT. The influence of preparation conditions of tin–antimony catalysts on their phase composition and olefin-oxidation activity is analysed. Special attention is paid to the influence of the starting compounds, the preparation method and the calcination temperature on the formation of the catalytic surface. The catalyst properties can be regulated by varying their synthesis conditions. Information about the effect of preparation conditions on the properties of the catalysts is scientifically and practically significant for their designed synthesis.

The bibliography contains 44 references.

Contents

I. Introduction 67
II. Influence of preparation method on catalytic activity of tin and antimony oxides 67
III. Influence of calcination temperature on the catalyst phase composition 69
IV. Dependence of catalyst properties on starting Sn- and Sb-containing reagents 69
V. Influence of synthesis conditions on formation of the catalytic surface 71
VI. Conclusion 73

I. Introduction

The economy requires highly active and selective catalysts of reactions, including oxidations, of organic compounds in order to produce the necessary chemical commodities.

The development of a process is an important but not the only condition for preparing an effective catalyst. The synthesis itself is an exceedingly complicated and delicate problem. It requires the strictest observance of the ratio of starting compounds, succession of operations and technical process parameters. This is necessary because the specific structure and given physicochemical, mechanical and catalytic properties are formed during the catalyst preparation. Therefore the numerous investigations of heterogeneous catalysts intentionally include careful studies of the synthesis process, the influence of the preparation method, the nature of the starting materials, the medium, the heat-treatment temperature, and other process parameters on the properties of the synthesised catalysts. An analysis of the results obtained is certainly of interest.

In the present review an attempt is made to generalise and analyse literature data for the influence of such factors on the structure and properties of the tin–antimony oxide system, which is known to contain highly active and selective catalysts of oxidation of olefins into unsaturated aldehydes.

II. Influence of preparation method on the catalytic activity of tin and antimony oxides

Tin–antimony catalysts are especially sensitive to the synthesis conditions. This is particularly evident in the contradictory data for the influence of composition on activity in oxidation and oxidative dehydrogenation of low-molecular-weight olefins.

Traditional preparation methods of such catalysts are rather complicated. They are usually prepared from Sn and Sb oxides that are precipitated separately by the action of boiling concentrated HNO_3 on the metals (or their oxides)[1–4] or of ammonia on HCl solutions of Sn^{IV} and Sb^{III} or Sb^{V} chlorides[5–9] followed by drying of the hydroxide mixture at 120 °C and prolonged (up to 16 h) calcination at 500–1000 °C.[1–5] Vartanov, et al.[10] suggest that the active catalyst phase is formed during the early stages of preparation and possibly even at the time of mixing of the hydroxides.

The prepared catalyst is a complicated heterogeneous system consisting of miscible Sn and Sb oxides over a wide range of Sn/Sb ratios. Data on the boundaries of the miscibility of the oxides are contradictory. Thus, the limiting Sb concentration in the SnO_2 lattice, according to the literature,[2,3,5,8,11–15] varies from 3 to 30 at.%. Such a wide range of concentrations can be explained on one hand by the different methods of determining the oxide solubility limits. X-Ray investigations indicate that Sb is dissolved in the catalyst lattice up to 20–30 at.%. The solid-solution region is limited to 7–8 at.% Sb according to electrical conductivity. On the other hand, the solubility of Sb in SnO_2 depends on the duration and temperature of calcination. It increases with increasing temperature up to 900 °C and then decreases at $t > 100$ °C.[5,13,16]

The question of whether the catalyst components undergo a chemical reaction has not been answered. A chemical compound in the Sn–Sb oxide system could not be detected by X-ray diffraction.[2,3,11] However, it could possibly exist in an X-ray amorphous form. This was confirmed by IR spectrosocpic studies that enabled Alkhazov to detect formation of a chemical compound of proposed composition $8SnO_2.Sb_2O_4$.[17]

Precipitation produces rather highly active and selective Sn–Sb catalysts of mild oxidation of olefins such as propylene into acrolein, isobutene into methacrolein, and oxidative dehydrogenation of butene into divinyl.[10,17–19] Thus, the yield of methacrolein and divinyl is 70% with a selectivity of 80–90% at 400 °C and a gas-mixture flow rate of 3600 h^{-1}. Solid solutions of Sb in SnO_2 in the range 10–20 at.% Sb are most active in mild oxidations.

The method for synthesising Sn–Sb catalysts mentioned above also has drawbacks. It includes many steps and involves formation of toxic and corrosively aggressive side products. The method of synthesising Sn–Sb catalysts from the metal oxides consisting of calcining their mixtures is technically simpler and devoid of these shortcomings. There were concerns about whether the components

reacted in this instance and whether it was extensive enough to form the active phases. Vartanov, et al.[10] confirm that oxides of Sn (SnO_2) and Sb do not react during joint calcination. The possibility of a solid-state reaction between SnO_2 and Sb oxides leading to a solid solution based on rutile has been demonstrated in other studies.[5,13,20]

Rather detailed studies of Sn–Sb catalysts prepared by calcining a mechanical mixture of Sn and Sb oxides have been carried out.[19–21] Oxides of $Sn^{II,IV}$ and $Sb^{III,V}$ were used as starting materials. A moist paste of their mixture was dried at 120 °C and calcined in air at 800 °C for 8 h. Thermographic analysis of the resulting oxide mixtures and X-ray phase analysis of the catalysts suggested with certainty that the starting components reacted during catalyst synthesis. This formed two types of solid solutions. One was based on rutile with the limiting solubility of Sb in SnO_2 of ~15 at.%. The other was a solid solution of Sn (15 at.%) in Sb_2O_4. X-Ray diffraction also detected an X-phase different from each of the starting oxides.

Tests of the samples for gas-phase oxidation of isobutene suggested that the products of reaction of Sn and Sb oxides are the active catalysts. The individual oxides do not catalyse formation of methacrolein. The binary compositions are rather active in this reaction.[19,22] Samples synthesised from SnO_2 and Sb oxides are slightly active.

Systems prepared from SnO and Sb oxides are very active for partial oxidation of isobutene. Compositions in the range of oxide solid solutions 80–90 at.% Sn and 70–80 at.% Sb are most active. The sharp reduction in the yield of CO_2 with the addition of even a small amount of antimony to tin oxides likewise confirms the existence of inter-reaction between the original oxides, but it does not explain the results for dilution of SnO_2 with antimony oxides.

In Fig. 1, the activity for isobutene oxidation of catalysts synthesised from Sn and Sb oxides is compared with that of those prepared by coprecipitation from their metallic powders. The ratios Sn/Sb in the starting materials, the heat-treatment conditions and the isobutene oxidation process are in all instances identical. Catalysts prepared from SnO_2 and Sb oxides have greater selectivity than those synthesised by the usual coprecipitation method. However, they give poorer yields of methacrolein. Samples prepared by calcination of a mixture of SnO and Sb oxides are slightly more selective than those prepared from SnO_2 and Sb oxides although the latter are nonetheless sufficiently selective. The activity of the former for methacrolein formation is much greater than that of the latter and comparable to that of catalysts of metallic Sn and Sb.

Therefore, oxides of $Sn^{II,IV}$ and $Sb^{III,V}$ react when their mixture is calcined. Phases that are active in partial olefin oxidation are formed. Differences in the activity of various series of catalysts indicate that the extent of reaction of the catalyst components and the phases formed are apparently different. These properties depend on the oxides chosen as starting materials and more accurately on the valence of the metal forming the oxide, among other factors. The valence of Sn in the starting oxide has a greater effect on catalyst formation than the Sb valence. In fact, it can be seen from Fig. 1 that samples prepared from various Sb oxides differ little in activity for isobutene oxidation whereas catalysts synthesised for SnO are much better (by about two times) than those prepared from SnO_2.

It is possible that Sn^{2+} becomes easier to oxidise after formation of a solid solution of Sb in the lattice of SnO, which is though to be responsible for oxidation of an olefin to a aldehyde.[13,14] Dissolution of Sb in the previously formed SnO_2 is apparently more difficult. This leads to enrichment of the catalyst surface in Sb as dispersed Sb_2O_4. According to the literature[23] this ensures the high selectivity. The role of surface Sb in selective partial olefin oxidation is also evident in a comparison of the catalytic properties and the surface composition of the Sn–Sb–O system. The experimental data obtained previously[19,21,22] show that samples over a wide range of compositions (10–90 at.% Sb) are sufficiently selective in mild oxidation of isobutene into methacrolein. The selectivity is practically independent of the ratio of starting Sn and Sb oxides. Structural studies of these samples by XPS demonstrated that the surface layer was enriched in Sb by at least two times compared with the bulk.

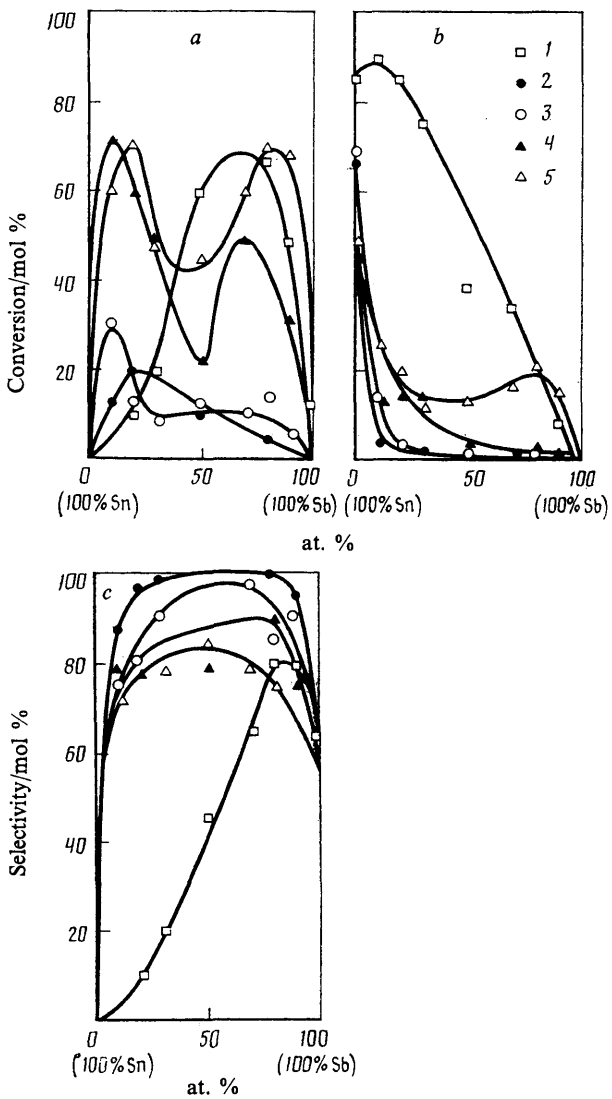


Figure 1. Activity of tin–antimony catalysts of oxidation of isobutene (400 °C): conversion into methacrolein (*a*), conversion into CO_2 (*b*), selectivity for methacrolein (*c*). Catalysts of metallic Sn and Sb (*1*), $SnO_2-Sb_2O_3$ (*2*), $SnO_2-Sb_2O_5$ (*3*), $SnO-Sb_2O_3$ (*4*), $SnO-Sb_2O_5$ (*5*).

III. Influence of calcination temperature on catalyst phase composition

One of the most important process parameters in synthesising catalysts is the calcination temperature, which has a substantial effect on their structure and phase composition and eventually determines their catalytic activity.

The need for high-temperature activation of Sn–Sb catalysts in order to achieve high selectivity for mild oxidation products in olefin oxidations has repeatedly been pointed out.[6,14,16,20,24,25] Various explanations of this need for high-temperature calcination have been offered. According to some,[20,24,26] it is required to increase the solubility of Sb in the SnO_2 lattice. This increases the number and stability of free electrons at high temperatures and also the stability of Sb^V to calcination and redox processes. The improved catalytic properties of the mixed oxides may be a result of both of these factors or only one of them.

Godin, et al.[14] view the role of high-temperature treatment as the destruction of microporosity. This increases the crystallinity and the particle size of the rutile.[9]

In the opinion of Roginskaya, et al.,[16] such heat treatment is necessary to effect the conversion of Sb^V into Sb^{III}.

Sala and Trifiro[20] think that the high-temperature calcination has three different types of effect on the mixed Sn–Sb oxides: a) It sharply increases the extent of SnO_2 modification by Sb, exhibited as increased absorption in the visible spectral region and a greater amount of butadiene formed after oxidative dehydrogenation of *n*-butenes. b) It sharply increases the isomerisation ability due to migration of Sb^V into the SnO_2 lattice and subsequent surface dehydrogenation. c) It decreases the irreversible catalyst mass loss in the redox process caused by the reduction of Sb oxide and partial sublimation of the metallic Sb formed.

The conclusions supported by the experimental data that the solubility of Sb in the SnO_2 lattice increases with increasing calcination temperature are still rejected by certain investigators. According to the literature,[8,15] Sn–Sb catalysts calcinated at high temperatures show a reduced tendency to incorporate Sb into the SnO_2 lattice. Thus, as demonstrated previously,[27–30] the catalytic surface is enriched in Sb. Several authors think[8,15,29,30] that a high calcination temperature induces migration of Sb from the bulk of the rutile to the surface. This forms an equilibrium solid solution of Sb in Sb oxide through thermally excited aggregation of SnO_2 octahedra. The Sb oxide readily volatilises at high temperatures. This leaves on the surface a crystalline solid solution of the rutile type that contains 4 at.% Sb in SnO_2 and up to 25% Sb in the catalyst.

Investigations of Sn–Sb catalyst[27] containing 4 at.% Sb, which according to the literature[8,27] corresponds to the limiting solubility of Sb in SnO_2, did not detect a segregated crystalline Sb oxide phase on the surface of the solid solution, as was described previously.[29] This suggested to Berry and Smith[27] that the enrichment of the surface of Sn–Sb catalyst in Sb after high-temperature calcination is due to concentration of Sb, possibly completely surrounded by Sn, on the SnO_2 rutile surface and is not accompanied by formation of a segregated crystalline surface phase of Sb oxide.

Samples with a high Sb content consist, after calcination at 1000 °C, as demonstrated before,[9] of a rutile solid solution, a small amount of a crystalline substance different from rutile, and significant quantities of an amorphous substance containing Sb. Several investigators[9,30] think that the amorphous phase is formed from Sb that did not enter the solid solution and did not act as a nucleus for formation of Sb_2O_4, which is readily volatiled at high temperatures. The crystalline phase different from rutile was not identified.

Thus we can see that there are various ideas about the surface phase composition formed during high-temperature calcination of Sn and Sb oxides. The question of which phases are responsible for the selective partial olefin oxidation in this catalytic system remains unanswered. The increase of selectivity for mild oxidation of butene[31,32] and propylene[29] of Sn–Sb catalysts due to their high-temperature calcination and the resulting enrichment of the surface in Sb is connected by some authors[14,24,26,32,33] with a solid solution of Sb in SnO_2 and by others[29,34] to the presence on the surface of a catalyst of this solid solution in combination with an Sb oxide phase or to an Sb_2O_4 phase.[23,35] It is also thought[8] that the bulk crystalline SnO_2 lattice is just as important to the occurrence of the catalytic reactions as the presence on the catalytic surface of Sb and Sn ions in close contact with each other.

The majority of investigations of the Sn–Sb oxide system have been carried out with compositions enriched in Sn. The middle region of compositions are still largely unexplored. In the opinion of Kustova, et al.[5] a compound of Sn and Sb oxides is not formed in samples calcined at 500–950 °C. This agrees with previous results.[14] However, Roginskaya, et al.[16] think that an unidentified phase containing 50–80 at.% Sb in addition to a solid solution of Sn is formed in the Sb_6O_{13} structure at 700 °C or in Sb_2O_4 at 900 °C. Structural relationships are unclear even for the Sb–O system in compositions enriched in Sb.

IV. Dependence of catalyst properties on Sn- and Sb-containing starting materials

The choice of Sn- and Sb-containing reagents is an important factor in catalyst formation during its synthesis. This last condition can often change even the influence of heat treatment on the catalyst properties. An investigation of this problem demonstrated[36,37] that high-temperature treatment can produce, depending on the Sn- and Sb-containing compounds chosen as starting materials for the catalyst synthesis, in one instance, samples differing substantially in phase composition and properties. This occurs regardless of an identical Sn/Sb ratio. In another instance catalysts with very similar properties are produced from components with an identical starting ratio.

Lemberanskii, et al.[36,37] studied catalysts of two extreme compositions in which Sn/Sb = 1/9 and 9. These were prepared from metallic Sn and Sb (series A) and from the metal chlorides (series B).

In the region enriched in Sb, the density of series A samples was approximately constant in the calcination temperature range 300–1000 °C at about 6.5–7.0 g cm^{-3}. The specific surface decreased from 6.4 to 4.0 m^2 g^{-1}. The mass change was insignificant. A stronger temperature effect is observed in series B. The density of this series increases continuously and substantially with increasing heat-treatment temperature. It is three times greater for a sample with a calcination temperature of 1000 °C than for one calcined at 300 °C and 1.5 times greater than that of the series A sample of analogous composition. Series B catalysts are more intensely coloured. A large mass loss is observed during heat treatment of series B samples. A significant amount of sample volatilises at all calcination temperatures.

X-Ray phase analysis of calcined catalysts and the phases that were vapourised and then condensed (Fig. 2) showed that series A samples are solid solutions based on Sb_2O_4 (curve *1*). The series B catalysts after calcination at 300 °C are a complicated mixture consisting apparently largely of various chloride compounds. Bands belonging to the pure Sn and Sb oxides are not observed by X-ray diffraction. Starting at 600 °C bands characteristic of SnO_2 (curve *2*) appear in the diffraction patterns and are observed up to 1000 °C. Lines belonging to other Sn and Sb oxides are practically absent. Thus, even at 600 °C the sample is exclusively SnO_2 (poorly formed). At 1000 °C it is already well crystallised SnO_2. The presence of a solid solution of Sb in SnO_2 is possible. It is thought that a significant part of the Sb volatilises as oxides during the calcination. Strong bands of Sb_2O_4 in addition to lines of the other Sb oxides Sb_2O_3 and Sb_2O_5 (curve *4*) are clearly evident in the diffraction patterns of the sublimed phases.

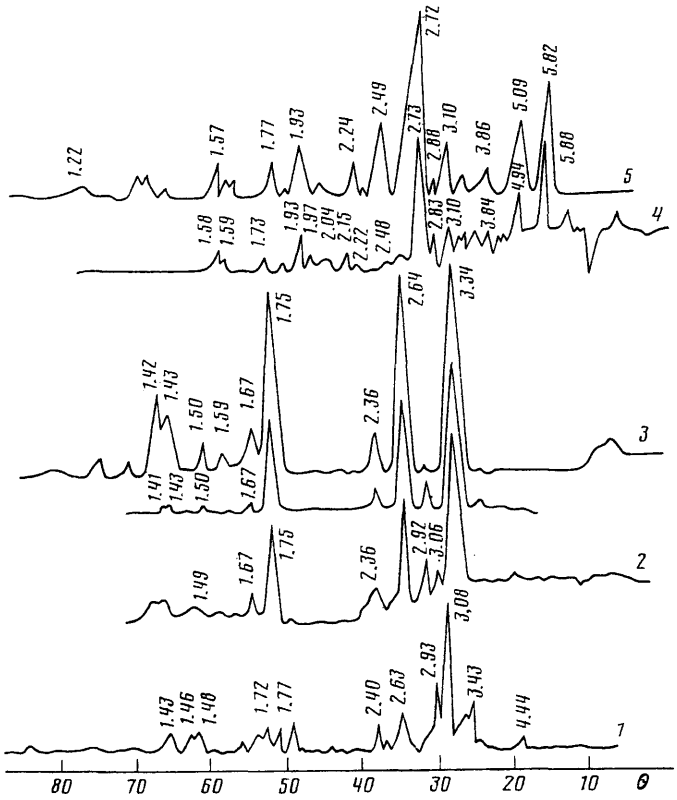


Figure 2. Diffraction patterns of tin–antimony catalysts and sublimed phases: catalysts of metallic Sn and Sb, t_{pr} = 1000 °C, Sn/Sb = 1/9 (*1*); for the curve over the curve *2*, Sn/Sb = 9. Samples of Sn and Sb chlorides, t_{pr} = 1000 °C, Sn/Sb = 1/9 (*2*), 9 (*3*). Sublimed phases of samples of Sn and Sb chlorides, t_{pr} = 600 °C, Sn/Sb = 1/9 (*4*), 9 (*5*).

In the region of compositions enriched in Sn (Sn/Sb = 9), the influence of heat-treatment temperature on catalyst formation depends little on the starting materials and is seen mainly as an intense volatilisation and a large amount of volatilised material. Whereas series A samples lose 5–7% of their mass, series B samples lose 70–80% at 600–1000 °C. The density and bulk mass of samples calcined in the temperature range 600–1000 °C are practically constant. The samples are dark blue, i.e. the catalyst is practically formed even at 600 °C. X-Ray phase analysis of samples with Sn/Sb = 9 demonstrated that the catalyst prepared from the metals is a solid solution of Sb in SnO_2 and that the maximal possible Sb concentration reaches 10–15 at.%.[38] Bands of SnO_2 (curve *3*) are also noted in the diffraction pattern of the sample synthesised from the metal chlorides. Bands characteristic of Sb oxides are not observed and they are not found in the diffraction patterns of the sublimed phases. The amount of sublimed phase is rather large. A comparison of the observed diffraction bands (curve *5*) with previous results[39,40] suggests that this phase contains mainly ammonium chloride and ammonium chlorostannate(IV). Therefore, it seems that all of the Sb is dissolved in the Sn oxide and that the catalyst is a solid solution based on SnO_2, probably in combination with SnO.

Thus, the phase composition of the Sn–Sb catalysts substantially depends on the synthesis conditions. Stucture formation in series A samples, which are prepared from metallic Sn and Sb, is mainly finished up to 600 °C. For series B samples, which are prepared from Sn and Sb chlorides, a longer time and higher temperatures are required and the process is accompanied by a significant loss of catalyst mass. According to thermographic and thermogravimetric analyses, water is lost up to 200 °C. Endotherms are observed in the range 400–500 °C. These are accompanied by large mass losses (65–85%). A Sn compound containing ammonium and chlorine (Sn/Sb = 9) and Sb oxides (Sn/Sb = 1/9) are vapourised. The oxide SnO_2 is more stable.

The high volatility of Sb oxides during heat treatment of series B samples is surely explained by the preparation method. The rate of migration of Sb oxides in series A samples is not so fast and leads only to concentration of Sb on the catalyst surface. Many authors use this to explain the high-temperature activation of Sn–Sb catalysts that is necessary to increase their selectivity for mild oxidation products in olefin oxidation reactions.[6,14,16,20,24,25] therefore, depending on the migration rate of Sb cations, which in turn depends on the starting materials and the catalyst preparation method, the surface of samples in one instance becomes enriched in Sb (series A). In the other instance, even with a high starting Sb content, the surface is depleted of Sb during heat treatment due to volatilisation and becomes enriched in Sn (series B). It is interesting to compare the diffraction patterns of catalysts prepared from Sn and Sb chlorides that have a different ratio of starting materials. In both cases only bands corresponding to SnO_2 are seen (Fig. 2, curves *2* and *3*).

Naturally this cannot affect the catalytic properties of the samples. The test results for isobutene oxidations that are plotted in Fig. 3 confirm this hypothesis.

It can be seen from Fig. 3 that the activity of catalysts of various compositions synthesised from the metals are substantially different. The sample with a high Sn content is significantly more active. Thus, an isobutene conversion of 70 mol% under the chosen oxidation conditions is achieved already at 350 °C whereas it does not exceed 20 mol% at this same temperature on the second sample (Sn/Sb = 1/9). However, the methacrolein yield is much greater at Sn/Sb = 1/9 (60 mol%) than for Sn/Sb = 9, where it does not reach 10 mol%. The sample enriched in Sn in practice catalyses the complete oxidation whereas conversion of olefin into the destructive oxidation products is less than 10 mol% (at 450 °C) on the catalyst

enriched in Sb. This catalyst is selective (up to 90 mol%) for methacrolein formation.

However, a sample of this same composition (Sn/Sb = 1/9) but prepared from metal chlorides is much more active than the series A sample for complete oxidation. It is much less selective for mild oxidation. These samples differ substantially in phase composition. The surface of the series B catalyst is enriched in SnO_2 due to volatilisation of Sb oxides.

In comparing samples with an identical ratio of components that are prepared from different starting materials, it is found that series B samples are always more active than series A samples for oxidation of isobutene to CO_2. The selectivity for methacrolein on them is much lower due to combustion of both isobutene and the methacrolein that is formed (methacrolein is not observed in the reaction products in the studied temperature range on the series B sample with Sn/Sb = 9).

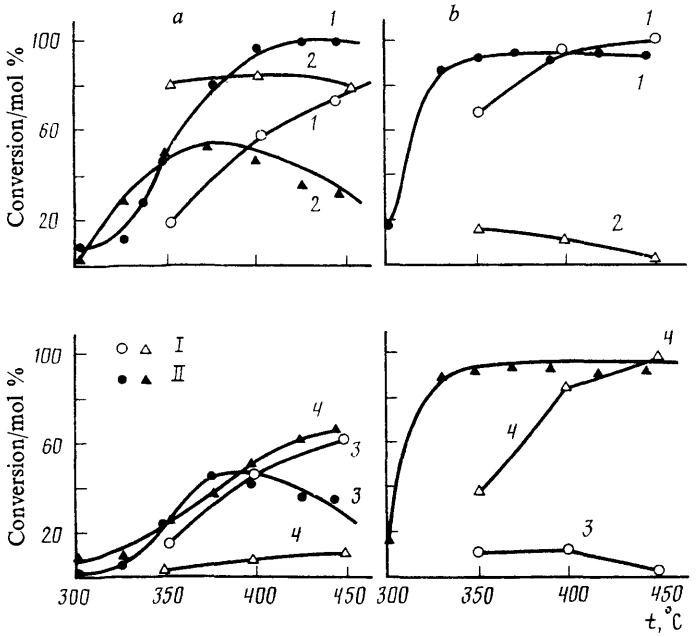


Figure 3. Activity of tin–antimony catalysts [Sn/Sb = 1/9 (*a*) and 9 (*b*)] for oxidation of isobutene (3600 h^{-1}, 5 mol% of *iso*-C_4H_8): series A (from metallic Sn and Sb) (*I*), series B (from Sn and Sb chlorides) (*II*). Total conversion of isobutene (*1*), selectivity for methacrolein (*2*), conversion into methacrolein (*3*), conversion into carbon oxides (*4*).

V. Influence of synthesis conditions on formation of the catalytic surface

The substantial difference in the activity of catalysts prepared by various methods is mainly due to the different nature of the catalytic surface formed under given catalyst synthesis conditions.

High-temperature migration of Sb from the crystal bulk to the catalyst surface has been observed.[8,15,27–30,36,37] The rate of migration and the resulting effects substantially depend on the preparation method of the catalyst. In particular, the starting Sn- and Sb-containing compounds are important. Oxygen necessarily migrates with the Sb and then is redistributed in its various forms on the surface. All of this should change the acid–base characteristics of the catalyst surface and eventually the catalytic properties.

According to Lemberanskii, et al.[36,37] the high oxidising capability of samples prepared from Sn and Sb chlorides, which markedly exceeds that of catalysts from metallic Sn and Sb, is largely controlled by the surface acid–base properties and is explained by their high surface acidity.

This argument is supported by the known fact that the products of complete oxidation are formed at acidic surface centres that depend on surface Sn cations for the Sn–Sb oxide catalysts.[7]

Data for the isomerisation of butene-1 into butene-2 (Fig. 4) confirm this hypothesis.[36,37] The isomerising capability of samples prepared from the chlorides is greater than that for catalysts prepared from the metals. It also appears at lower temperatures. This difference is especially large for the composition with Sn/Sb = 1/9, in which a sharp difference in the phase composition is observed according to X-ray structural analysis.

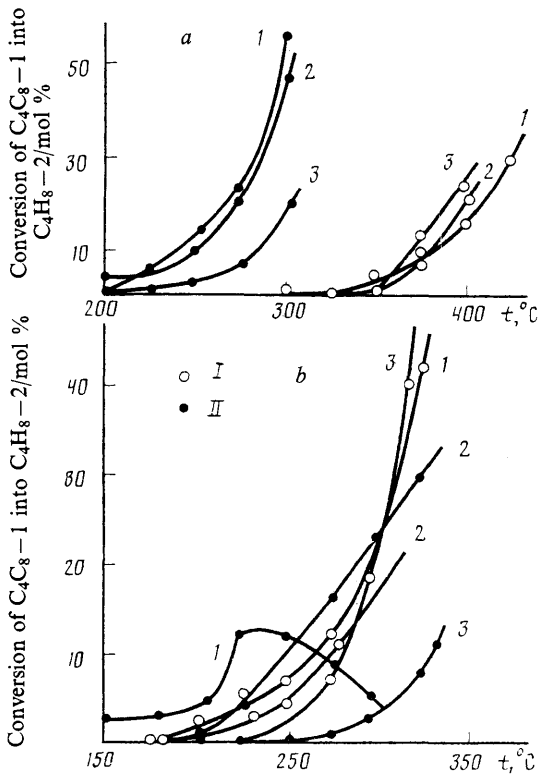


Figure 4. Isomerisation of butene-1 and butene-2 on tin–antimony catalysts (3600 h^{-1}, 5 mol% C_4H_8): Sn/Sb = 1/9 (*a*), Sn/Sb = 9 (*b*). Series A (from metallic Sn and Sb) (*I*), series B (from Sn and Sb chlorides) (*II*); t_{pr}, °C: 600 (*1*), 800 (*2*), 1000 (*3*).

Such results agree with previous studies[20] in which the strong isomerising capability of Sn–Sb catalysts prepared from metal chlorides is explained by the increase in the number of Lewis acid centres formed after dehydration of the surface. This is confirmed

by studies of the isomerisation of butene-1 into butene-2 in an oxidising atmosphere without oxygen in the reaction mixture.[36,41] The experiments were carried out by a response method. An olefin–air mixture was continuously passed at a volume rate of 3600 h^{-1} through a catalyst. After each half minute (analysis time) the reaction products were analysed. After a steady state was attained, the oxygen flow rate was replaced by an equivalent amount of nitrogen to maintain the given volume flow rate. The response of the system to removal of oxygen from the gas phase was followed by continuously analysing the reaction products. After a new steady state was attained, the oxygen flow was started, expelling the nitrogen from the system. The product analyses were stopped after the system again reached a steady state.

Catalysts were prepared by calcining at 800 °C Sn and Sb hydroxides prepared in one instance by the action of concentrated HNO_3 on metallic Sn and Sb and in another by the action of ammonia on the metal chlorides.

It can be seen in Fig. 5*a* that *cis*-butene-1 is formed in greatest yield in an oxidising atmosphere (region *I*) on samples enriched in Sn (curves *1* and *2*). The different activities of the catalysts of the two compositions Sn/Sb = 1/9 and 9 is especially large for samples prepared from the metals (curves *1* and *3*). It is interesting that the isomerisation of butene-1 into *cis*-butene-2 stops on all samples after oxygen is taken out of the gas mixture (region *II*). Subsequent addition of oxygen (region *III*) restores the activity of samples with Sn/Sb = 1/9 to the original value whereas that of samples enriched in Sn (Sn/Sb = 9) does not quite reach the initial value.

Catalysts with a high Sb content are most active in the isomerisation of butene-1 into *trans*-butene-2 (Fig. 5*b*). The yield of *trans*-butane-2 is much less than that of the *cis*-isomer and does not depend on the presence of oxygen in the reaction mixture.

The following conclusions were made by Lemberanskii, et al.[36,41] after analysing their experimental data and results of earlier experiments.

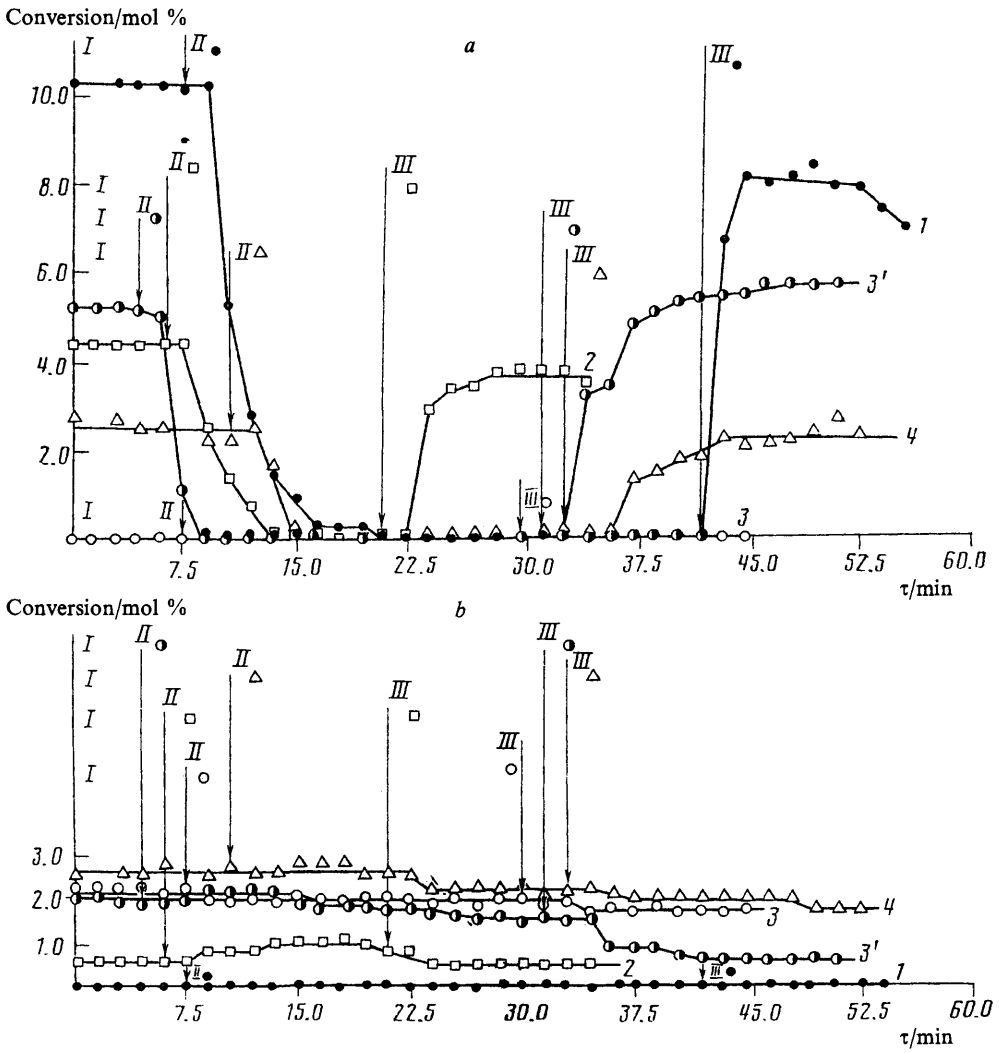


Figure 5. Isomerisation of butene-1 into *cis*-butene-2 (*a*) and *trans*-butene-2 (*b*) on tin–antimony catalysts. Sn/Sb: 9 (*1*, *2*), 1/9 (*3*, *4*). From metallic Sn and Sb (*1*, *3*), from Sn and Sb chlorides (*2*, *4*). O_2 in the gas mixture (*I*, *III*), N_2 in the gas mixture (*II*).

Butene-1 is isomerised into *cis*- and *trans*-butene-2 on Sn–Sb catalysts in an oxidising atmosphere. The yield of *cis*-butene-2 is much greater than that of the *trans*-isomer. Without oxygen in the gas mixture the isomerisation of butene-1 into *trans*-butene-2 continues practically unabated whereas the formation of *cis*-butene-2 is completely inhibited. This certainly indicates that butene-1 is isomerised into *cis*- and *trans*-butene-2 by different mechanisms. In particular, weakly adsorbed molecular oxygen is surely involved in the formation of the *cis*-isomer.

It follows from the experimental data presented that butene-1 is isomerised into *cis*-butene-2 on the catalytic surface enriched in Sn. This is clearly seen by comparing samples prepared from metallic Sn and Sb that differ sharply in composition (Sn/Sb = 1/9 and 9). In the first instance conversion of butene-1 into *cis*-butene-2 is greater; in the second, the *cis*-isomer is not formed under the selected experimental conditions (t = 275 °C). Formation of *cis*-butene-2 is observed on the sample of analogous composition (Sn/Sb = 1/9) that is synthesised from the metal chlorides. However, this does not contradict the preceding observations. It must be considered that according to physicochemical investigations this sample is relatively enriched in Sn due to the fast rate of migration of Sb to the surface and the subsequent volatilisation of Sb, which does not enter the solid solution.[37] The comparison is made with the catalyst of the same nominal composition but prepared from metallic Sn and Sb, where the slower rate of migration of the Sb cations from the bulk limits volatilisation and ensures concentration of Sb on the surface. Therefore, these samples differ in ability to isomerise butene-1 to *cis*-butene-2.

The requisite presence of oxygen in the gas in combination with the catalytic surface enriched in Sn for isomerisation of butene-1 into *cis*-butene-2 indicates that Sn ions are responsible for weakly adsorbed molecular oxygen. This conclusion is confirmed by data for the high activity of SnO_2 and also of Sn–Sb catalysts with surfaces enriched in Sn due to their specific synthesis conditions in complete oxidation reactions requiring the participation of oxygen weakly bound to the catalyst surface.[11,18,22,37,42]

An analysis of previous experimental data[36,37] also suggests that Sb cations are responsible for the conversion of butene-1 into *trans*-butene-2. In fact, butene-1 isomerises into *trans*-butene-2 on the sample enriched in Sb (Sn/Sb = 1/9). No isomerisation is observed on the catalyst with the minimal Sb content (Sn/Sb = 9). This is clearly evident for catalysts prepared from metallic Sn and Sb that are solid solutions of the oxides (Fig. 5*b*, curves *1* and *3*). For samples synthesised from the metal chlorides, formation of the *trans*-isomer becomes noticeable even at Sn/Sb = 9. This is not unexpected if the enrichment of the catalyst surface in Sb as a result of migration from the crystal bulk is considered.

The established fact that Sn and Sb ions are responsible for *cis*- and *trans*-isomerisation, respectively, of butene-1 is of definite interest. It is known that the isomerisation of butene-1 is proposed as a qualitative test for the determination of the total acidity of an oxide catalyst.[43] The study of the acidity of Sn–Sb catalysts by IR spectroscopy of adsorbed ammonia[44] suggested that the Brönsted acidity is caused by Sb ions; the Lewis acidity, by coordinatively unsaturated Sn ions on the surface. Keeping this in mind and recalling the data mentioned above, isomerisation of butene-1 into *cis*- and *trans*-butene-2 can be recommended as a test for Lewis and Brönsted acidity, respectively.

VI. Conclusion

It can be seen from the material presented that the synthesis conditions of Sn–Sb catalysts play such an important role in the formation of their structure and properties that they often dominate over the chemical composition. In fact, the choice of starting Sn- and Sb-containing reagents can affect the rate of high-temperature migration of Sb from the crystal bulk to the surface. This can produce samples with similar or sharply differing catalytic properties depending on the starting ratio of components. In one instance highly selective catalysts of partial oxidation of isobutene into methacrolein are obtained; in the other, active catalysts of complete oxidation.

The optimal synthesis method can be selected on the basis of data for the influence of the method and preparation conditions on the catalyst properties. This method would be fully responsive to economic, technical and ecological demands. For the Sn–Sb oxide system, an analysis of the experimental data indicates that solid-state high-temperature reaction of Sb oxides with SnO should be considered the most rational method of catalyst preparation. This method is technically simple and produces catalysts with sufficiently high activity and selectivity for mild oxidation of olefins that is free of toxic and corrosive starting materials and side products.

References

1. J L Barclay, J R Bethell, J B Bream, D J Hadley, R H Jenkins, D G Stewart, B Wood *Acrolein and Methacrolein by Oxidation of Propylene and Isobutene*, B P No. 964 666, The Distillers Co. Ltd. Applied for Feb. 17, 1959; Issued April 6, 1961
2. S S Stroeva, A I Gel'bshtein, N V Kul'kova, et al. *Neftekhimiya*, 1966, **6**(3) 412
3. T G Alkhazov, M S Belen'kii, R I Alekseeva *Osnovy Predvideniya Kataliticheskogo Deistviya* (Principles for Predicting Catalytic Activity), in: *Trudy IV Mezhdunarodnogo Kongressa po Katalizu* (Proceedings of the Fourth International Congress on Catalysis), Nauka, Moscow, 1970, p. 232
4. Kh Z Sekushova, A A Vartanov, T G Alkhazov, M S Belen'kii *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1970, **13**(1) 102
5. G N Kustova, D V Tarasova, I P Olen'kova, N N Chumachenko *Kinet. Katal.*, 1976, **17**(3) 744
6. J-M Herrmann, J-L Portefaix, M Forissier, et al. *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**(6) 1346
7. J G McAteer *J. Chem. Soc., Faraday Trans. 1*, 1980, **75** 2762
8. D R Pyke, R Reid, R J D Tilley *J. Chem. Soc., Faraday Trans. 1*, 1980, **76** 1174
9. D J Smith, L A Bursill, F J Berry *J. Solid State Chem.*, 1982, **44** 326
10. A A Vartanov, Kh Z Sekushova, K M Mekhtiev, T G Alkhazov *Kinet. Katal.*, 1972, **3**(3) 792
11. V I Lazukin, M Ya Rubanik, Ya V Zhigailo, A A Kurganov *Kataliz i Katalizatory* (Catalysis and Catalysts), Naukova Dumka, Kiev, 1967, 54 pp.
12. R A Lemberanskii, I B Annenkova, E G Rostevanov *Azerb. Khim. Zh.*, 1975, (4) 10
13. K Wakabayashi, Y Kamiya, N Ohta *Bull. Chem. Soc. Jpn.*, 1968, **41** 2776

14. G W Godin, C C McCain, E A Porter *Proc. 4th Int. Congr. Catal. Moscow, 1968,* Akad. Kiado, Budapest, 1971, Vol. 1, p. 271
15. L Portefaix, P Bussiere, M Forissier, F Figueras *J. Chem. Soc., Faraday Trans. 1*, 1980, **76** 1652
16. Yu E Roginskaya, D A Dulin, S S Stroeva, et al. *Kinet. Katal.*, 1968, **9**(5) 1143
17. T G Alkhazov, Doctoral Dissertation in Chemical Sciences, AzINEFTEKhIM, 1968
18. R A Lemberanskii, E G Rostevanov, I B Annenkova, et al. *Azerb. Khim. Zh.*, 1974, (4) 24
19. R A Lemberanskii, I B Annenkova, Z A Bakhshieva "Voprosy kinetiki i kataliza. Mekhanizm i kinetika formirovaniya katalizatora" (Problems of kinetics and catalysis. Mechanism and kinetics of catalyst formation), in: *Mezhvuz. Sb. Nauchn. Tr.*, Ivanovo, 1986, p. 42
20. F Sala, F Trifiro *J. Catal.*, 1974, **34**(1) 68
21. R A Lemberanskii, I B Annenkova *Vliyanie Sposoba Prigotovleniya na Svoistva Olovo–Sur'myanykh Katalizatorov* (Influence of Preparation Method on Properties of Tin–Antimony Catalysts), deposited paper No. 1552-84, March 21, 1984, VINITI, Moscow, 1983, 25 pp.
22. R A Lemberanskii, I B Annenkova, F M Poladov "Nauchnye osnovy prigotovleniya katalizatorov" (Scientific bases for catalyst preparation), in: *Tezisy Dokladov Vsesoyuznogo Soveshchaniya* (Abstracts of Papers of an All-Union Conference), Novosibirsk, 1983, p. 47
23. Y Boudeville, F Figueras, M Forissier, et al. "I. Kataliticheskaya aktivnost chistykh i nanesennykh metallov. II. Kataliticheskaya aktivnost ionov perekhodnykh metallov v kompleksakh i okisnykh matritsakh" (I. Catalytic activity of pure and deposited metals. II. Catalytic activity of transition metal ions in complexes and oxide matrices), in: *Tr. IV Sovetsko-Frants. Seminara po Katalizu* (Proceedings of the Fourth Soviet-French Seminar on Catalysis), Tbilisi, 1978, p. 51
24. K Wakabayashi, Y Kamiya, N Ohta *Bull. Chem. Soc. Jpn.*, 1967, **40**(9) 2172
25. M Crozat, J E Germain *Bull. Chem. Soc. Fr.*, 1972, 3526
26. M Crozat, J E Germain *Bull. Chem. Soc. Fr.*, 1973, 1125
27. F Berry, D Smith *J. Catal.*, 1984, **88**(1) 107
28. P A Cox, R G Egdell, C Harding, et al. *Surf. Sci.*, 1982, **123**(2/3) 179
29. Y Boudeville, F Figueras, M Forissier, et al. *J. Catal.*, 1979, **58** 52
30. Y Cross, D Pyke *J. Catal.*, 1979, **58** 61
31. J C McAteer *J. Chem. Soc., Faraday Trans. 1*, 1979, **75** 2768
32. H J Herniman, D R Pyke, P Reid *J. Catal.*, 1979, **58** 68
33. N Zenaidi, M Formanti, M Budel, et al. *Tezisy Dokladov V Sovetsko-Frants. Seminara po Katalizu* (Abstracts of Papers of the Fifth Soviet-French Seminar on Catalysis), Lille, 1980, p. 15
34. J M Herrmann, J L Portefaix *React. Kinet. Catal. Lett.*, 1979, **12**(1) 51
35. F Figueras, M Forissier, J L Portefaix, et al. *Tezisy Dokladov V Sovetsko-Frants. Seminara po Katalizu* (Abstracts of Papers of the Fifth Soviet-French Seminar on Catalysis), Lille, 1980, p. 8
36. R A Lemberanskii, I B Annenkova, Z A Bakhshieva *Issledovanie Vliyaniya Uslovii Prigotovleniya Olovosur'myanykh Oksidnykh Katalizatorov na ikh Fiziko-Khimicheskie i Kataliticheskie Svoistva* (Investigation of the Influence of Preparation Conditions of Tin–Antimony Oxide Catalysts on their Physico-Chemical and Catalytic Properties), deposited paper No. 1602-A3, AzNIINTI, Dec. 24, 1990, Baku, 1990
37. R A Lemberanskii, I B Annenkova, F M Poladov, Z A Bakhshieva *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, 1990, **33**(5) 71
38. R A Lemberanskii, E R Gilbert Ortis, K M Mekhtiev, I B Annenkova *Azerb. Khim. Zh.*, 1977, (6) 66
39. M Havigherst *J. Am. Chem. Soc.*, 1924, **46** 2362
40. NBS Circular, 1955, **539**(5) 4
41. R A Lemberanskii, I B Annenkova, F M Poladov, Z A Bakhshieva *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1991, **34**(5) 51
42. A I Gel'bshtein, Yu A Mishchenko, P P Nechiporuk, N D Gol'dshtein *Preprinty Dokladov Vsesoyuznoi Konferentsii po Mekhanizmu Geterogenno-Kataliticheskikh Reaktsii* (Preprints of Papers of the All-Union Conference on the Mechanism of Heterogenous Catalytic Reactions), Moscow, 1974, Preprint 89
43. G O Tuarsheva, Candidate's Dissertation in Chemical Sciences, AzINEFTEKhIM, Baku, 1989
44. R A Lemberanskii, F M Poladov, I B Annenkova, A A Davydov *IK-Spektroskopicheskoe Issledovanie Poverkhnostnykh Kislotnykh Tsentrov Olovosur'myanogo Katalizatora* (IR-Spectroscopic Investigation of Surface Acid Centres of a Tin–Antimony Catalyst), deposited paper No. 3102-B, April 28, 1986, VINITI, Moscow, 1986, 6 pp.

Translated from *Uspekhi Khimii* **61** 139–160 (1992) U.D.C. 541.64:542.952

Recent trends in research into ionic polymerisation

B L Erusalimskii
Institute of Macromolecular Compounds, USSR Academy of Sciences, St Petersburg

ABSTRACT. The results of original studies on the mechanism of formation of macromolecules in ionic systems are discussed. Amongst these are polmerisation involving living carbocation chains, cationic processes that occur via the activation of a monomer, anionic polymerisation initiated by aluminium and zinc porphyrins, group transfer polymerisation, and polymerisation of olefins using homogeneous Ziegler–Natta catalysts that exhibit high activity.

The bibliography includes 76 references.

Contents

I. Introduction 75
II. Cationic processes 75
III. Anionic processes 80
IV. Processes initiated by Ziegler–Natta catalysts 83

I. Introduction

During the last ten years the range of agents capable of initiating the ionic polymerisation of various monomers has increased considerably. Many agents have been successfully used to solve important practical problems, such as the preparation of novel polymers, simplifying the conditions for the synthesis of narrowly dispersed macromolecules, and the development of highly effective polymerisation processes. The properties identified in original initating systems have had a marked influence on existing ideas about the mechanism of formation of macromolecules in ionic processes. In the present article particular attention is given to this very question. The desirability of discussing it arises from the fact that the trends in research which will be considered below have so far not been reflected in the Russian review literature.

We should mention that in comparing cationic with anionic polymerisation it was customary to emphasise the marked difference in stability of the active sites. The specific features of polymerisation occurring via active anionic sites are as follows: a linear increase in molecular weight (MW) of the polymers with conversion, and a narrow molecular weight distribution (MWD). These characteristics, which had been established for a number of specific processes, were for a long time considered unattainable for active cationic sites.

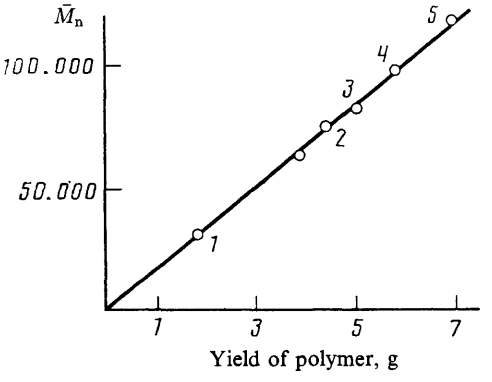


Figure 1. Polymerisation of isobutylene by the system dimethoxy-*p*-dicumyl (DMDC)–$TiCl_4$ in the mixed solvent $CH_3Cl-C_6H_{14}$ (40:60 by volume) at −80 °C.[9] Concentration, mol litre^{-1}: $TiCl_4$ 1×10^{-3}, DMDC 6.4×10^{-5}; total volume 25 ml; conversion 100%; values of $\overline{M}_w/\overline{M}_n$: *1*, 1.11; *2*, 1.10; *3*, 1.17; *4*, 1.10; *5*, 1.09.

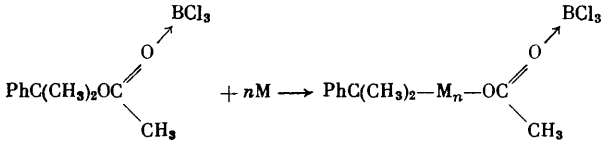
II. Cationic processes

1. Mechanisms of cationic processes

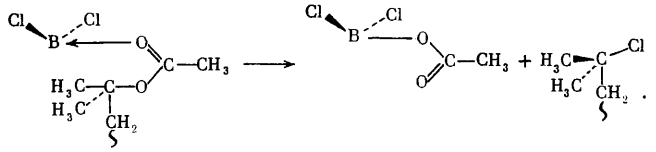
A comparison of the practical significance of the results that characterise cationic and anionic polymerisation has often pointed to the considerable advantage of the latter. This has mainly been connected with the possibility of synthesising various block and multiblock copolymers with a widely controlled range of physicomechanical properties in anionic rather than cationic systems. The development of novel cationic initiators has substantially altered this situation in recent years, and this contrasting position has now lost its original importance.

Studies undertaken in recent years led to a revision of this idea. The basis for this was provided by the studies by Kennedy et al. that developed from previous research by the same authors which focused on the so-called "quasi-living" chains. The results of these studies were examined in a previous review.[1] We shall confine ourselves to the following observation: the distinctive features of polymerisation processes involving quasi-living chains are governed by slow batching of the monomer into the reaction mixture ($3-5 \times 10^{-3}$ mol min^{-1}); this technique results in a marked narrowing of the molecular weight distribution compared to polymerisation under normal conditions. For example, in the case of *p*-t-butylstyrene with the use of boron chloride–cumyl chloride as initiating system in dichloromethane at −50 °C and a conversion of 100%, the $\overline{M}_w/\overline{M}_n$ ratios were 6.53 and 1.38 respectively for introduction of monomer in a single batch and gradually.

The characteristics of the growth of living chains were identified when initiating systems containing Lewis acids in combination with cumyl ethers or esters were used.[2–25] Boron chloride and cumyl acetate (CA) or methyl cumyl ether were used most frequently as components of these systems. For this type of polymerisation the formation of polymers with $\overline{M}_w/\overline{M}_n$ almost equal to 1.1 is typical as is a retention of the linear dependence of $\overline{M}_n$ on the degree of conversion up to 100%. This is shown in Fig. 1 in the case of the polymerisation of isobutylene. The following scheme[4] illustrates the mechanism for polymerisation of this monomer (M) with the system boron chloride–CA

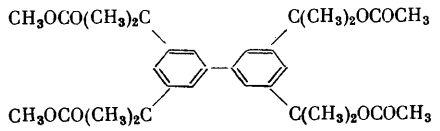


Deactivation of the living polymers, which is caused in particular by an increase in temperature of the reaction mixture, results in the formation of macromolecules with a terminal chlorine atom, which has been interpreted in the following way:[2]



It is worth noting that terminal chlorine atoms have also been found in polymers deactivated by nucleophilic reagents; no details about the mechanism of this effect were given by Faust and Kennedy.[2]

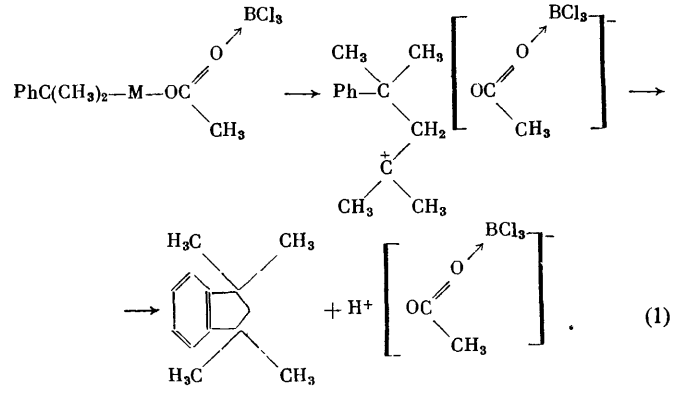
Interesting results are obtained by replacing CA and methyl cumyl ether with the di-, tri- and tetra-functional analogues of these compounds.[4,6–8,11] The last of these has the structure (I):



(I)

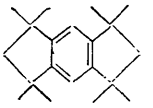
"Tetrablock" macromolecules were obtained from this compound. Polymerisation in the system isobutylene–(I)–BCl_3–CH_2Cl_2 at –80 °C gave this result.[11]

The above processes are accompanied by side reactions that result in the formation of indane rings. This is typical for growing cationic chains containing aromatic rings. Such cases are illustrated by the following scheme:[6]



(1)

For bifunctional initiators the formation of diindane structures is possible:



The relative role of these reactions depends on the temperature and nature of the medium. A reduction in the polarity of the solvent and temperature may lead to their being completely excluded, as depicted in Fig. 2.

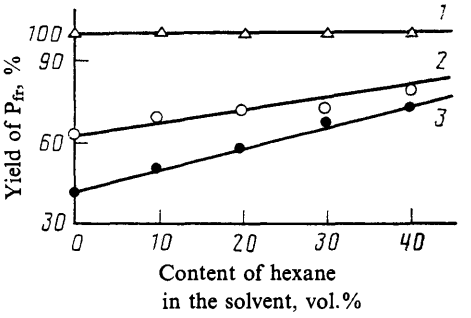


Figure 2. Effect of polarity of the medium and temperature on the formation of polyisobutylene free of indanyl groups (P_{fr}).[6] Initiating system BCl_3–DMDC; temperature, °C: *1*, –70; *2*, –50; *3*, –30.

Let us consider the preferred use of boron chloride compared to other Lewis acids in initiating systems by the authors of these studies. This also refers to the above-mentioned polymerisation processes involving quasi-living chains.[1]

The characteristics of boron chloride are revealed when it is compared with certain aluminium derivatives that form highly active initiating systems with the compounds R_3CCl or HCl. The former do not yield any suitable initiators with BCl_3 while the combination of BCl_3 and HCl constitutes an equilibrium system with a low initiating activity. According to Kennedy and Chen,[12] the reason for this is the low stability of the BCl_4^- counterion, which undergoes reaction (2*c*):

$$HCl \cdot BCl_3 \underset{a}{\rightleftarrows} H^+, BCl_4^- \xrightarrow[b]{(CH_3)_2C=CH_2} (CH_3)_3\overset{+}{C}, BCl_4^- \xrightarrow{c} \longrightarrow (CH_3)_3CCl + BCl_3. \quad (2)$$

The features that are typical of living carbocation chains are also found in the polymerisation of styrene monomers. In this respect the best results have been obtained for 2,4,6-trimethylstyrene,[10] whose structure excludes side reactions of the type (1).

In some studies titanium tetrachloride has been used as a component of the initiating systems. A combination of it and *p*-dimethylcumyl ether (DCE) proved active towards isobutylene

down to −80 °C.[9] The introduction of $TiCl_4$ into a reaction mixture containing all the remaining components achieves good results ($\bar{M}_w/\bar{M}_n$ = 1.1, $\bar{M}_n \sim 10^5$). The use of a previously prepared complex of $TiCl_4$ and DCE gives rise to the formation of indane rings on one or on both ends of the chain. This effect led the authors to make the following assumptions.

When the initial complex is allowed to stand, it gives rise to the formation of the ion pair $\geqslant C^+ [OTiCl_4]^-$, for which an intramolecular conversion to $H^+ [OTiCl_4]^-$ is possible, accompanied by the development of an indane ring at the end of the chain. The contribution of such a conversion must depend on the length of time of storing the initial complex until its introduction into the solution of monomer, which is what actually occurs. With an increase in time for allowing the complex to stand, the content of indane rings in the polymers increases (for example, in one study[9] data is given for times of 30, 75, and 90 s). The relatively slow ionisation of the complex may be attributed to the low polarity of the solvent — a mixture of methyl chloride and n-hexane in the ratio 2:3 was used.

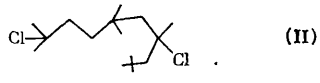
We should mention a further route for the exclusion of side reactions of the type (1) as described by Biswas and Kennedy.[3] In this case the ability of boron chloride to interact with 2,5-dichloro-2,5-dimethylhexane (DDH) was established, leading to the formation of an active initiator for the polymerisation of isobutylene. The absence of a similar effect in the case of monohaloalkanes led the authors to conclude that the bifunctionality of DDH has a special role, making it possible for a cyclic halonium ion to be formed:

$$Cl{-}C(CH_3)_2CH_2CH_2C(CH_3)_2{-}Cl \xrightleftharpoons{BCl_3} (CH_3)_2C\begin{array}{c}CH_2{-}CH_2\\ |\quad\quad |\\ \quad Cl,\ BCl_4^-\end{array}C(CH_3)_2 \quad (3)$$

The propagating chains formed by the action of this sytem undergo spontaneous termination by the normal route (4), but the characteristic signs of reinitiation could not be detected

$$\geqslant C^+,\ BCl_4^- \longrightarrow \geqslant C{-}Cl + BCl_3. \quad (4)$$

The combination of spontaneous termination and lack of reinitiation is indirect confirmation of mechanism (3). Positive evidence for it is also provided by the formation of the dihalide (II) on reaction of 2,2,4-trimethyl-1-pentene (TMP) with DDH and BCl_3 in CH_2Cl_2 at −20 °C, namely, with conditions under which TMP does not polymerise. For the sake of brevity, we shall use the skeletal structural depicted by Biswas and Kennedy,[3]



(II)

It follows from the above that replacement of cumyl chloride as a component of the initiating systems by cumyl ethers gives rise to a change in behaviour of quasi-living and living chains in the majority of cases. Similar qualitative effects were subsequently obtained when another method was used, namely, the addition of a catalytic quantity of a strong electron donor (ED) to binary systems of the type Lewis acid — t-alkyl chloride. The result of such an addition are illustrated by data on the polymerisation of isobutylene in a mixed solvent of n-hexane — methyl chloride (3:2) at −40 °C on treatment with the system 2-chloro-2,4,4-trimethylpentane — $TiCl_4$ in the absence and in the presence of an ED:[5]

Polymerisation conditions	$\bar{M}_w/\bar{M}_n$ of polymer
In the absence of an ED	1.21
In the presence of dimethyl sulphoxide	1.05.

In this case 2,5-di-t-butylpyridine, which acts as a proton trap but which is inert towards carbocations, was also included amongst the components of the reaction mixture. Its presence leads to removal of the proton component of the initiation reaction, which results from an uncontrolled number of proton donors. (For further details, see the review of Erusalimskii).[1] Dimethylacetamide was used as an ED in other systems of a similar type.

These compounds may be regarded as agents stabilising the active cationic sites. The hypothetical structure (III), relating to a system based on boron chloride,[4] has been put forward to explain this theory:

$$\sim\overset{\delta+}{\underset{CH_3}{\overset{CH_3}{C}}}{-}Cl\cdots ED\cdot n\,BCl_3\cdots\overset{\delta-}{BCl_4} \quad (III)$$

Evidence for polymerisation occurring on living chains was found by Kennedy et al. in the case of certain chlorine-substituted styrene monomers.[3,4] In particular, in the system *p*-chlorostyrene — $TiCl_4$ — 2-chloro-2,4,4-trimethylpentane — methyl chloride — cyclohexane — dimethylacetamide — di-t-butylpyridine, polymerisation at −80 °C is characterised by a linear dependence of $\bar{M}_n$ on the degree of conversion.[13] However, $\bar{M}_w/\bar{M}_n$ in this case is not less than 1.26, which may be due to side reactions.

Results of practical significance were obtained by polymerisation of *p*-chlorostyrene via mono-, di-, and tri-functional living polyisobutylene chains.[14] In this way linear and three-arm block copolymers containing comparable proportions of blocks of both types were synthesised with a total value of $\bar{M}_n$ of the order of 5×10^4. Their properties are typical of thermoplastic elastomers — polymers with rubber-like and "glass-like" sequences. They have a considerable advantage over block copolymers based on butadiene and styrene that are similar in general type, but they differ from them by virtue of their increased stability towards atmospheric oxygen and lower combustibility (due to their chlorine content) while having similar physicomechanical parameters.

An assessment of the degree of success obtained from the studies carried out in this area has been given in a general summary by Kennedy,[15] in which considerable attention is given to the applied aspects.

Before the series of studies by Kennedy was published, only the polymerisation of vinyl ethers by the initiating system HI — I_2 could be classed as a cationic process occurring via living chains. The first studies in this area, which were carried out by Higashimura et al., have been discussed in an earlier review.[1] Let us consider more recent studies by these same authors, which extended the range of systems of a similar type and their applicability to other monomers.

A number of novel systems based on HI were obtained when I_2 was replaced by different zinc halides.[16] Their effect in relation to the polymerisation of vinyl isobutyl ether (VIBE) is briefly illustrated

by the results obtained in toluene at 0 °C and with complete conversion of monomer at concentrations (mol litre^{-1}) of: 0.38 (VIBE), 5×10^{-3} (HI), and 1×10^{-4} (ZnX_2):

X	I	Br	Cl
$\bar{M}_w/\bar{M}_n$	1.05	1.04	1.05 .

The introduction of a second equal portion of monomer after polymerisation of the first portion was complete led to the formation of polymers with $\overline{M}_n$ of the order of 1.5×10^4 while preserving a linear dependence of this value on conversion and with only a slight broadening of the molecular weight distribution ($\overline{M}_w/\overline{M}_n$ 1.07–1.08).

The possibility of replacing both the iodine components by others was demonstrated in the case of the polymerisation of VIBE in toluene by the system $(CH_3)_3SiI-ZnI_2$. Effects that were typical of polymerisation via living chains were found at −40 °C.[17] The dependence of the final result on temperature, with complete conversion of monomer and concentrations of VIBE, trimethyliodosilane, and zine iodide equal to 0.38, 0.005, and 0.001 mol litre^{-1} respectively was as follows:

t, °C	−40	0	25
M_n	8200	640	470
$\bar{M}_w/\bar{M}_n$	1.06	1.14	1.26 .

The active sites that are effective in $HI-ZnX_2$ systems have been attributed a structure containing the fragment $(I\cdots I_2)^-$ proposed for the active sites formed by interaction of monomer with a combination of HI ands I_2.[1] Generation of active sites in the last of the above-mentioned systems may be viewed in a similar manner—activation by ZnI_2 of the C–I bond in the adduct between the silane component and monomer.

The polymerisation processes of VIBE initiated by the system $HI-ZnI_2$ have been studied in the greatest detail. Of the other properties, the lifetime of the growing chain in relation to the conditions selected has been determined. We shall list the results obtained with VIBE, HI, and ZnI_2 concentrations of 0.38, 0.01, and 0.0001 mol litre^{-1} respectively:[18]

Solvent	t, °C	half-life* of active sites, min
Dichloromethane	−15	270
Toluene	−15	390
Toluene	0	180
Toluene	25	30

*The period of time over which the concentration of the active sites is halved through deactivation reactions.

The use of different iodine-containing initiating systems for the polymerisation of vinyl ethers with polar substituents [$CH_2=CHO(CH_2)_2Cl$, $CH_2=CHO(CH_2)_2CH(COOC_2H_5)_2$, $CH_2=CHO(CH_2)_2OC_6H_4X$, where X = OCH_3 or Cl] gave narrowly dispersed polymers.[19–21] Some of these were used for the synthesis of block oligomers with a given sequence of monochain residues corresponding to different monomers. An interesting example of this type is the heterotetramer obtained in toluene at −40 °C using the system $HI-ZnI_2$:[22]

$$CH_3CH(O-n\text{-}Bu)-CH_2CH[OCH_2CH_2CH(COOEt)_2]-CH_2CH\cdot$$
$$\cdot(OCH_2CH_2OCOPh)-CH_2CH[OCH_2CH_2OCOC(CH_3)=CH_2]OCH_3.$$

It is formed as a result of the activation of the adduct of vinyl n-butyl ether and hydrogen iodide by zinc iodide and the step-wise introduction of equimolar quantities of the other three monomers into the reaction mixture. By using 2-(vinyloxy)ethyl methacrylate as one of these (the last one in this case) this tetramer may be considered capable of undergoing addition polymerisation.

Table 1. Synthesis of block copolymers through living polymers corresponding to monomer M_1.[23]

M_1	M_2	Properties of block copolymers	
		$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
VIBE(38)*	*p*-(*t*-Butoxy)styrene, TBS(100)	17.5	1.08
TBS(38)	*p*-Methoxystyrene, MS(38)	12.0	1.05
MS(38)	TBS(100)	19.0	1.04

Note. Process conditions: initiating system $HI-ZnI_2$ (2:1); toluene as solvent: temperature −15 °C; 100% conversion of each monomer.
*The degree of polymerisation of the monomers is given in brackets.

Block copolymers containing alkoxy derivatives of styrene have recently been obtained using the same initiating system (Table 1). The interaction of the active sites corresponding to different $CH_2=CHOR$ monomers (where R is C_2H_5, iso-C_4H_9, or n-$C_{16}H_{33}$) with a small quantity of the bifunctional vinyl ether $(CH_2=CHOCH_2CH_2OC_6H_4)_2C(CH_3)_2$ as a cross-linking agent resulted in the formation of more complex structures such as star-shaped polymers. Polymers that were completely soluble in toluene and THF were thus obtained with the number of branches ranging from 3 to 60, controlled by the ratio of reagents and the total concentration of the living chains.[24] The value of $\overline{M}_w$ of star-shaped polymers synthesised in this manner is in the region of 2×10^4 to 3.8×10^5 with an average degree of polymerisation of the branches ranging from 38 to 114.

It was pointed out by Higashimura et al.[23,24] that the wide range of polymers synthesised provides a sound basis for their use for various practical objectives.

Let us consider two further points concerning the exact nature of the active sites occurring in the processes described in the studies of Kennedy and Higashimura. Their substantially longer lifetime compared to the carbocations formed in normal cationic systems does not make it possible to identify both these agents. The authors of these studies have taken this into account. The view of Plesch,[25,26]

according to which these processes should be classed as pseudocationic, is stated with considerable clarity in this connection. We should mention that the mechanism of pseudocation polymerisation put forward in the 1960s by Gandini and Plesch (for further details, see four studies)[25–28] is based on the concept of the covalent nature of the active sites occurring in such processes.

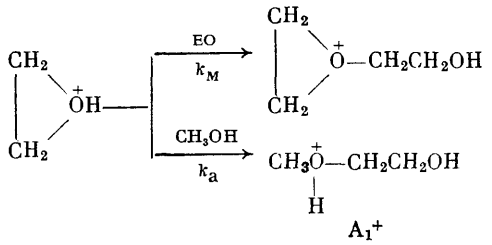
The second point, which is of a more fundamental nature, touches on the question as to whether it is legitimate to define these same active sites as living polymers. This was called into question by Sigwalt in the middle of the 1980s,[29] as was briefly mentioned in an earlier review.[1] In maintaining his point of view subsequently, Sigwalt[30] emphasised that for relatively low values of the degrees of polymerisation (in several of the cited studies they do not exceed 100) the possibility of chain transfer is not excluded, which in cationic polymerisation is usually characterised by C_M constants that do not exceed 10^{-4}. This argument is contradicted by the known facts[15] about the increase of $\overline{M}_n$ with conversion up to values of the order of 10^5 and the possibility of synthesising different block copolymers in these processes with the active sites corresponding to monomer M_1 being completely used up in the formation of products $(M_1)n-(M_2)_m$.[31,32]

Certain deviations from results of this type[1,31] merely attest to the influence of the monomer on the final effect.

2. Mechanism of the cationic polymerisation of oxygen-containing heterocycles

In recent years Penczek et al.[33–37] formulated a new mechanism for the cationic polymerisation of oxygen-containing heterocycles, which the authors called polymerisation via an activated monomer (PAM). This denotes the generation of active sites for propagation via the formation of a protonated monomer (HM^+), which then transfers the proton to a more active acceptor. The protonated acceptor then reacts with a further molecule of monomer. This sequence has been studied in detail in the case of the system $EO-BF_3-CH_3OH$, where EO is ethylene oxide.[33]

For the product HM^+ the following reactions are possible:



(5)

(6)

Route (5), which occurs provided that

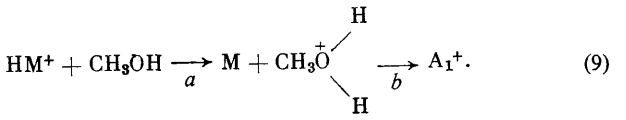
$$k_M[M] > k_a[CH_3OH], \tag{7}$$

leads to active sites of the tert-oxonium ion type, namely, to a trivalent mechanism for cationic polymerisation processes of such monomers. In the presence of a nucleophile with high activity another situation is feasible, namely

$$k_M[M] < k_a[CH_3OH], \tag{8}$$

i.e., the condition under which route (6) occurs.

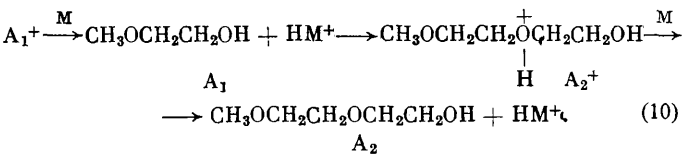
We should note that from the definition by Penczek et al. of route (6) as proton transfer from HM^+ to a nucleophile, this stage may be assumed to occur in two steps



(9)

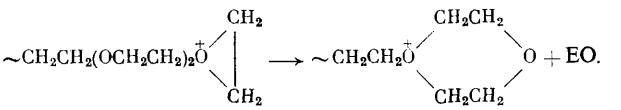
On the basis of the greater nucleophilicity of methanol compared to EO, the authors evidently do not regard stage (9*b*) as probable and assume that there is a concerted single-stage mechanism for formation of a secondary oxonium ion. In the studies cited above this question was not considered.

The subsequent course of this process is given by the scheme



(10)

Its validity is supported by the formation of product A_2. As noted in one study,[33] this compound may also be formed by mechanism (5), but only together with the elimination of a 1,4-dioxan. This possibility arises for active sites of the tert-oxonium ion type which can undergo the following rearrangement:



However, in reaction mixtures obtained by polymerisation in the presence of a sufficient quantity of methanol, only a small amount of dioxan was detected.[33] From this the contribution of the PAM route could be assumed to exceed 98%.[38]

The amount of A_2 in the system, in accordance with condition (8), decreases during the process as a result of its consumption by mechanism (10). The dependence of the contribution of this route to the total process of the methanol content in the system also provides support for mechanism (6). A reduction in its content causes an increase in the role of route (5), which is suggested by the increased yield of dioxan that occurs at the same time (Table 2). The PAM mechanism starts to predominate only when there is a large concentration of methanol. The unfavourable results of these conditions for the molecular-weight characteristics of the polymers can be avoided by operating at a very low concentration of monomer, which is achieved by slow batching of it into the reaction mixture. How this is reflected in a decrease in the role of side reactions and the values of $\overline{M}_n$ of the polymers is indicated by the results of polymerisation of epichlorohydrin by the system boron fluoride–ethylene glycol with complete conversion of monomer[33] (no details were given about the other experimental conditions in this study):

Method of introducing the monomer	Yield of tetramer	$\overline{M}_n$ (calc)	$\overline{M}_n$ (experiment)
Single batch	21	2350	1530
Slow batching	0.01	2100	2100

Results of a similar type were obtained in the polymerisation of propylene oxide (PO) in dichloromethane by $HBF_4 \cdot Et_2O$ in the presence of 1,6-hexanediol. In this case the yield of PO tetramer, which amounts to about 50% when the diol is absent, decreases to 4% when the ratio of monomer to diol is equal to 10.[36] Slow batching of monomer (0.02 ml min^{-1}) reduces the yield of tetramer to 1%. These results relate to room temperature and to a total concentration of monomer of 2.0, initiator of 5×10^{-3}, and diol of 0.2 mol $litre^{-1}$.

Table 2. Effect of methanol on the formation of 1,4-dioxan in the polymerisation of ethylene glycol by $BF_3 \cdot CH_3OH$ in dichloromethane.[33]

[M], mol $litre^{-1}$	$[CH_3OH]/[M]$	Yield of dioxan, %
1.1	2.0	1.1
1.1	3.2	13.4
1.2	6.0	39.5
1.3	17.0	66.5

Note. Process conditions: concentration of initiator 0.03 mol $litre^{-1}$; temperature 25 °C; 100% conversion of monomer.

We should note the effect discovered during polymerisation in the systems $EO-HSbF_6-CH_2Cl_2-CH_3(OCH_2CH_2)_nOH$ at 30 °C. The results presented below represent the total rate constant of polymerisation (k_t, litre mol^{-1} min^{-1}) in the presence of these hydroxyl derivatives (0.5 mol $litre^{-1}$) with a concentration of monomer and initiator of 0.5 and 4×10^{-4} mol $litre^{-1}$ respectively:[36]

n	0	1	2
k_t	8±1	13±2	22±3 .

This result has been interpreted by the authors as the consequence of an increase in the number of processes of type (6) as the oxygen-containing residues in the proton acceptor increase in length.

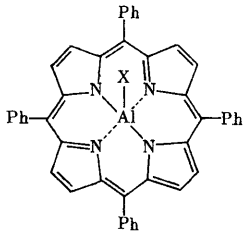
Conditions favouring a PAM mechanism can be used for the synthesis of block copolymers. This has been demonstrated[39] in the polymerisation of cyclic acetals in the presence of poly(ethylene oxide glycol) (PEOG). Thus, in the case of dioxolane and dioxepane on treatment with trifluoromethanesulphonic acid, the formation of products of the general type $HO-M_n-PEOG-M_n-OH$ and their corresponding multiblock copolymers was established.

A general review of the kinetics of PAM processes has recently appeared.[40]

III. Anionic processes

1. Initiating systems based on porphyrin

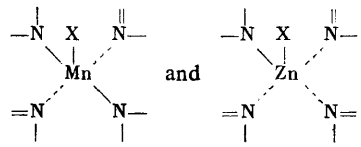
At the beginning of the 1980s the first results were published on the ability of aluminoporphyrin derivatives of the type (IV) to cause the efficient polymerisation of different types of oxygen-containing heterocycles



(IV)

In compounds (IV) the substituent can be a halogen, alkyl, OR or COOR group. These initiators will subsequently be denoted by the symbols TPhPAl–X, with substituent X being specified.

Development of these studies extended the range of initiators of a similar type and their use in the polymerisation of other monomers, including acrylic compounds.[44–48] Subsequently results were published on the initiating activity of certain tetraphenylporphyrin derivatives of manganese[49] and zinc[50,51] towards three-membered heterocycles. These compounds contain central groups that are similar to (IV)



in which X = $OCOCH_3$ in the case of manganese and X = C_2H_5, iso-C_3H_7S, or iso-C_3H_7O in the case of zinc.

Polymerisation of heterocycles. Let us first consider the validity of classifying the mechanism of these processes as anionic. The following circumstance can cast doubts in this respect. Effective polymerisation of the simplest epoxides is achieved when it is carried out in dichloromethane by the action of initiator (IV) with X = Cl. Under these conditions a cationic mechanism for the process could formally be expected. The result obtained in a model system, i.e., with an equimolar ratio of initiator and propylene oxide, would also appear to lend support to this argument. According to the PMR data, this reaction in dichloromethane gives the product $TPhPAl-OCH(CH_3)CH_2Cl$. The insertion of monomer into an Al–N bond would be more natural in anionic polymerisation. On the other hand, the further stages of chain propagation occur through polarisation of the $O^{\delta-}-Al^{\delta+}$ bond. An active $Cl^{\delta-}-Al^{\delta+}$ bond, respectively for initiation, should evidently be regarded in a similar light.

A general characteristic of initiators (IV) with different substituents X is the lack of chain termination in polymerisation caused by them and the formation of narrowly dispersed polymers with $\overline{M}_w/\overline{M}_n$ = 1.05–1.10. This relates, in particular, to epoxides[41] and lactones.[44,45] The individual nature of the initiators is most clearly revealed in the latter case. For example, the compounds

TPhP–AlCl and TPhP–AlCOOR are only active towards β-lactones, and not towards higher lactones. Compounds (IV) with an OR substituent are noted for their initiating activity towards the latter.[48,49]

The polymerisation of δ-valerolactone has been studied in greater detail, and in this case the following noteworthy effect has been identified. The low rate of polymerisation caused by the methoxy derivative of (IV) increases markedly in the presence of TPhPAl–Cl, which by itself is inert under the same conditions towards the same monomer. The scale of this effect is illustrated in Fig. 3.

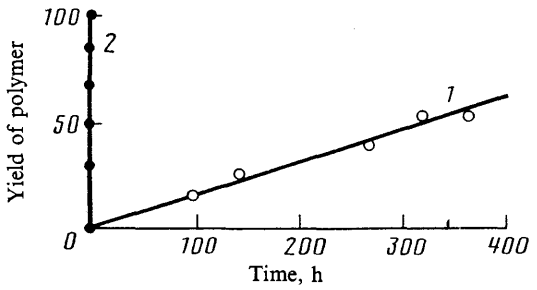


Figure 3. Polymerisation of δ-valerolactone in the absence of a solvent at 30 °C.[48] Initiators: *1*, TPhP–$AlOCH_3$; *2*, TPhP–$AlOCH_3$–TPhP–AlCl. Molar ratios: monomer/TPhP–$AlOCH_3$ = 200:1; TPhP–$AlOCH_3$/TPhP–AlCl = 2:1.

The effect of this chloride has been attributed by Aida et al.[43] to its high complexing activity towards the monomer, as was concluded from the PMR spectroscopic data. The conclusion that this type of complexation has a promoting role is consistent with the order of reaction in the absence and in the presence of this reagent:

$$v = k[\text{TPhPAl}{-}\text{OCH}_3]^2[\text{M}],$$
$$v = k'[\text{TPhPAl}{-}\text{OCH}_3][\text{TPPhAl}{-}\text{Cl}][\text{M}].$$

The effects revealed in a study of the interaction of the active sites corresponding to these initiators with typical deactivators of anionic chains (HCl, ROH, H_2O, etc.) are unusual. In these systems deactivation of the active sites occurs at the same time as regeneration of the initiator, for example

$$\text{TPhAl}{-}\text{M}_n{-}\text{Cl} \overset{\text{HCl}}{\rightleftarrows} \text{TPhPAl}{-}\text{Cl} + \text{H}{-}\text{M}_n{-}\text{Cl}.$$

The high frequency of these exchanges, exceeding the rate of propagation, leads to results that are typical of polymerisation via living chains. This is achieved by the introduction of a mixture of proton donor and monomer into a solution of initiator. Several examples are given in Table 3. A second portion of monomer introduced after complete conversion of the initial portion results in an increase in the molecular weight of the polymer while retaining a narrow molecular weight distribution. This result has been obtained in particular for the system PO–TPhPAl–Cl–CH_2Cl_2–CH_3OH; the final value of $\overline{M}_w/\overline{M}_n$ in this case was 1.09.

Similar results were obtained in the polymerisation of lactones and also with the introduction of a "foreign" monomer into the reaction mixture at the second stage of the process. An EO–PO block copolymer was synthesised in this manner.

Table 3. Polymerisation in R–CH(O)–CH_2–TPhPAl–Cl–CH_3OH systems in the absence of a solvent.[48]

R	Time, h	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
H	48	700	1.05
CH_3	48	1300	1.08
CH_3CH_2	96	1200	1.10
CH_2Cl	48	1500	1.04

Note. Process conditions. Molar ratios: monomer/initiator = 200, methanol/initiator = 9; room temperature; 100% conversion of monomer.

On the basis of these characteristics, Inoue et al.[45] introduced the term "immortal polymerisation" for such processes.

Similar effects were recently found in systems incorporating zinc derivatives of tetraphenylporphyrin. This was demonstrated, in particular, for the polymerisation of PO by the system TPhP–$Zn(C_3H_7)S$–CH_3OH. In this case the value of $\overline{M}_w/\overline{M}_n$ corresponding to 100% conversion of monomer was 1.08.

The molecular-weight characteristics suggest that the rate of exchange between active sites and proton donor molecules is much higher than the rate of propagation.

Polymerisation of polar unsaturated monomers. Some of the initiators under discussion have proved active towards methacrylates, but only in the light, according to the original findings.[42] It was subsequently shown to be possible to carry out polymerisation also in the dark provided that initiators (IV) with substituents X = OR or SR were used.[46] An example of this is the polymerisation of methyl methacrylate (MMA) in dichloromethane at 35 °C by TPhP–$AlSC_3H_7$. With a ratio of MMA:(IV) = 200:1 and complete conversion of monomer, a polymer with $\overline{M}_n = 2.2 \times 10^3$ and $\overline{M}_w/\overline{M}_n = 1.12$ was obtained.

Use of initiator (IV) with X = SPh achieves results of a similar type. A linear dependence of $\overline{M}_n$ on the degree of conversion and formation of polymer with $\overline{M}_n = 3 \times 10^4$ and $\overline{M}_w/\overline{M}_n = 1.1$ has been established in this case.

Information on nitrile monomers is currently limited to data on the polymerisation of methacrylonitrile (MAN) by propagating MMA chains. An MMA–MAN block copolymer was obtained in this case.

We should note that the possibility of polymerising these monomers in the dark depends not only on the nature of the initiator but also on the selected reaction temperature. Thus,

polymerisation of PO by TPhPZn–SC_3H_7 occurs in the light at 25 °C but is also achieved in the dark at 70 °C; the $\overline{M}_w/\overline{M}_n$ values in these cases were 1.05 and 1.07 respectively.[51]

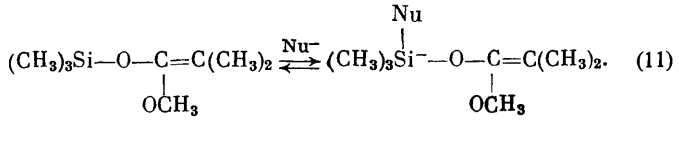
2. Group transfer polymerisation

The first publication of Webster et al.[52] concerning a new method of anionic polymerisation, established under the name of group transfer polymerisation (GTP), appeared in 1983. The mechanism of GTP differs fundamentally from other known polymerisation processes in that each stage of addition of the next monomer molecule to the growing chain combines initiation and propagation, concluding with reproduction of the structure that in principle matches that of the original initiator.

The method is based on the use of mixtures of *O*-silyl ketals of ketenes with nucleophilic or electrophilic compounds. According to the accepted terminology, the first of these components are called initiators and the second are known as catalysts. Nucleophiles such as HF_2K, $FNBu_4$, and certain others or electrophilic compounds of the Lewis acid type such as zinc halides can function as catalysts. Nucleophilic catalysts have proved more convenient for the polymerisation of methacrylates, to which most of the studies on GTP have been devoted.

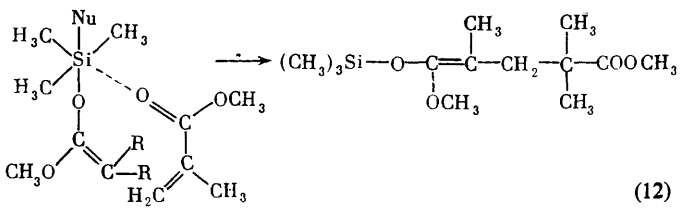
An important advantage of these processes over polymerisation of the same monomers using conventional anionic initiators (organometallic compounds) is that propagation of the living chains is not complicated by side reactions† even at room temperature. This characteristic of GTP considerably simplifies the synthesis of narrowly dispersed polymers—a task of considerable practical significance. Even with the normal technique (simultaneous introduction of the whole portion of monomer into the reaction mixture), $\overline{M}_w/\overline{M}_n$ for the MMA polymers is equal to 1.3, while with slow batching of the monomer, $\overline{M}_w/\overline{M}_n$ = 1.01. This property has substantially simplified the synthesis of block copolymers of different methacrylates, including hybrid macromolecules of the type A–B–C.

The scheme put forward by Webster et al.[54,55] to interpret the mechanism of GTP involves the formation of a pentacoordinate silicon derivative in the reaction between initiator and catalyst, which has been demonstrated for the simplest example of ketene *O*-silyl ketals and a nucleophile (Nu^-), which may be an F^- or HF_2^- ion.



(11)

The product of this reaction interacts with the monomer to form an intermediate hexacoordinate silicon derivative, rearrangement of which completes the propagation step. We can illustrate this in the case of methyl methacrylate (MMA), where R = CH_3:



(12)

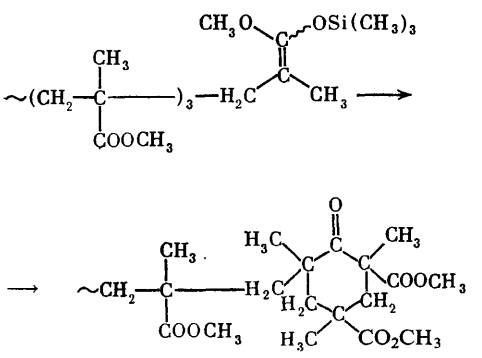
† The mechanism and results of these reactions are examined in detail in another review.[53]

The existence of an intermediate has not been confirmed experimentally, but the results of nonempirical calculations, referred to in a study by Müller,[56] provide evidence for it. However, the conclusion that there is a combination of initiation and propagation steps at each stage of the insertion of monomer into the polymer chain is valid. The final product of reaction (12) interacts with the nucleophile according to scheme (11), thus achieving the further progression of polymerisation.

In practice, tris(dimethylamino)sulphonium difluoride (DSDF) has been used to a relatively greater extent than other nucleophiles. Amongst the reaction products in systems in which it involved, triple block copolymers of MMA with n-butyl and allyl or glycidyl acrylates have been synthesised. Kinetic studies were carried out with DSDF and the simplest of the ketene *O*-silyl ketals. Let us consider the results of Müller et al.[57]

Standard conditions were selected: THF as solvent, temperature 20 °C, concentrations of monomer, initiator, and catalyst equal to 0.18, 1×10^{-3}, and 2×10^{-6} mol litre^{-1} respectively. One of these parameters was varied, keeping the remaining conditions constant. With a concentration of catalyst $\leqslant 3 \times 10^{-6}$ mol litre^{-1}, rapid initiation occurred with a propagation reaction that was first-order with respect to this reagent. With a concentration of catalyst $> 3 \times 10^{-5}$ mol litre^{-1} the initial stage of polymerisation was characterised by an induction period and the rate of reaction then passing through a maximum. However, the decrease in rate of polymerisation due to termination stages did not prevent the complete conversion of monomer. When the concentration of initiator was varied, similar effects—an induction period and a curve with a maximum on the conversion/time coordinates—occurred in the region of higher concentrations of this reagent. The authors assume that in this case these are due to the deactivating effect of excess initiator rather than as a result of termination.

A study by Brittain and Dicker,[58] in which the behaviour of short-chain oligomers of this type was studied under standard conditions, has shed light on the question of the mechanism of termination reactions in GTP processes. MMA–(1-methoxy-2-methyl-1-propenyl)oxytrimethylsilane (P_1^*) was chosen as the initial system, with ratios of MMA/P_1^* equal to 2 and 3. Under the conditions employed (THF, tetrabutylammonium dibenzoate as catalyst, room temperature) oligomerisation of MMA is complete after 2 min. The IR characteristics of deactivated samples of the reaction mixture taken after different intervals of time indicated a gradual decrease in intensity of the absorption band due to the C=C bond (1687 cm^{-1}) together with the appearance and increase in intensity of an absorption band due to a carbonyl group (1716 cm^{-1}). These effects were attributed to intramolecular cyclisation of the active sites:[58]



In a determination of the rate of cyclisation of the oligomers based on the change in intensity of these bands, good agreement was obtained for the results calculated for each of the IR properties: 0.009 and 0.010 mol litre^{-1} s^{-1} for the C=O and C=C groups respectively. The authors emphasised that the role of this reaction is important only in the absence of monomer. According to their results, under real polymerisation conditions the ratio of the rate of propagation to the rate of deactivation by this mechanism is 2600.[58]

Of the other monomers that display an ability to undergo GTP, acrylates, methyl vinyl ketone, acrylonitrile, and pentadiene- and hexadiene-carboxylate esters are mentioned in the literature.

GTP processes are of definite practical value because of the possibility of using such initial reagents that can be used to synthesise polymers with reactive terminal groups. In particular, initiators containing the group $\geqslant C(OSi(CH_3)_3)O(CH_2)_2OSi(CH_3)_3$ are of this type. On hydrolysis of the polymers obtained by GTP involving these initiators, macromolecules with terminal OH groups are formed.

An interesting development for GTP processes was made in a study by Miller et al.,[59] the subject of which was an investigation of the possibility of extending the rate of nucleophiles through the reaction of different crown ethers with alkali metal salts. This was successfully carried out in the case of a system containing $(CH_3)_3Si-O-C=C(CH_3)_2$ (OCH$_3$), dibenzo-18-crown-6, and potassium acetate. When the crown ether was absent, this system was inert towards MMA, whereas by using a three-component system with this composition it was possible to obtain PMMA in 92% yield with $\overline{M}_w/\overline{M}_n$ = 1.9 (acetonitrile as solvent, temperature 50 °C).

A comprehensive description of the experimental details of the synthesis of the initial reagents, the effects on GTP of varying them, and the characteristics of the resulting polymers appear in a study.[55] Replacement of Si initators by their Sn and Ge analogues is included amongst the points mentioned in it.

A detailed comparison of the process characteristics of normal anionic polymerisation of methacrylates and the behaviour of the same monomers in GTP processes has been carried out by Müller.[56,60] The distinct nature of the latter does not prevent them from being classified under the general title of anionic-type reactions.

IV. Processes initated by Ziegler–Natta catalysts

In the Russian literature of recent years that has been devoted to problems of catalytic polymerisation,[61–64] there has been no review of the polymerisation of olefins by homogeneous Ziegler catalysts, which has undergone a particular rapid development during these years.

At the early stage of research into these processes, homogeneous systems were regarded as a convenient subject for studying the mechanism of polymerisation. For a long time they had no practical use, since all of the known systems of this type were considerably inferior to heterogeneous systems of a similar nature, differing from them through having much lower values of the rate constants of propagation and by their inability to form stereoregular polymers.

At the beginning of the 1980s the development of homogeneous Ziegler systems acquired a "second wind" as a result of the production of catalytic complexes of extremely high activity, surpassing the activity of heterogeneous systems of the same type. The replacement of aluminium alkyl and haloalkyl compounds, which were extensively used as components of a large number of Ziegler–Natta catalysts, by aluminoxanes in combination with derivatives of certain transition metals led to this situation.

The first results on highly active soluble catalysts of this type were obtained by Sinn, Kaminsky et al.[65,66] for systems containing aluminoxanes and zirconium or titanium compounds. In particular, in the polymerisation of ethylene by an initiating system based on a cyclic methylaluminoxane containing 10–20 OAl(CH$_3$) groups and the compound $Cp_2Zr(CH_3)_2$, where Cp = cyclopentadienyl, the value of the propagation constant k_p was 10^5 litre mol^{-1} s^{-1} (data for 90 °C).[67] It is approximately 10^4 times higher than those values which are known for conventional homogeneous initiating systems and $10^1-10^{1.5}$ times higher than the kinetic parameters relating to heterogeneous catalysts.[68] The relative activity of certain other systems based on the same type of aluminoxane are briefly indicated by the data in Table 4.

Table 4. Polymerisation of ethylene by soluble complexes of methylaluminoxane with compounds of Group IV metals with a constant pressure of monomer.[67]

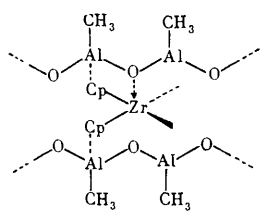
Compound	Concentration, mol litre^{-1}	t, °C	Activity of system, g polymer (g M*)$^{-1}$ h 100 kPa
$Cp_2Ti(CH_3)_2$	$3\cdot10^{-6}$	20	500
$Cp_2Ti(CH_3)Cl$	$3\cdot10^{-6}$	20	50 000
$Cp_2Zr(CH_3)_2$	$1\cdot10^{-7}$	20	9 000
$Cp_2Zr(CH_3)_2$	$1\cdot10^{-7}$	70	700 000
Cp_2ZrCl_2	$3\cdot10^{-8}$	70	1 000 000
$Cp_2Hf(CH_3)_2$	$3\cdot10^{-8}$	70	60 000

Note. process conditions: concentration of aluminoxane based on a single unit 1.5×10^{-2} mol litre^{-1}; monomer pressure 800 kPa.

*Transition metal.

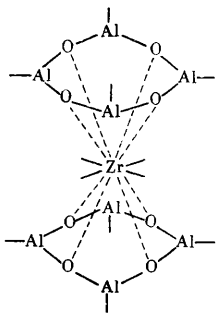
We should note the considerably higher concentration ratio of Al to transition metal in these examples compared to those normally used in Ziegler processes. The above-mentioned high efficiency of the alumino-zirconium system is provided by the very small concentration of the transition metal compound but only with a large excess of aluminoxane (see Table 4). When its concentration is reduced to a value exceeding that of the zirconium component even by a factor of 10^2-10^3, the activity of the system decreases sharply.[66]

On the basis of this phenomenon, Kaminsky et al.[66] attributed to the active agents structure (V), the formation of which requires a large excess of aluminoxane.

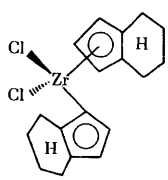


(V)

The kinetics of formation of the catalytic complex, corresponding to first and second order with respect to the zirconium and aluminium components respectively, are consistent with this. We should note, however, that structure (V) has no experimental support, although it seems plausible for linear aluminoxanes. For cyclic aluminoxanes it is necessary to take into account the increase in promoting effect of these compounds together with the increase in the number of >Al−O− residues contained in it.[65] It may be assumed from this that polyligand structures are formed in systems involving cyclic aluminoxanes, as is shown schematically in the case of a four-unit aluminoxane:[69]



Many of the same catalysts have been used for efficient polymerisation of propylene,[67] but it was only possible to improve on the synthesis of atactic polymers when a zirconium bis(indenyl) derivative with ligands rigidly connected by an ethylene bridge was used:[70]



The use of the *l*-enantiomer of this compound in combination with methylaluminoxane resulted in the formation of polypropylene with the following properties (toluene as solvent, temperature 10 °C)

Fraction*	Content of isotactic triads, %	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-3}$
Soluble in boiling heptane	96.0	1.77	4.96
Insoluble in boiling heptane	98.6	8.90	22.78

*Relative proportions of the fractions not indicated.

The above results contradict the idea that the use of insoluble Ziegler–Natta complexes is obligatory for carrying out the stereospecific polymerisation of olefins.

Recently Kaminsky[71] prepared a number of novel catalysts based on chiral zirconocenes in combination with methylaluminoxane that effected the synthesis of isotactic polyolefins. Some of these catalysts for the first time opened up the possibility of the polymerisation of cyclic olefins (cyclobutene, cyclopentene, etc.) without the complication of ring opening.

The studies of Kaminsky and Sinn[65–67,70,71] do not contain the physicochemical characteristics of the catalysts mentioned. Let us therefore introduce the data of Fink et al.[72,73] that relate to one of the simplest homogeneous aluminotitanium systems, namely, $Cp_2TiEtCl-EtAlCl_2$. They are worthy of attention mainly because they provide the first direct evidence for the insertion of monomer into the bond of the carbon atom of the active site with a transition metal. This follows from a detailed analysis of the ^{13}C NMR spectra of this system in the absence and in the presence of ethylene.[73] Kinetic studies by the same authors, which suggest that there is a two-stage mechanism for formation of the active sites in systems of the general type $Cp_2TiRCl-EtAlCl_2$, where R = alkyl, are of considerable interest.[74–76] This conclusion is based on the lack of initiating activity in the 1:1 complex indicated below as C_1:

$$Cp_2TiRCl + {}^1/_2(EtAlCl_2)_2 \overset{K_1}{\rightleftarrows} C_1. \qquad (13)$$

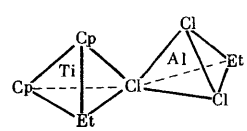
Only when it reacts with an excess of the aluminium component does it give rise to the formation of an active site (C*), which is accompanied by the formation of a dimeric aluminium derivative (Al_2') of an undetermined nature

$$C_1 + (EtAlCl_2)_2 \overset{K_2}{\rightleftarrows} C^* + Al_2'. \qquad (14)$$

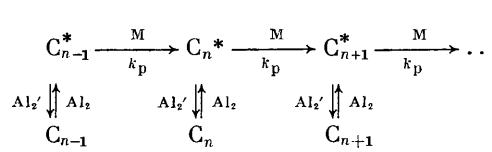
According to Eqns. (13) and (14), an increase in the original ratio of Al to Ti increases the initial rate of polymerisation of ethylene.

From the intensity of the ^{13}C NMR signals due to the $Ti-CH_2$ group, limiting values of $5 \times 10^{-3} \geqslant K_1 \geqslant 5 \times 10^{-4}$ litre mol^{-1} at −33 °C have been calculated for the equilibrium constants of Eqn. (13), while for K_2 a value of the order of 10^{-3} litre mol^{-1} was obtained.

The results that followed from an analysis of the ^{13}C NMR spectra (reduction in electron density on the titanium atom, absence of bridging methylene groups) led the authors to conclude that the C_1 complex probably exists in the form of the structure



The results of studies by Fink et al.[74–76] were used for mathematical simulation of the processes studied, which by neglecting chain termination and chain transfer made it possible to determine the rate constants of the successive propagation steps corresponding to the scheme



According to the calculations carried out, the value of k_p depends on the size of R up to R = C_5H_{11} in the component Cp_2TiRCl (data for ethylene at 283 K):[76]

Reaction	$C_2 \xrightarrow{M} C_4$	$C_3 \xrightarrow{M} C_5$	$C_4 \xrightarrow{M} C_6$	$C_5 \xrightarrow{M} C_7$	$C_6 \xrightarrow{M} C_8$
k_p, litre mol^{-1} s^{-1}	120—140	96	62	48	47.

By using a flow method with a rate of flow 2 m s^{-1} that made it possible to control the kinetics of oligomerisation and starting with a reaction time equal to 0.095 s, it was possible to characterise the dependence of the rate of the process on the concentration of monomer while retaining homogeneity of the reaction mixture. As a result the reaction was established as first-order with respect to monomer.[76]

* * *

Each of the trends in research examined here has developed rapidly, considerably strengthening ideas about the mechanism of the formation of macromolecules in ionic systems. Of no less importance are the studies reviewed here on the synthesis of polymers with practical value. This relates in particular to the preparation of various block and multiblock copolymers based on the use of different types of novel initiating systems.

References

1. B L Erusalimskii *Vysokomol. Soedin., Ser. A*, 1987, **29** 1795
2. R Faust, J P Kennedy *Polymer Bull.*, 1986, **15** 317
3. M Biswas, J P Kennedy *Makromol. Chem., Macromol. Symp.*,1986, **3** 113
4. R Faust, A Nagy, J P Kennedy *J. Macromol. Sci., Chem.*, 1987, **24** 595
5. M K Mishra, J P Kennedy *J. Macromol. Sci., Chem.*, 1987, **24** 933
6. M K Mishra, J P Kennedy *Polymer Bull.*, 1987, **17** 7
7. B Wang, M K Mishra, J P Kennedy *Polymer Bull.*, 1987, **17** 213
8. M K Mishra, B Wang, J P Kennedy *Polymer Bull.*, 1987, **17** 307
9. J Kaszás, G Puskás, J P Kennedy *Polymer Bull.*, 1987, **18** 23
10. R Faust, J P Kennedy *Polymer Bull.*, 1988, **19** 35
11. K J Huang, M Zsuga, J P Kennedy *Polymer Bull.*, 1988, **19** 43
12. J P Kennedy, F J Chen *Polymer Bull.*, 1988, **19** 201
13. J P Kennedy, J Kurian *Macromolecules*, 1990, **23** 2737
14. J P Kennedy, J Kurian *J. Polym. Sci., Polym. Chem. Ed.*, 1990, **28** 3725
15. J P Kennedy *Makromol. Chem., Macromol. Symp.*, 1990, **32** 119
16. K Kojima, M Sawamoto, T Higashimura *Macromolecules*, 1989, **24** 1522
17. M Sawamoto, M Kamigaito, K Kojima, T Higashimura *Polymer Bull.*, 1988, **19** 2923
18. W O Choi, M Sawamoto, T Higashimura *J. Polymer Sci. A*, 1990, **28** 2923
19. T Higashimura, Y-M Law, M Sawamoto *Polymer J.*, 1984, **16** 401
20. T Higashimura, T Enoki, M Sawamoto *Polymer J.*, 1987, **19** 525
21. W Choi, M Sawamoto, T Higashimura *Polymer J.*, 1987, **19** 889
22. M Masahiko, M Sawamoto, T Higashimura *Polymer Bull.*, 1990, **23** 133
23. K Kojima, M Sawamoto, T Higashimura *Macromolecules*, 1991, **24** 2658
24. S Kanaoka, M Sawamoto, T Higashimura *Macromolecules*, 1991, **24** 2309
25. P H Plesch *Eur. Polymer J.*, 1986, **22** 775
26. P H Plesch *Makromol. Chem., Macromol. Symp.*, 1988, **13/14** 389
27. A Gandini, H Cheradame *Adv. Polym. Sci.*, 1980, **34/35** 1
28. B L Erusalimskii, S G Lyubetskii *Protsessy Ionnoi Polimerizatsii* (Ionic Polymerisation Processes), Khimiya, Leningrad, 1974, p. 116
29. P Sigwalt *Polymer J.*, 1985, **17** 57
30. P Sigwalt *IUPAC Symposium on the Mechanism and Kinetics of Polymerization Reactions*, Paris, 1990, p. 31
31. M Sawamoto, T Higashimura *Makromol. Chem., Macromol. Symp.*, 1986, **3** 83
32. T Higashimura, M Aoshima, M Sawamoto *Makromol. Chem., Macromol. Symp.*, 1990, **32** 99
33. S Penczek, P Kubisa, R Szymanski *Makromol. Chem., Macromol. Symp.*, 1986, **3** 203
34. K Brzezinska, R Szymanski, P Kubisa, S Penczek *Makromol. Chem., Rapid Commun.*, 1986, **7** 1
35. M Wojtania, P Kubisa, S Penczek *Makromol. Chem., Macromol. Symp.*, 1986, **6** 21
36. S Penczek, P Kubisa *Makromol. Chem., Macromol. Symp.*, 1988, **13/14** 203
37. M Bednarek, P Kubisa, S Penczek *Makromol. Chem. Suppl.*, 1989, **15** 49
38. S Penczek *Frontiers of Macromolecular Science* (Edited by T Saegusa, T Higashimura), Blackwell, 1989, p. 107
39. L Reibel, H Zouine, K Franta *Makromol. Chem., Macromol. Symp.*, 1988, **13/14** 127
40. T Biedron, R Szymanski, P Kubisa, S Penczek *Makromol. Chem., Macromol. Symp.*, 1990, **32** 155
41. T Aida, S Inoue *Makromol. Chem., Rapid Commun.*, 1980, **1** 677
42. T Aida, S Inoue *Macromolecules*, 1981, **14** 1162, 1169
43. T Aida, R Mizuta, Y Yoshida, T Inoue *Makromol. Chem.*, 1981, **182** 1073
44. T Yasuda, S Inoue, T Aida *Macromolecules*, 1984, **17** 2217
45. K Shimazaki, T Aida, S Inoue *Macromolecules*, 1987, **20** 3076
46. M Kuroki, T Aida, S Inoue *J. Am. Chem. Soc.*, 1987, **109** 4737
47. L Trofimoff, T Aida, S Inoue *Chem. Lett.*, 1987, 991
48. S Inoue *Prog. Polym. Sci.*, 1988, **13** 63
49. M Kuroki, T Aida, S Inoue *Makromol. Chem.*, 1988, **189** 1305
50. W Yashihika, T Aida, S Inoue *Macromolecules*, 1990, **23** 2612
51. S Inoue *Polym. Prep.*, 1990, **31**(1) 70
52. O W Webster, W R Hertler, D Y Sogah *J. Am. Chem. Soc.*, 1983, **105** 5706
53. B L Erusalimskii *Vysokomol. Soedin., Ser. A*, 1985, **27** 1571
54. D Y Sogah, W R Hertler, O W Webster, G M Cohen *Macromolecules*, 1987, **20** 1475
55. W R Hertler, T V Rajan Babu, D W Ovenall *J. Am. Chem. Soc.*, 1988, **110** 5841
56. A H E Müller *Makromol. Chem., Macromol. Symp.*, 1990, **32** 87

57. A H E Müller *Recent Advances in the Mechanism and Synthetic Aspects of Polymerization* (Edited by M Fontanille, A Guyot), Reidel Publishing Co., 1987, p. 23
58. W J Brittain, J B Dicker *Macromolecules*, 1989, **22** 1054
59. J Miller, A D Jenkins, B Tsartolia *Polymer Bull.*, 1988, **20** 247
60. A H E Müller *Comprehensive Polymer Science* (Edited by G Allen, J C Bevington), Oxford, 1988, Vol. 3, p. 387
61. N G Marina, Yu B Monakov, S R Rafikov, V I Ponomarev *Usp. Khim.*, 1983, **52**(5) 733 [English translation in *Russ. Chem. Rev.*, 1983(5)]
62. K S Minsker, M M Karpasas, G K Zaikov *Usp. Khim.*, 1986, **55**(1) 29 [English translation in *Russ. Chem. Rev.*, 1986(1)]
63. B A Krentsel', F S D'yachkovskii *Vysokomol. Soedin., Ser. A*, 1989, **31** 1123
64. Yu B Monakov, G A Tolstikov *Kataliticheskaya Polimerizatsiya Dienov* (Catalytic Polymerisation of Dienes), Nauka, Moscow, 1990, p. 211
65. W Kaminsky, H Sinn *Adv. Organomet. Chem.*, 1980, **18** 99
66. W Kaminsky, M Miri, H Sinn, R Woldt *Makromol. Chem., Rapid Commun.*, 1983, **4** 417
67. W Kaminsky *Angew. Makromol. Chem.*, 1986, **149** 149
68. W Cooper *Comprehensive Chemical Kinetics* (Edited by C H Bamford), Elsevier, Amsterdam, 1976, Vol. 15, p. 133
69. B L Erussalimsky *Acta Polym.*, 1986, **37** 399
70. K Soga, T Shiono, S Takemura, W Kaminsky *Makromol. Chem., Rapid Commun.*, 1987, **8** 310
71. W Kaminsky *IUPAC Symposium on the Mechanism and Kinetics of Polymerization Reactions*, Paris, 1990, p. 17
72. G Fink, W Fenzl, R Mynott *Proceedings of the International Symposium on Olefin Polymerization*, Tokyo, 1986, p. 215
73. G Fink, R Rottler, C G Kreiter *Angew. Makromol. Chem.*, 1981, **96** 1
74. G Fink, D Schnell *Angew. Makromol. Chem.*, 1982, **105** 15
75. G Fink, D Schnell *Angew. Makromol. Chem.*, 1982, **105** 31
76. G Fink, D Schnell *Angew. Makromol. Chem.*, 1982, **105** 39

Translated from *Uspekhi Khimii* **61** 161–194 (1992) U.D.C. 678.02:66.095.3

Heterocyclic bifunctional monomers in the synthesis of polymers

R D Katsarava, D P Kharadze
Institute of Molecular Biology and Biological Physics, Georgia Academy of Sciences, Tbilisi

ABSTRACT. One of the variations of activated polycondensation, the "active ring" method is reviewed. The method consists essentially of the reaction of *bis*- and polyfunctional nucleophiles with monomers containing various heterocycles (three-, four-, five- and six-membered rings) as the electrophilic functional groups. Polyaddition reactions in which the heterocycle is opened are examined. It is demonstrated that many of the discussed reactions are promising for the synthesis of functionalised polymers that are often unattainable using traditional polycondensation methods.

The bibliography includes 139 references.

Contents

I. Introduction 87
II. Three-membered heterocycles 87
III. Four-membered heterocycles 90
IV. Five-membered heterocycles 90
V. Six-membered heterocycles 100

I. Introduction

Heterochain polymers traditionally are synthesised using high-temperature or low-temperature polycondensations. The latter is based on the use of activated monomers such as dichloroanhydrides, *bis*-chloroformates and *bis*-carbamoylchlorides, diisocyanates, etc.[1–5]

Recently new polycondensation methods based on novel methods of activating monomers and arbitrarily called "activated polycondensation" have become widespread. Five principal directions have been defined.[6] Two of the methods of activated polycondensation, "direct polycondensation"[7,8] and the "leaving group" method,[6] have been analysed in the cited references.

The present review treats a third type of activated polycondensation, the "active ring" method.

The method consists essentially of the polycondensation of heterocyclic compounds of increased reactivity due to intramolecular electronic effects or strain in the ring with nucleophiles. During the reaction the ring opens†, often under mild conditions. The resulting polymers are difficult to produce using other polycondensation methods. This is especially true of functionalised polymers. The review does not include reactions involving dianhydrides of tetracarboxylic acids, upon which the synthesis of thermally resistant polyimides is based. These have been thoroughly discussed in numerous monographs and reviews (for example, see Refs. 9–11). Reactions occurring without opening of the heterocycle, for example, copolymerisation (also a polyaddition process) or polycondensation involving the heterocycle, also are not included. These have been reviewed before.[12]

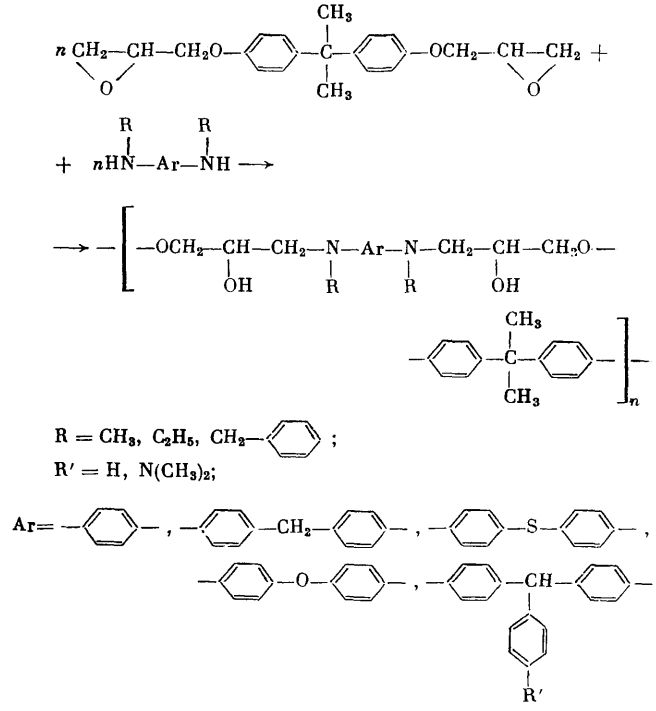
In the present review, we attempted to correlate examples of the use of various bifunctional heterocyclic monomers in polyaddition reactions with ring opening[12] and to describe some of the properties of the polymers formed.

Three-, four-, five- and six-membered heterocycles containing O, N, or O (more rarely S) and N together are discussed separately.

II. Three-membered heterocycles

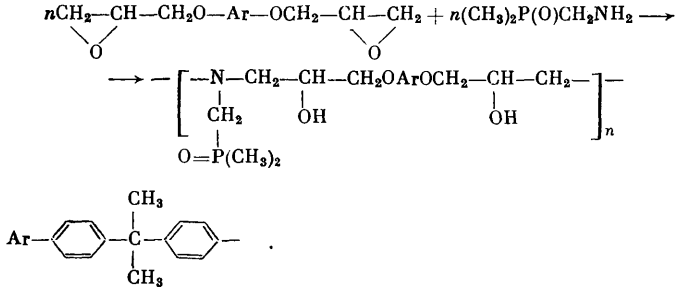
1. *bis*-Epoxides. The role of epoxides in the chemistry of high-molecular-weight polymers is well known. The present review is not concerned with the widespread processes that use epoxide resins. Only certain comparatively new polymer-synthesis reactions involving monomers containing oxirane rings are discussed.

It is known that diepoxides react with diamines by forming crosslinked polymers.[13,14] Hoerhold, et al.[15,16] successfully synthesised linear polymers ($M_n = 8-18 \times 10^3$) of polyamines with hydroxyl side groups by reacting *bis*-glycidyl ethers of *bis*-phenol-A with *N,N'*-alkyl-substituted aromatic diamines:

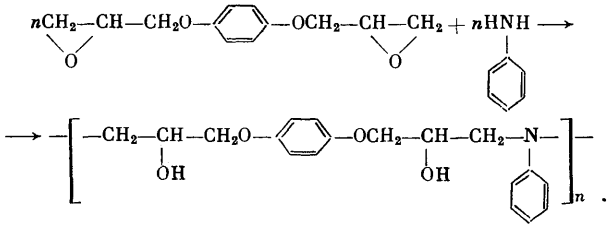


†Such polymerisation processes can be categorised as "multiple addition reactions with ring opening".

Using a phosphorus-containing primary monoamine as the monomer, linear polyaminohydroxy-ethers (M_n = 12.2 × 10^3) with increased fire-resistant properties are produced:[17]



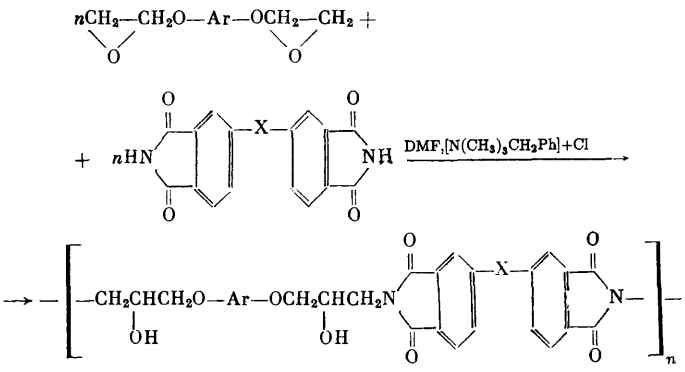
Iwakura, et al.[18] effected an essentially similar reaction by using aniline as the nucleophilic monomer:

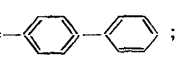


This resulted in linear polyhydroxyaminoethers capable of forming fibres.

An interesting feature of the above reactions is that the primary amines exhibit a practical functionality (Φ_{pr}) of two.[19]

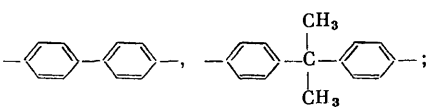
The reaction of bisimides with diepoxides[20] produces linear polyhydroxyalkylimides that are soluble in polar aprotic solvents (η_{inh} = 0.10–0.19 dl g^{-1}):

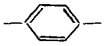
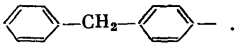


Ar =  ;

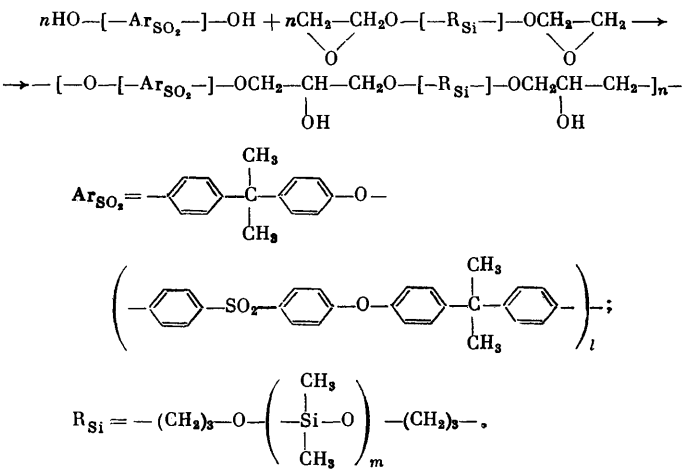
X = CO, COOROCO, CONHR'NHCO;

R = —$(CH_2)_2$—, —$(CH_2)_6$—, —$(CH_2)_{10}$—, , ,

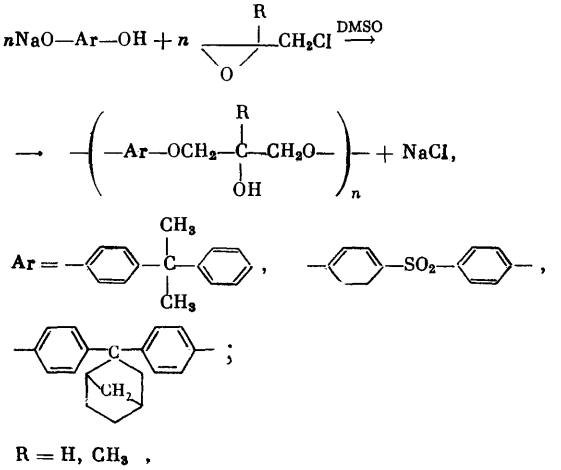
 ;

R' = —$(CH_2)_6$—, —$(CH_2)_{12}$—,  ,  .

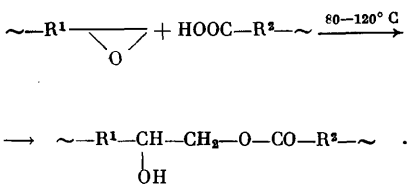
Having investigated in detail the model reaction between phenol and the epoxide ring in a melt,[21] Marechal, et al.[22] successfully used it to synthesise simple polyethers containing hydroxyls, in particular, block polyethers, through the reaction of α,ω-diphenyloligosulphones with α,ω-diepoxyoligosiloxanes:



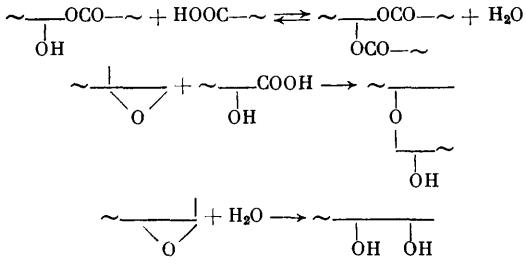
Rokicki and Kuran[23] prepared simple polyethers containing hydroxyls in one step without preliminary synthesis of the *bis*-glycidyl ethers:



Based on a detailed study of the reaction of epoxides with carboxylic acids, linear polyesters could be synthesised according to the scheme:[24–26]



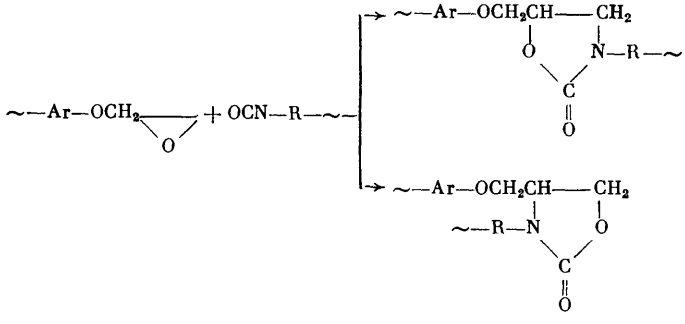
It was found that side reactions including those involving side hydroxyl groups that lead to crosslinked polymers occur only at higher temperatures.



Use of Cr^{III} diisopropylsalicylate instead of tertiary amines as catalyst helps to suppress these undesired reactions.

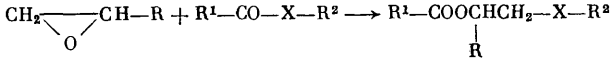
The prepared polyesters with side hydroxyl groups are capable of further polymeric conversions and can have practical application, for example, as biodegradable carriers of bioactive substances etc.

Frisch, et al.[27,28] established that the reaction of *bis*-glycidyl ethers with diisocyanates can be used to synthesise polyoxazolidones. Two isomeric rings are formed, the ratio of which depends on the reaction temperature:



The synthesis of polyoxazolidones through reaction of epoxides with isocyanates are examined in greater detail in a review.[29]

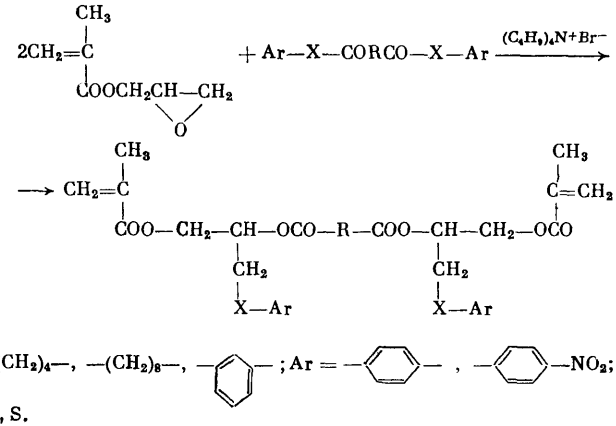
Korshak, et al.[29–32] discovered an interesting insertion reaction of oxirane rings into the bond to the heteroatom (esters and amides):



X = O, NH.

These reactions were used to modify the properties of polyesters and polyamides by reacting them with epoxide resins.

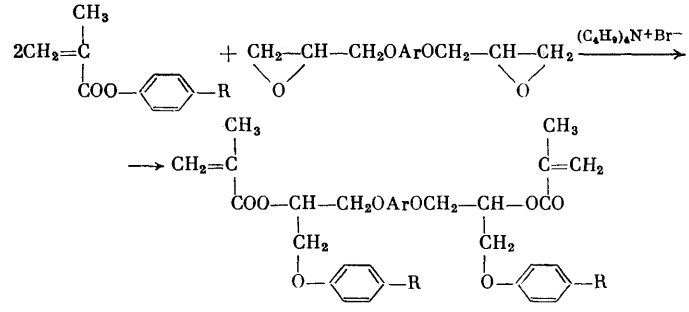
Nishikubo, et al.[33,34] also found that glycidyl ethers react with activated diesters of dicarboxylic acids according to the insertion scheme mentioned above. The reaction occurs under conditions enabling the readily polymerising double bonds to be preserved:

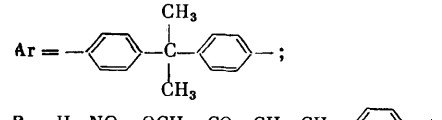


R = $-(CH_2)_4-$, $-(CH_2)_8-$, ; Ar =

X = O, S.

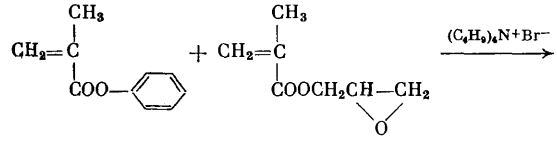
Bifunctional unsaturated monomers were also obtained by an alternative scheme:

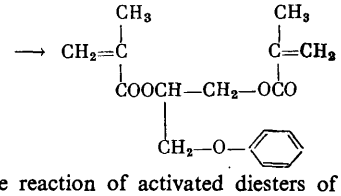




R = H, NO_2, OCH_3, CO—CH=CH— etc.

or

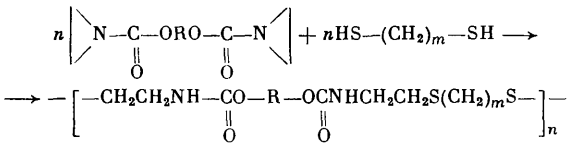




The reaction of activated diesters of dicarboxylic acids with the oxirane ring that occurs at elevated temperatures was also used to harden epoxide resins.[34]

The insertion reactions described above can apparently be used to synthesise linear polymers, converting them into bifunctional compounds. Such processes would be promising for preparation of functionalised polymers.

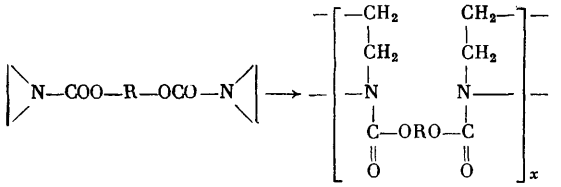
2. Aziridine derivatives. Iwakura, et al.[18,35] already at the start of the 1960s proposed an original synthesis of high-molecular-weight ([η] ≤ 1.4 dl g^{-1}) polyurethane sulphides. The method consists essentially of alkylation of dimercaptans with polymethylene-*bis*-(*N,N*-ethyleneurethanes) in DMF at 75–120 °C in the presence of triethylamine:



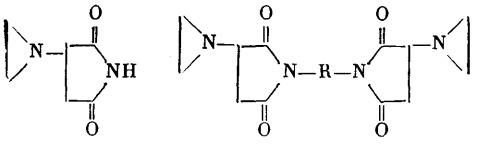
where R = $-(CH_2)_{4-6}$, *trans*-1,4-cyclohexyl, and *trans*-hexahydro-1,4-xylenyl.

It was found that the polyurethanesulphides prepared by this polyaddition scheme are slightly more heat resistant than analogous polymers synthesised by interphase polycondensation of the corresponding *bis*-chloroformates with polymethylene-*bis*-(β-aminoethylthioethers). The other characteristics of the polymers are completely identical.[35]

At elevated temperatures (in the absence of the dimercaptan), *bis*-(*N,N*-ethyleneurethanes) polymerise with ring opening to form polymers that are insoluble in organic solvents:



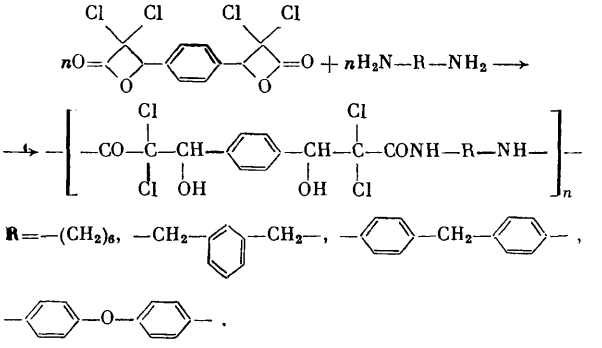
The molecules 3-(1-aziridinyl)succinimide and *N,N'*-alkylene-*bis*-(1-aziridinyl)succinimides were also suggested as monomers.[36]



These compounds polymerise at 125 °C in the melt with opening of the imide and imine rings to form crosslinked polymers. Under the appropriate conditions they can be used in linear polycondensation.

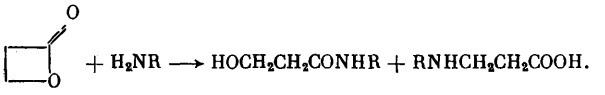
III. Four-membered heterocycles

***bis*-β-Lactones.** It is known that β-lactones are highly reactive toward nucleophiles due to strain in the four-membered ring.[37] This feature was successfully used by Ueda, et al.[38] to synthesise high-molecular-weight polyamides containing hydroxyls ($\eta_{inh} \leqslant$ 1.12 dl g^{-1}) through reaction of 3,3'-*p*-phenylene-*bis*-(2,2-dichloro-β-propiolactone) with diamines:



It is noteworthy that the high-molecular-weight polyamides are formed even with aromatic diamines under mild conditions (20 °C in nonpolar dioxane, although the reaction does indeed take 12 days).

It was found that aminolysis of this *bis*-β-lactone occurs exclusively with cleavage of the O-acyl bond whereas the O-alkyl bond also breaks in the unsubstituted propiolactone to form the *N*-substituted β-aminoacid:

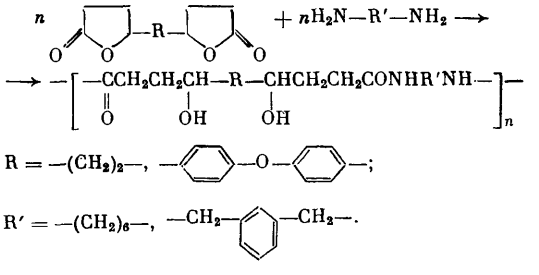


Apparently the two Cl atoms affect the *bis*-lactone and additionally activate the carboyl group.

IV. Five-membered heterocycles

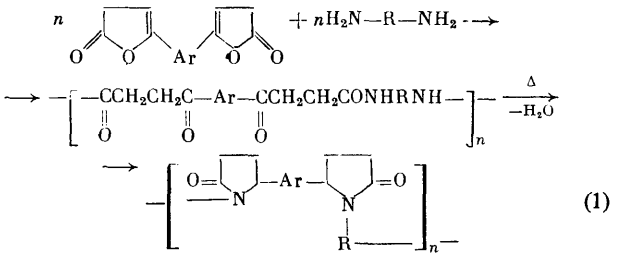
1. *bis*-γ-Lactones

Unsaturated γ-lactones are much less reactive than β-lactones. However, they are more reactive than the corresponding linear analogues, alkyl esters of carboxylic acids, which are exceptionally unreactive toward aminolysis.[39–43] Reaction of a *bis*-γ-lactone with aliphatic diamines (65–80 °C, 20 days, in alcohols and diethyleneglycol) produces hydrophilic polyamides containing hydroxyl groups with $\eta_{inh} \leqslant 0.53$ dl g^{-1}.[44,45]

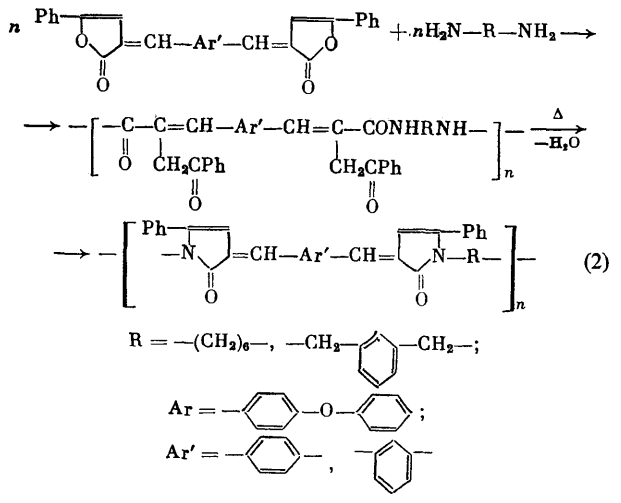


Unsaturated *bis*-γ-lactones are more reactive toward aminolysis. They react with aliphatic diamines to produce polyamides with $\eta_{inh} \leqslant 0.8$ dl g^{-1}.[45,47] In this instance the effect of ring strain is apparently not "innocent" since the unsaturated lactones are cyclic

analogues of vinyl esters, which are more reactive toward aminolysis than their saturated analogues.[39] This is due to the greater electronegativity of a vinyl group compared with an alkyl group. An additional driving force for starting with an unsaturated alcohol is the ease of isomerisation into a stable ketone. Here we note that whereas the reaction of diamines with unsaturated *bis*-lactones forms polyamides containing hydroxyl groups, reaction with unsaturated *bis*-lactones produces polyketoamides containing keto groups in the main [Reaction (1)][47] or side [Reaction (2)] chain:[46]

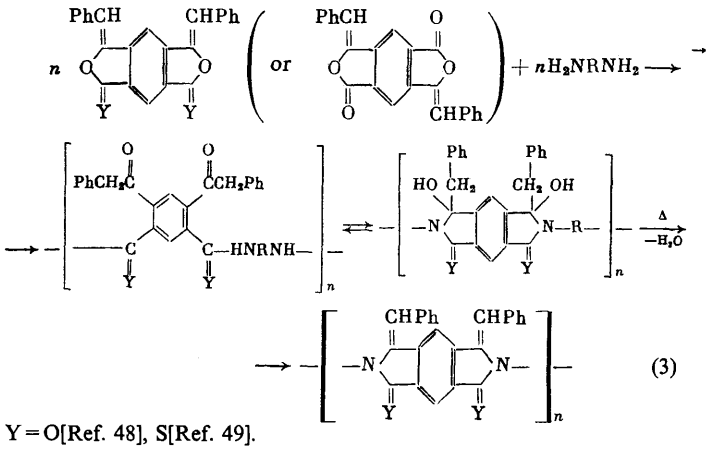


(1)



(2)

The *bis*-benzylidene derivatives of pyromellitic[48] and pyromellitdithioic[49] anhydrides (pyromellitides) react analogously with diamines:



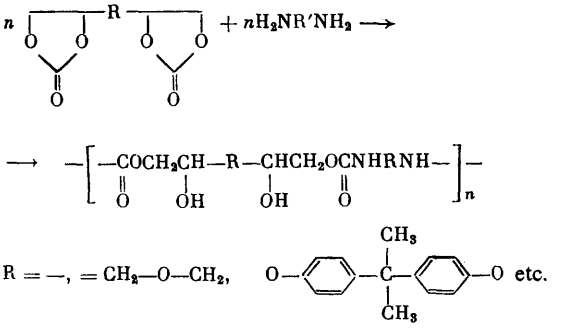
(3)

Y = O[Ref. 48], S[Ref. 49].

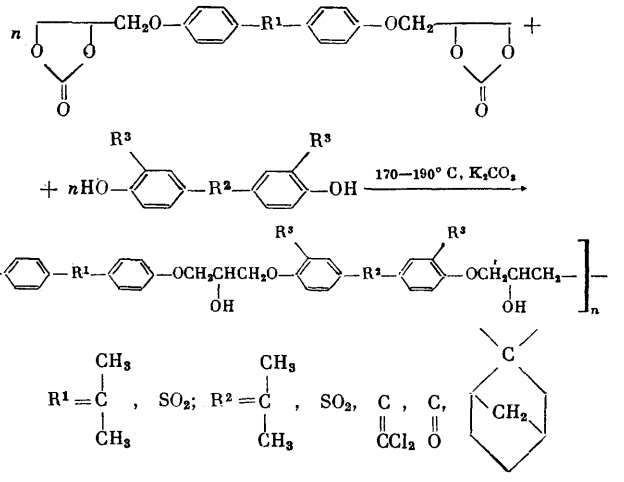
Other 3,5- and 3,7-disubstituted pyromellitides (for example, see Ref. 49 and references cited above) have also been synthesised. It has been demonstrated that benzylidene-substituted pyromellitides are more reactive toward diamines than phenyl-substituted ones and that those containing S are more reactive than the analogues containing O. Polyimidines with good heat resistance and solubility in organic solvents are obtained by cyclodehydration of the intermediate polyketoamides [or the cyclic hydroxy forms, see Reaction (3)]. It is noteworthy that the polyketoamides mentioned above [see Reactions (1) and (2)] also undergo cyclodehydration to the corresponding polymeric heterocyclic compounds.

2. Cyclic *bis*-carbonates

Cyclic *bis*-carbonates also readily react by ring opening and polycondensation with aliphatic diamines. Thus, hydrophilic polyurethanes ($[\eta] \leqslant 1.0$ dl g^{-1}) containing hydroxyl groups are formed:[50–53]



It was found[54] that cyclic *bis*-carbonates in the melt or in a polar aprotic solvent (DMSO, sulpholane) at 170–190 °C in the presence of K_2CO_3 alkylate *bis*-phenols, forming simple polyethers‡ containing hydroxyl groups ($[\eta]$ = 0.3–0.7 dl g^{-1}):



R^3 = H, CH_3.

The synthesis of polymers through reaction of anhydrides of unsaturated dicarboxylic acids (maleic, itaconic, cyclohexen-1,2-dicarboxylic, etc.) with cyclic carbonates (ethylene- and

‡ Polymers of this class are also obtained through reaction of *bis*-phenols with diepoxides or epichlorohydrin (cf. Part II).

propylenecarbonate) has been reported. Depending on the reaction conditions, either crosslinked or linear polymers with $\eta_{inh} \leqslant 0.21$ dl g^{-1} are formed.[55] This reaction apparently can be extended to cyclic *bis*-carbonates.

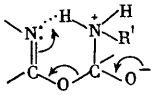
Syntheses involving cyclic *bis*-carbonates are rather attractive since, on one hand, monomers are obtained through reaction of diepoxides (of independent interest as starting monomers, cf. Part II) with CO_2 and, on the other, polymers, in particular, polyurethanes, are obtained by a scheme avoiding use of highly toxic phosgene.

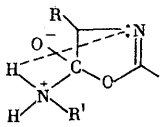
3. *bis*-Azlactones

a) Saturated *bis*-azlactones

Some of the first representatives of cyclic bifunctional monomers of this class were saturated azlactones, 2,2′-*p*-phenylene (or polymethylene)-*bis*-(oxazoline-5-one). These were first synthesised by cyclisation of *N,N′*-diacyl-*bis*-α-aminoacids§ and used to synthesise polymers by Cleaver and Pratt in 1955.[56,57]

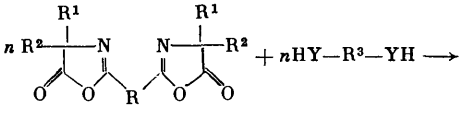
It is noteworthy that azlactones contain the isoimide structural moiety $-N=C-O-CO-$, which is distinguished by a great propensity to react with nucleophiles.[58–60] Adducts of carbodiimides and carboxylic acids containing analogous structural elements also are exceptionally reactive toward nucleophiles.[61,62] This feature along with the ring strain apparently is responsible for the high acylating potential of azlactones. However, it must be mentioned that aminolysis in linear isoimides can be accelerated owing to the freedom of intramolecular rotation taking into account anchimeric assistance from the isoimide N atom in the transition complex. This should be hindered in the cyclic analogues (azlactones) although the existence of a similar effect in the latter instance also cannot be completely ruled out:



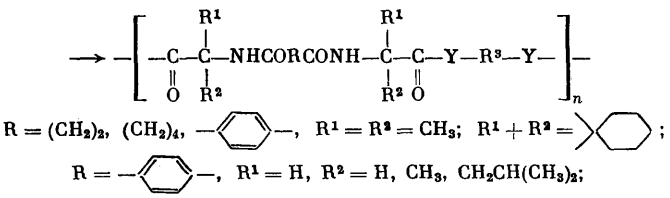


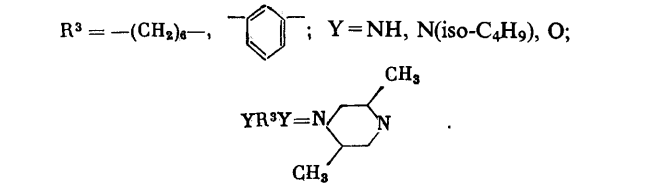
A study of the kinetics of anilinolysis of 4,4′-R-substituted 2,2′-*p*-phenylene-*bis*-(oxazoline-5-ones) demonstrated[63] that they are comparable in reactivity to *p*-nitrophenyl esters of aliphatic carboxylic acids.[64,65] Thus, it was also demonstrated that 2,2′-*p*-phenylene-*bis*-(oxazoline-5-ones) are monomers with an independent reactivity of functional groups and that the radical R in the 4-position of the azlactone ring has comparatively little effect on their reactivity.

Cleaver and Pratt[57] used various 2,2′-*p*-phenylene-*bis*-(oxazoline-5-ones) to synthesise regularly alternating polymers, mainly polyamides, containing α-aminoacid moieties in the principal macromolecular chains:



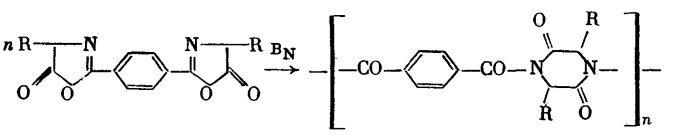
§Obtained through reaction of the dichloroanhydrides of dicarboxylic acids with α-aminoacids.[56]





High-molecular-weight polyamides were prepared based on aliphatic diamines. An aromatic diamine and aliphatic diol were used to synthesise low-molecular-weight polymers.

It was found[57] that 2,2′-*p*-phenylene-*bis*-oxazolinones in the presence of a tertiary amine (B_N) undergo homopolymerisation to form poly(*N,N′*-terephthaloyl-diketopiperazine):



These compounds are polymeric acyllactams (activated amides) and are very reactive toward nucleophiles.[6] In analogy with polyanhydrides,[66] they can be used as quickly decomposing materials for medical and biological applications.

Other investigators[67–70] subsequently also prepared various 2,2′-*p*-phenylene-*bis*-(oxazoline-5-ones) and used them to synthesise ordinary polyamides. A slightly different path to *N,N′*-diacyl-*bis*-α-aminoacids, reaction of dinitriles with an α-hydroxyacid (benzylic) according to Ritter, has been proposed.[68]

The variety of α-aminoacids used to synthesise 2,2′-*p*-phenylene-*bis*-(oxazoline-5-ones) has been significantly expanded.[71] As a result, polyamides and copolyamides that contain enzyme-specific side groups in the macromolecules and are susceptible to biodegradation have been prepared.[72] These polyamides exhibit good biocompatibility and are promising as surgical materials.[73,74] The rapid rate of reaction of 2,2′-*p*-phenylene-*bis*-(oxazoline-5-ones) with aliphatic diamines[71] determined the ability to prepare block-copolymers based on telechelic oligopeptides containing terminal amino groups. Such block-copolymers undergo biodestruction at an incresed rate[72,75] and are promising as drug delivery systems.

Table 1. Saturated five-membered *bis*-azlactones used to synthesise polymers.

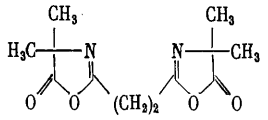
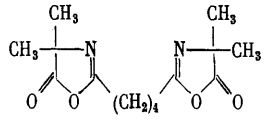
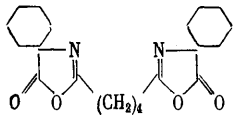
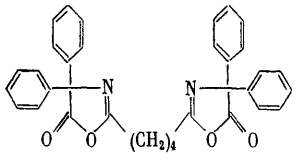
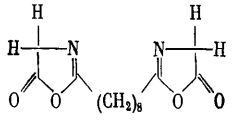
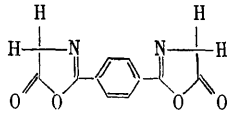
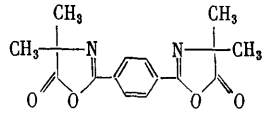
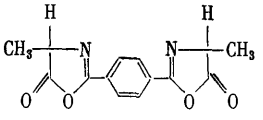
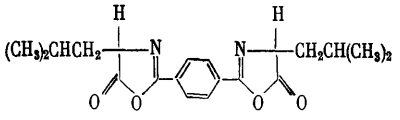
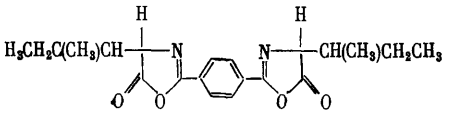
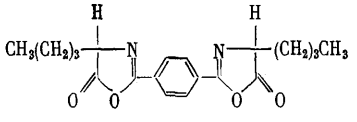
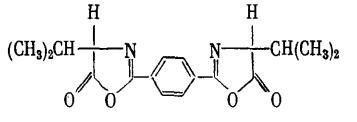
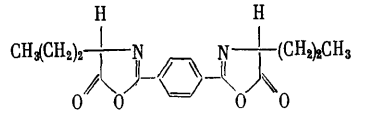
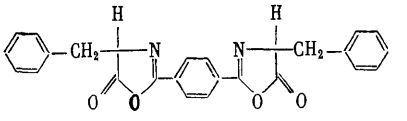
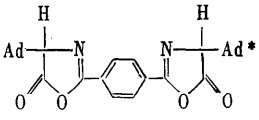
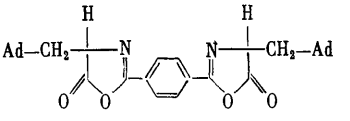
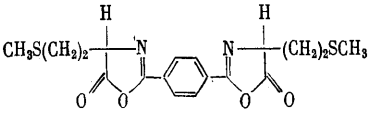
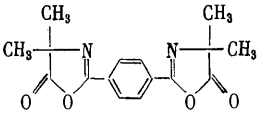
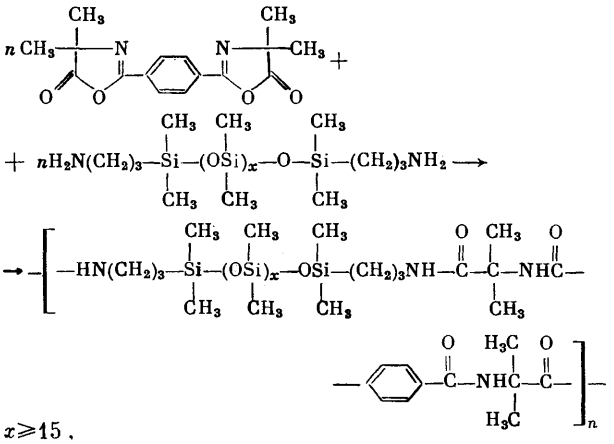
bis-Azlactone	Reference
	[56]
	[56, 57]
	[56, 57]
	[68—70]
	[67]
	[56, 57, 71, 78, 79]
	[56, 57, 78, 79]
	[46, 47, 71, 75]
	[56, 57, 67, 71, 75]
	[71, 75]
	[71, 75]
	[71, 75]

Table 1. (contd.)

bis-Azlactone	Reference
	[71, 75]
	[71, 75]
	[75]
	[75]
	[71, 75]
	[78, 79]

*Ad = adamantyl

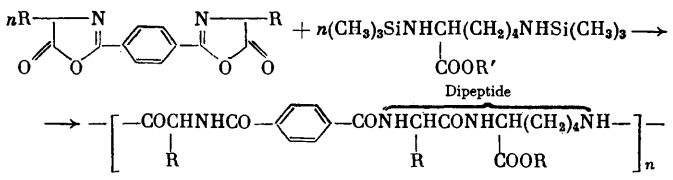
An alternating block-copolymer was also prepared on the basis of telechelic oligosiloxanes:[76]



$x \geqslant 15$.

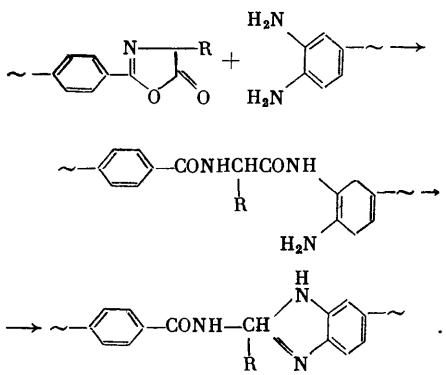
It has been demonstrated that *bis*-(oxazoline-5-ones) react with *N,N'*-trimethylsilylated diamines to form high-molecular-weight polyamides ($[\eta] \leqslant 0.68$ dl g^{-1}).[75]

This reaction was successfully used to prepare polyamides with dipeptide fragments using alkyl esters of N^{α},N^{β}-*bis*-trimethylsilyl-L-lysine as the diamine:[75,77]



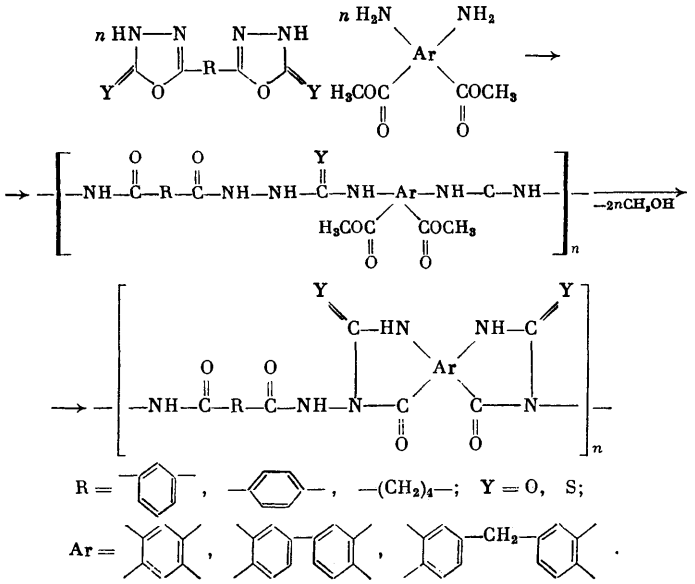
R′ = CH_3, C_2H_5.

Polyamidobenzimidazoles have been prepared through reaction of 2,2′-*p*-phenylene-*bis*-(oxazoline-5-ones) with tetraamines:[78,79]



The saturated five-membered *bis*-azlactones used to synthesise polymers are presented in Table 1.

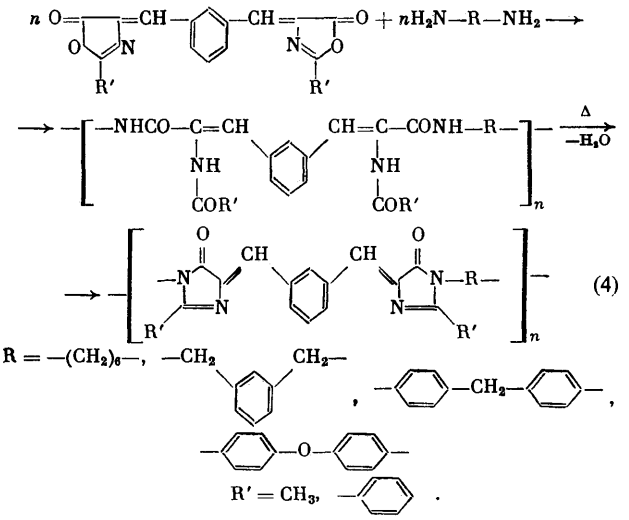
Iwakura, et al.[80,81] used five-membered azlactones with two N atoms in the ring, 2,2′-arylene (or alkylene)-*bis*-(1,3,4-oxadiazoline-5-ones) and 2,2′-arylene (or alkylene)-*bis*-(1,3,4-oxadiazoline-5-ones), as bifunctional cyclic monomers in polycondensation with *bis*-*o*-aminoesters:



The reaction was carried out in *m*-cresol at 180 °C (Y = O;[80] [η] of the obtained polyamidequinazolinediones is 0.09–0.27 dl g^{-1}) or at 150–160 °C (Y = S;[81] [η] of the obtained polyamidequinazoline-4-one-2-thiones is 0.07–0.31 dl g^{-1}). The comparatively mild reaction conditions in the latter instance may be related to the greater reactivity of the analogue containing S.

b) Unsaturated azlactones

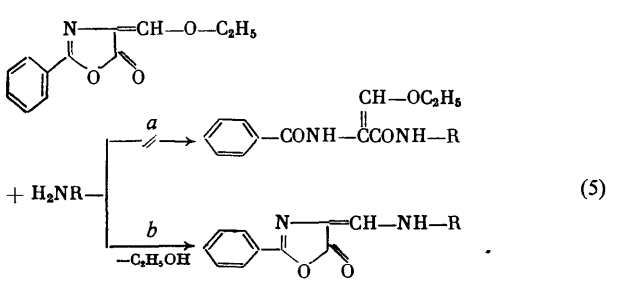
Ueda, et al., who have greatly contributed to the development of the active-ring method, synthesised unsaturated *bis*-azlactones[82] and investigated their polycondensation with diamines:



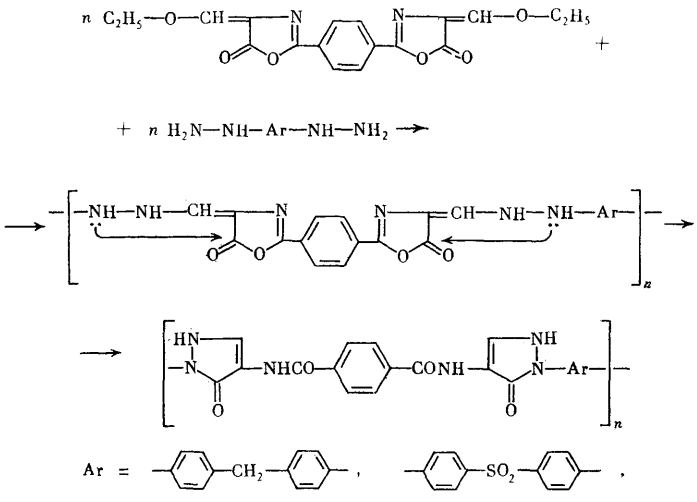
It was found that unsaturated *bis*-azlactones are sufficiently reactive to synthesise polymers (η_{inh} = 0.17–0.51 dl g^{-1}). However, as should have been expected,[83] they are inferior to the saturated analogues. In all probability the reason for the poorer reactivity of the unsaturated azlactones should be sought both in the conjugation of the heterocyclic carboxylic group with the C–C double bond, which decreases its electrophilicity, and in the ring conjugation of the electrons that stabilises the azlactone ring in general.

It was suggested that the unsaturated polyamide that was formed with pendant amide groups undergoes cyclodehydration with formation of the corresponding polyimidazolone [Reaction (4)] near 200 °C for R = $(CH_2)_6$ and R′ = CH_3.

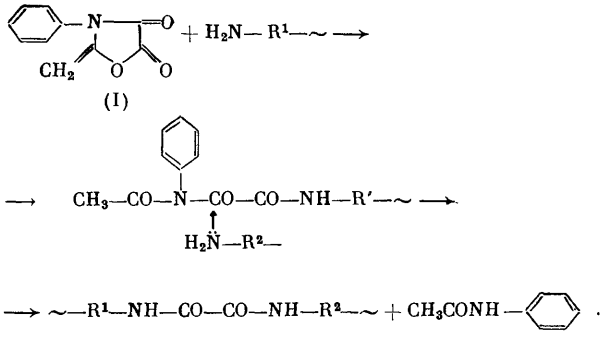
It is interesting that the ring is stabilised so much if the 2,2′-*p*-phenylene-*bis*-azlactone contains an ethoxymethylene group as the substituent in the 4,4′-positions that it is not opened by amines. Instead of acylation [Reaction (5*a*)], nucleophilic substitution occurs [Reaction (5*b*)]:



This fact was established by Imai, et al.,[84–87] who prepared high-molecular-weight polyenamines containing azlactone rings in the principal chains of the macromolecules instead of the expected polyamides through reaction of the corresponding *bis*-azlactone with diamines. The polycondensation of a *bis*-azlactone with aromatic dihydrazines occurs analogously in the first step. However, in this instance the reaction proceeds further with involvement of a second N atom of the hydrazine and is accompanied by opening of the azlactone ring and intramolecular rearrangement.[86] As a result, high-molecular-weight (η_{inh} = 0.5–1.23 dl g^{-1}) polyamide-pyrazolines are formed:



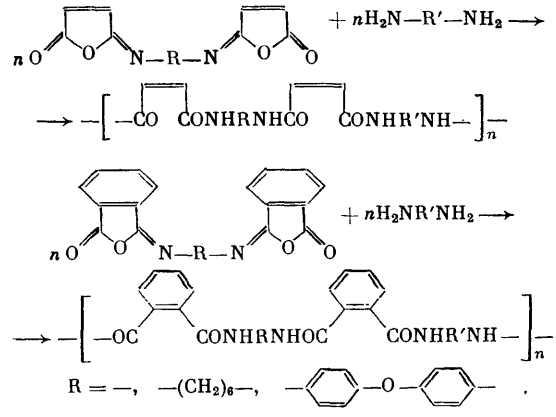
An original method of synthesising polyoxamides is based on use of an unsaturated monoazlactone, 2-methylene-3-phenyloxazolidine-4,5-dione (I), exhibiting Φ_{pr} = 2. The ring opens in the first step of the reaction of this compound with diamines. In the second, aminolysis occurs with loss of acetanilide and the polyoxamide forms ($\eta_{inh} \leqslant$ 0.35 dl g^{-1}):[88]



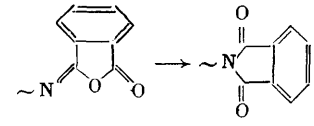
This process is a unique combination of two methods of activated polycondensation. These are the active-ring method and the leaving-group (active-amide) method.[6]

4. Cyclic *bis*-isoimides and *bis*-imides

The synthesis of various *bis*-isoimides has been reported.[89–91] These are structural isomers of the *bis*-azlactones examined above. As was expected, the isoimides react readily with aliphatic diamines in aprotic polar solvents at room temperature to give the corresponding polyamides:

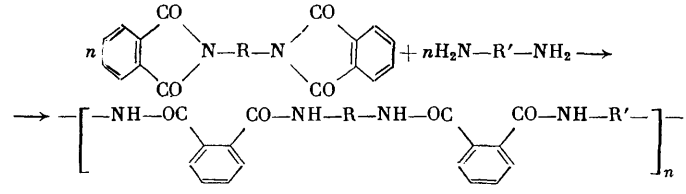


The *bis*-maleic isoimides were more reactive. Reaction of these with *m*-xylylenediamine in *N*-methylpyrrolidone is complete after 1 h.[89] They react with aromatic 4,4′-diaminodiphenyloxide much more slowly. The reaction is complete only after three days. Polyamides based on *bis*-maleic isoimides had higher viscosities ($\eta_{inh} \leqslant$ 0.7 dl g^{-1}) than those based on *bis*-isophthalimides ($\eta_{inh} \leqslant$ 0.26 dl g^{-1}). This and the slow rate of the principal reaction are related to the ease of isomerisation of the latter to the corresponding phthalimides. This inhibits chain propagation:[90]



For this reason the use of high temperature to accelerate the reaction of *bis*-isophthalimides with diamines is undesirable.

However, it was demonstrated that under certain conditions (in dry organic solvents, e.g. toluene at 20–95 °C) the ring opens during reaction of polymethylene-*bis*-phthalimides with aliphatic diamines. This leads to polyphthalimides ([η] $\leqslant$ 0.32 dl g^{-1}):[92,93]



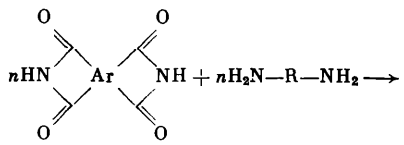
(6)

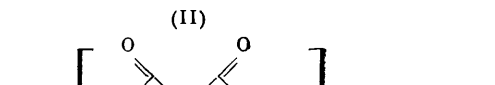
where R = $-(CH_2)_2-$, $-(CH_2)_4-$, $-(CH_2)_6-$, and $-(CH_2)_{10}-$.

It is noteworthy that Reaction (6) does not occur in the presence of water. Furthermore, other *bis*-imides (see above) react better with diamines in aqueous medium.

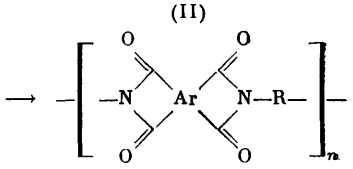
For example, Zhubanov, et al.,[94,95] synthesised the polyamido-amides (II) through reaction of imides of aromatic tetracarboxylic acids with aliphatic diamines in aqueous suspension at room

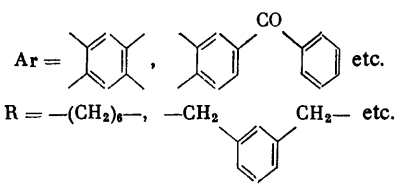
temperature. Alkylaromatic polyimides were prepared by cyclisation of these at 200–250 °C:



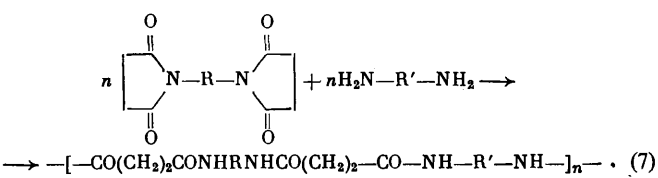


(II)





In contrast with aromatic phthalimides (the imide ring is stabilised by conjugation with the benzene ring), the ring of aliphatic imides, in particular, *N,N'*-alkylene-*bis*-succinimides, tends to open during reaction with aliphatic diamines. This forms the corresponding polysuccinamides:

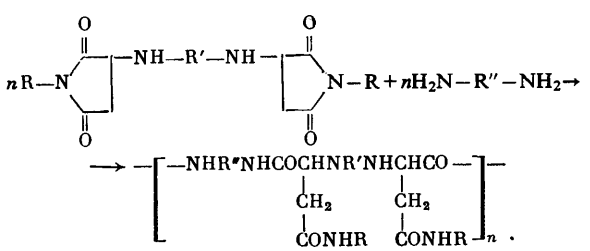


(7)

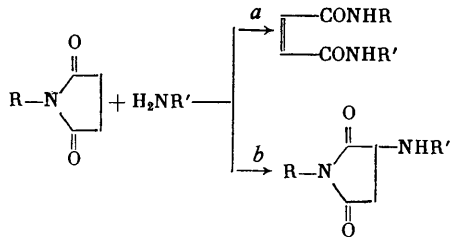
Kagiya, et al.[96] carried out this reaction in the melt at 200 °C and produced polyamides with $[\eta] = 0.2-0.5$ dl g^{-1}.

It has been found[97] that this reaction occurs better (under mild conditions of 0–20 °C) in aqueous ethanol to produce polysuccinamides with a relative molecular mass up to 20×10^3. It is interesting that Reaction (7), in contrast with Reaction (6), practically does not occur in dry and in polar aprotic solvents.

Diimides of *bis*-aspartic acid have also been used as starting monomers in reactions analogous to Reaction (7):[98]

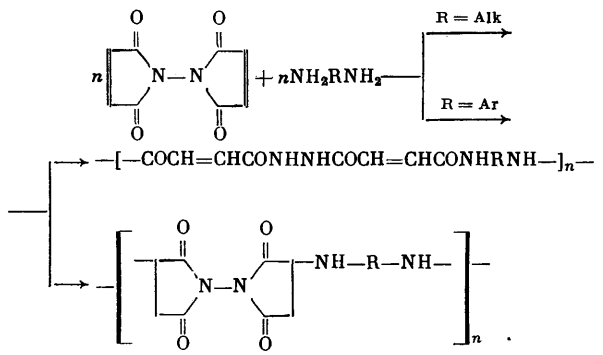


Cycloimides based on unsaturated acids, e.g. maleic and citraconic,[99] are also capable of being opened by amines. This reaction also occurs in aqueous medium [Reaction (8*a*)]. The amine adds to the double bond in anhydrous organic solvents [Reaction (8*b*)]:[100]



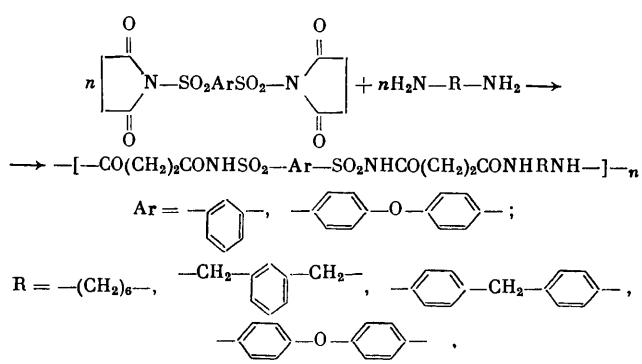
(8)

The direction of the reaction depends on the nature of the amine.[100] For example, *N,N'-bis*-maleimide in *m*-cresol at 65 °C with aliphatic diamines forms polyamides ($\eta_{inh} \leqslant 0.98$ dl g^{-1}) whereas addition to the double bond occurs for aromatic diamines to form polysuccinimides ($\eta_{inh} \leqslant 0.56$ dl g^{-1}):

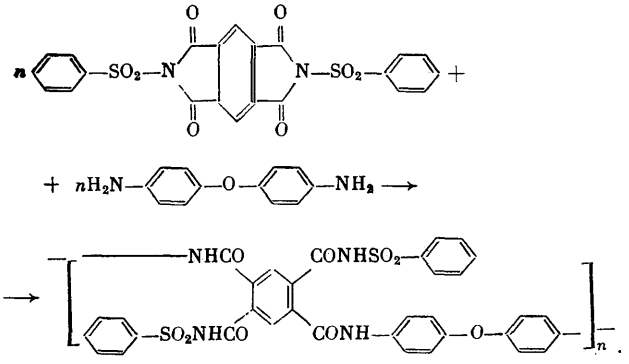


It is noteworthy that polyamides based on 1,2-dicarboxylic acids are promising as self-destructive polymers since the neighbouring amide groups facilitate hydrolytic decomposition of each other.[101]

Activated imides containing electron acceptor groups on the N atom were more reactive toward amines. For example, it was found that *N,N'*-arylenedisulphonyl-*bis*-succinimides react with diamines in *N*-methylpyrrolidone at 10–20 °C to form polyamides with $\eta_{inh} \leqslant 0.4$ dl g^{-1}.[102]

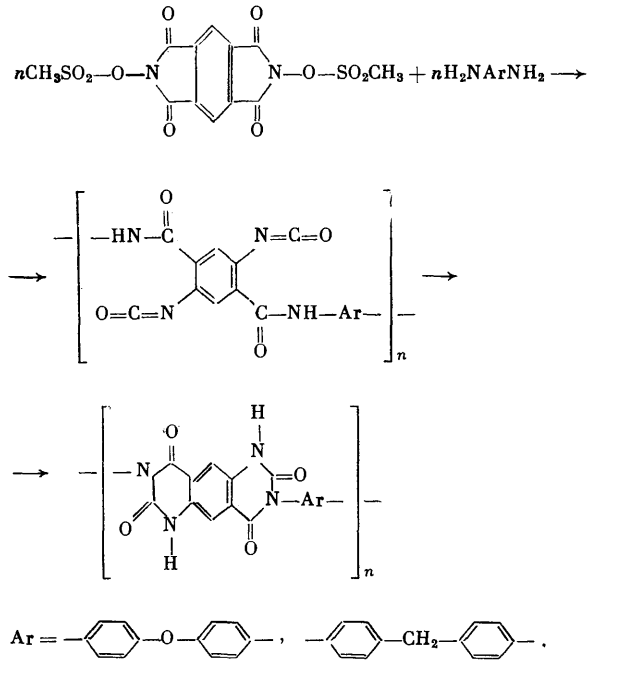


The reaction of *N,N'-bis*-(phenylsulphonyl)pyromellitimide with an aromatic diamine (η_{inh} of the polyamide formed = 0.74 dl g^{-1}) occurs analogously at room temperature:[103]

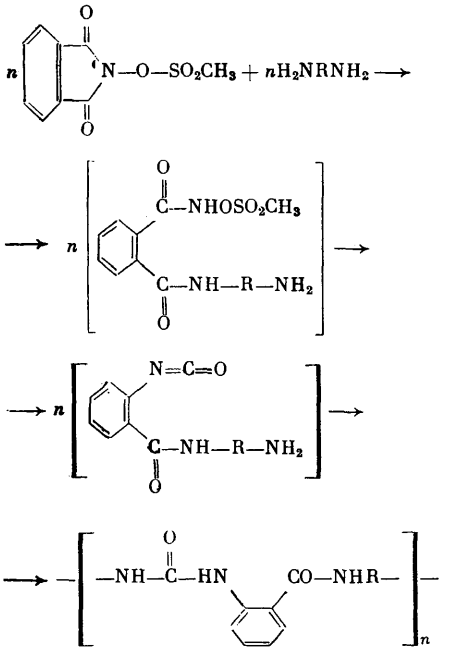


It is noteworthy that the reaction of *N*-arylsulphonylimides and diamines occurs with ring opening and without cleavage of the $=N-SO_2-$ bond whereas the exocyclic $=N-CO-$ bond primarily cleaves during aminolysis of *N*-acylimides with loss of the corresponding imide.[6]

The mesyloxy group also substantially activates the imide ring. In this instance the mesylhydroxamic acid formed undergoes the Lossen rearrangement. Polyquinazolinediones ($\eta_{inh} \leqslant 0.25$ dl g^{-1}) are formed as a result:[104]

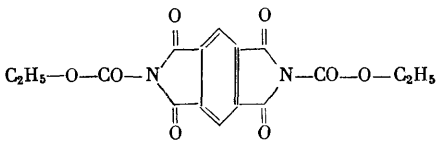


Thanks to the rearrangement mentioned above the *N*-mesylphthalimide exhibits $\Phi_{pr} = 2$ with diamines (at a 1 : 1 mole ratio). This leads to formation of polybenzamidoureas:[105]



The synthesised polymers have low viscosities (η_{inh} = 0.12–0.34 dl g^{-1}). Apparently this is due to chain breaking as a result of cyclisation of the intermediate isocyanate to the corresponding quinazolinedione.

An ethoxycarbonyl group also activates the phthalimide ring towards reaction with amines.[106] For example, *N,N'-bis*-(ethoxycarbonyl)pyromellitimide



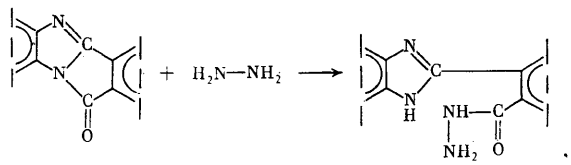
is significantly more reactive than the unsubstituted pyromellitimide; however, it is less so than the *N,N'-bis*-phenylsulphonyl derivative examined above. The latter in turn is less active than pyromellitic dianhydride. The *N*-substituted pyromellitimides, like pyromellitic dithioanhydride, were polymerised[107] during a search for better methods of synthesising pyromellitimides. An important advantage of these compounds is the ease of cyclisation of the prepolymers prepared from them compared with the polyamido acid synthesised through pyromellitic dianhydride.

The polymerisation involving cycloimides (both with opening and without opening of the imide ring) are discussed in more detail in a review.[12]

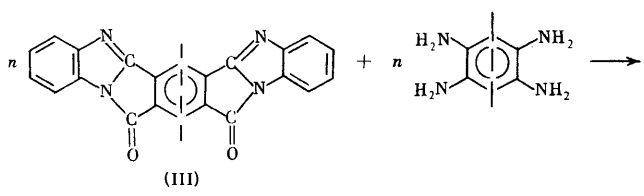
5. Cyclic *bis*-amides

Korshak, et al.[108] found in 1969 that benzoylenebenzimidazoles (benzimidazopyrrolones) are intramolecularly activated amides (their acyclic analogues have since been widely used to synthesise

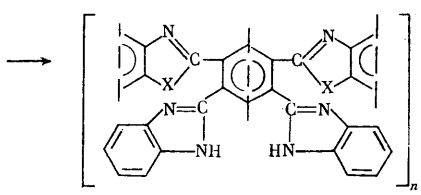
polyamides[6]) and readily react with a highly basic nucleophile (hydrazine) under mild conditions:



Then *bis*-benzoylenebenzimidazoles (III, IV) were successfully used as monomers both for the synthesis of various polybenzazoles with *o*-benzimidazole substituents in the principal chains of the macromolecules:[109–111]

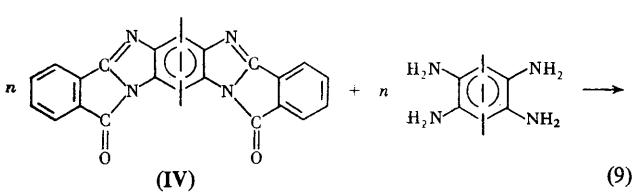


(III)

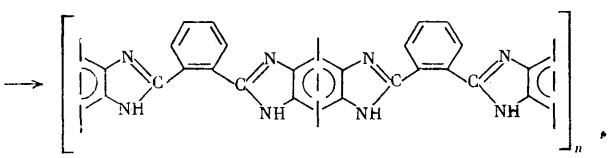


X = O, S, NH.

and for the synthesis of copolymers of polybenzimidazoles[112] with a regular alternation of two tetraamine residues.

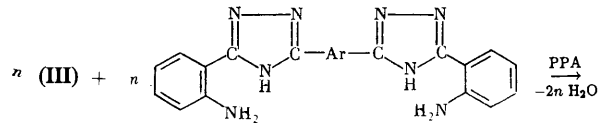


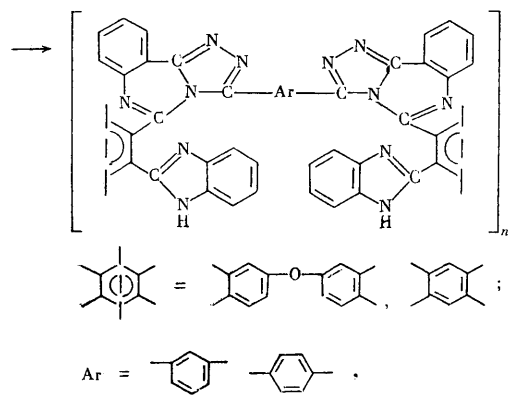
(IV) (9)



These reactions were carried out in polyphosphoric acid (PPA) at 180–200 °C. The prepared polymers are soluble in organic solvents and are capable of forming layers.

In analogous reactions in PPA, *bis*-[5-(*o*-aminophenyl)-*s*-triazolyl-3]phenylenes were used with III as tetrafunctional nucleophiles.[113] This resulted in block-ladder soluble polytriazoloquinazolines with *o*-benzimidazole side groups:





In contrast with the five-membered benzoyleneimidazoles, six-membered naphthoylenebenzimidazoles containing the structural element

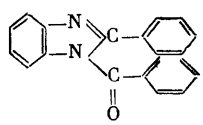
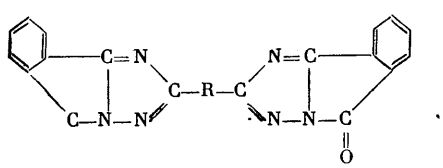
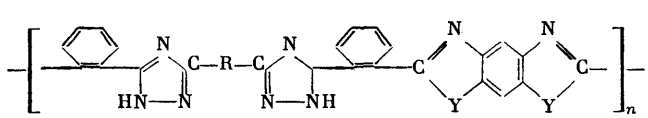


exhibit high chemical resistance[114] and do not undergo analogous reactions.

It has been demonstrated[115] that *bis*-benzoylenetriazoles of the general formula below can be used as bifunctional cyclic activated amines to synthesise polyheteroarylene through Reaction (9):

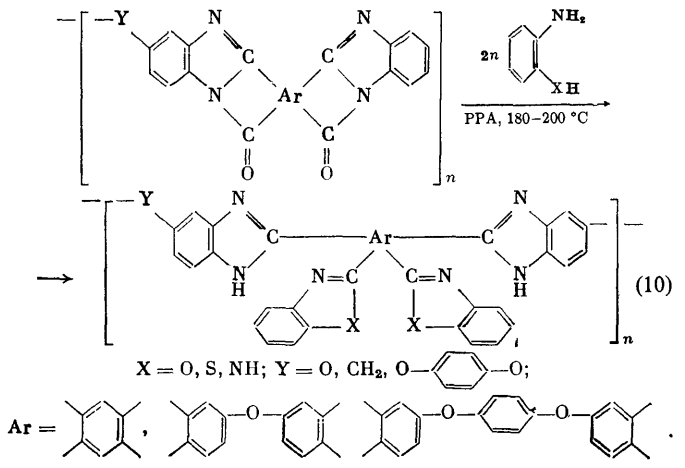


Copolymers with a regular alternation of benzazole and triazole rings in the principal chains of the macromolecules are produced:

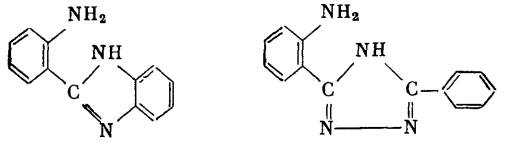


Y = O, S, NH.

Reactions similar to those given above have also been used for polymer-like conversions of polybenzoylenebenzimidazoles in order to prepare modified polybenzimidazoles:[116]

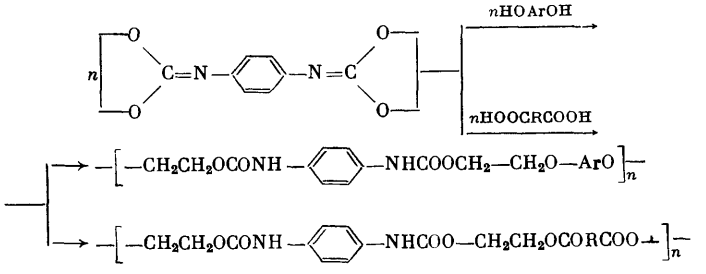


In order to increase the heat resistance and solubility of the polymers, 2-(*o*-aminophenyl)-benzimidazoles and 3-phenyl-5-(*o*-aminophenyl)-1,2,4-triazoles have been employed as the *o*-substituted anilines in Reaction (10):[117]

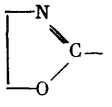


6. Cyclic *bis*-iminoesters and their analogues

An interesting method of synthesising polyesterurethanes consisting of the reaction of a bifunctional cyclic iminocarbonate with *bis*-phenols[118] and dicarboxylic acids[119] has been proposed by Mukayama, et al.

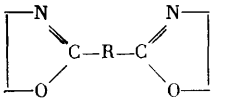


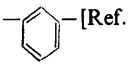
Bifunctional oxazolines containing the structural element



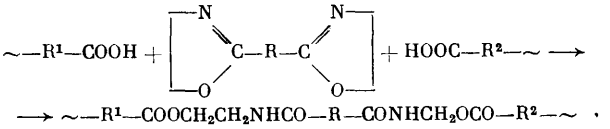
were used to synthesise hetero-chain polymers by various authors. These can be viewed as cyclic iminoesters.

bis-Oxazolines of general formula



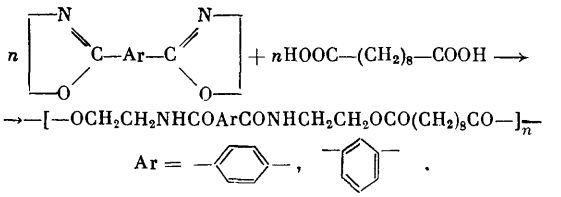
R = —[Ref. 120],  —[Ref. 121];

have been used[120,121] as chain extenders of polyesters with terminal carboxylic groups:

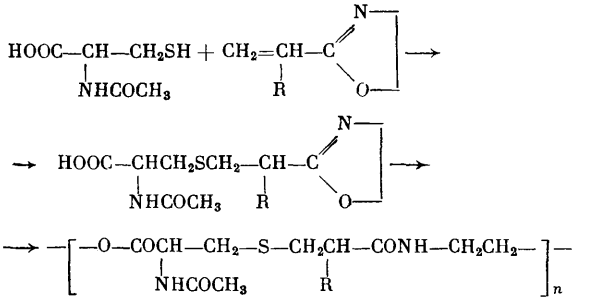


It is noteworthy that the reaction was carried out at elevated temperatures (200—280 °C) in the polyester melt. Under these conditions the stable *bis*-oxazolines are more suitable chain extenders than their more thermally resistant analogues, the *bis*-oxazolinones examined in part 4.

The reaction of oxazolines with carboxylic acids was investigated in detail and used successfully by Sano[122] to synthesise high-molecular-weight polyesteramides ($[\eta] \lesssim 1.21$ dl g^{-1}) in the mass at 185—240 °C:

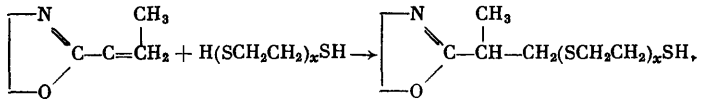


An original synthesis route to polyesteramides employing unsaturated 2-alkylene-2-oxazoline has been proposed.[123] An AB-type monomer is first prepared by its reaction with *N*-acetyl-L-cysteine:

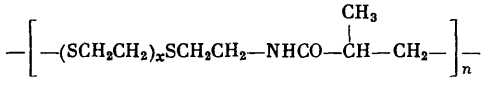


where R = H and CH_3. This is then polymerised with the terminal carboxylic and oxazoline group (analogously to the reactions mentioned above). The mechanism involves polyaddition in DMF at 50—100 °C and produces an optically active polymer with a relative molecular mass up to 13.8×10^3.

An essentially similar process has been carried out.[124] Reaction of 2-isopropenyl-2-oxazolines with H_2S or a dithiol was used to synthesise AB-monomers with SH- and oxazoline groups:

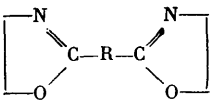


where $x = 0$ and 1. The latter was polymerised in the melt or DMF at 100–200 °C. Polyamidethioethers were prepared with the structure:



with $M_n \leqslant 4300$ depending on the reaction conditions.

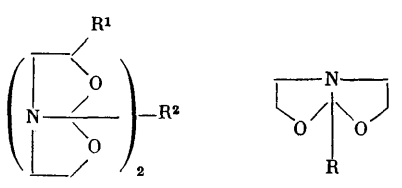
The nucleophilic substitution reaction on which the processes described above are based was also used to prepare polyamides containing simple ether bonds through reaction of *bis*-oxazolines of general formula



where R = alkylene C_{1-20} and arylene C_{6-20}, with polyphenols at 170 °C using $Ph_3(C^+X^-$ (X = BF_4, PF_6, SbF_6, AsF_6, BPh_4, or ClO_4) as catalysts.[125] High-melting thermally reactive polyamidoethers with a 5% mass loss at 390 °C (TGA) were obtained.

The *bis*-oxazolines also react with aromatic diamines to form prepolymers that undergo intermolecular crosslinking in the presence of strong acids as catalysts.[126] These systems are useful for preparing thermally reactive formed compositions with good strength indicators.

Bicyclic amidacetals of the general formula shown below with structures similar to the iminoethers were also used as cyclic monomers to prepare polymers:



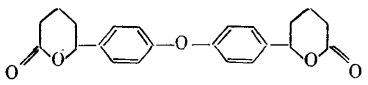
Reaction of these with alkanolamines produces oligomeric polyols that are used to synthesise polyurethanes.[127]

Polyurethanes are also synthesised through reaction of bicyclic amidacetals with polyols and diisocyanates[128] or directly with diisocyanates.[129]

V. Six-membered heterocycles

1. *bis*-δ-Lactones

Six-membered *bis*-δ-lactones are unreactive in aminolysis reactions, like their five-membered analogues (see Part IV). The *bis*-δ-valerolactone shown below has been synthesised:[130]



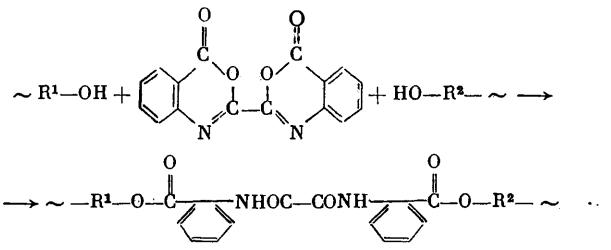
It was found that a polyamide containing hydroxyl groups with $\eta_{inh} \leqslant 0.26$ dl g^{-1} is formed through its reaction with hexamethylenediamine (65–80 °C, 10 days, in methanol, *m*-cresol or *N*-methylpyrrolidone).

2. *bis*-Benzoxazinones

Ueda and Imai[131] synthesised various *bis*-(3,1-benzoxazine-4-ones) (Table 2, compounds Nos. 1–6) from *bis*-anthranilic acids. These are six-membered analogues of isoimide azlactones (Part IV). During a study of model reactions it was established that these compounds at room temperature comparatively easily react with aliphatic amines (butylamine, benzylamine). More forcing conditions are required with an aromatic amine (aniline). This is probably due to both the decrease of electrophilic reactivity of the isoimide fragment (its carbonyl group) and the significant stabilisation of the heterocycle owing to conjugation with the condensed benzene ring. It was found that 2-methyl-substituted benzoxazines are more active than the 2-phenyl-substituted analogues. This may also indicate the importance of conjugation in determining the acylating potential of a given heterocyclic system.

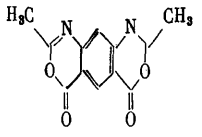
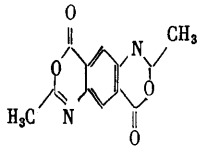
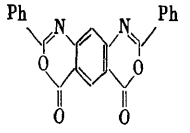
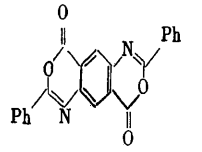
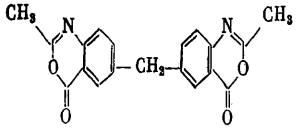
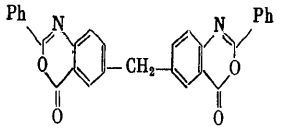
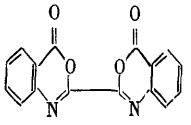
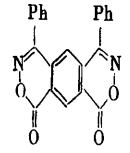
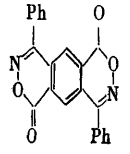
High-molecular-weight layer-forming polyamides with $\eta_{inh} \leqslant 0.6$ dl g^{-1} are produced through reaction of *bis*-benzoxazinones with hexamethylenediamine and *m*-xylylenediamine in polar aprotic solvents (DMF, hexametapol, DMSO, etc.).[131]

Inata and Matsumura[132] also synthesised the novel isoimide benzoxazinone 2,2′-*bis*-(4H-3,1-benzoxazine-4-one) and used it as a chain extender of polyethyleneterephthalate:



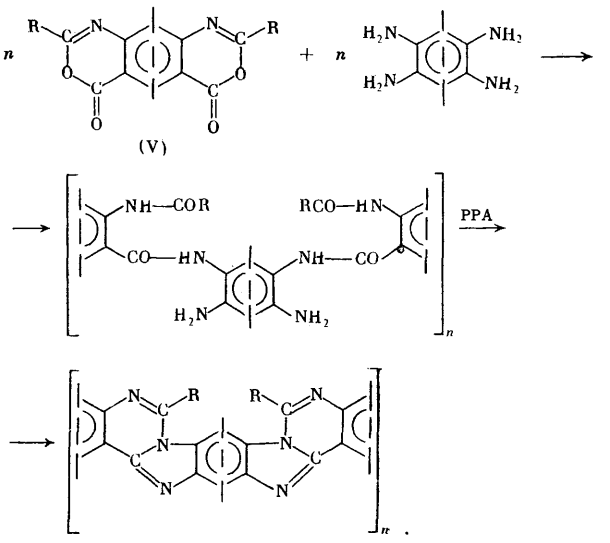
The reaction was carried out in the melt at 280 °C. A linear polymer with an elevated molecular mass was prepared. It is appropriate to mention here that *bis*-oxazinones, as was expected, react with OH groups with more difficulty than five-membered azlactones.

Table 2. *bis*-Oxazinones used to synthesise polyamides.

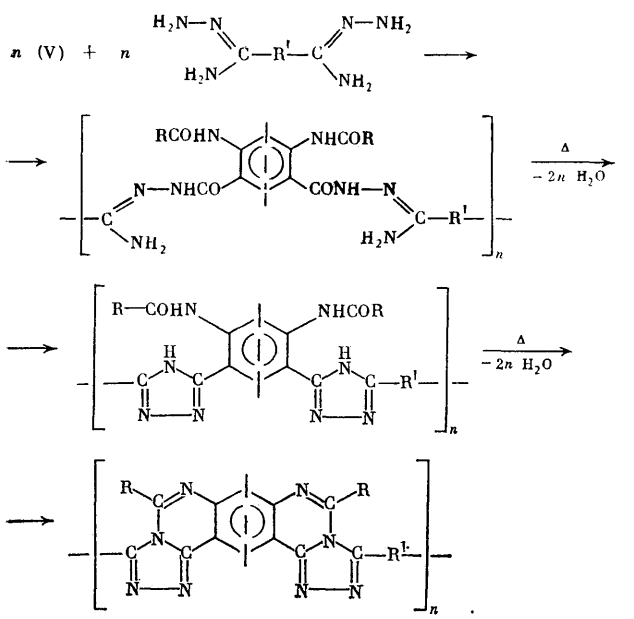
Sample No.	*bis*-Oxazinone	Reference
1		[131]
2		[131]
3		[131]
4		[131]
5		[131, 133]
6		[131]
7		[132]
8		[137]
9		[137]

Quinazoloneimide¶[133] copolymers with an initial decomposition temperature of 380–396 °C are obtained through reaction of 6,6′-methylene-*bis*-(2-methyl-3,1-benzoxazine-4-one) (Table 2, compound No. 5) with 4,4′-diaminodiphenyloxide and 3,3′,4,4′-benzophenonetetracarboxylic acid in *m*-cresol in the temperature range 130–180 °C.

The reaction of isoimide *bis*-benzoxazinones with *bis*-*o*-phenylenediamines (aromatic tetraamines) was used to synthesise full or partial ladder polymers, polybenzimidazolequinazolines:[134,135]



Korshak, et al.[136] used *bis*-amidrazones as tetrafunctional nucleophiles in the reaction with *bis*-benzoxazinones to synthesise partial ladder (block–ladder) polytriazoloquinazolines:

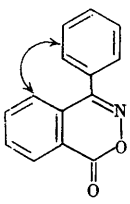


The isomeric *bis*-oxazinones *bis*-4-phenyl-2,3-benzoxazine-1-ones (Table 2, compounds Nos. 8 and 9) were also synthesised.[137] In contrast with the benzoxazinones examined above that contain isoimide moieties, the reactive structural elements of the

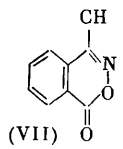
¶Adducts of *bis*-benzoxazione and diamines undergo thermal cyclodehydration to form polyquinazolones.

benzoxazinones that are isomeric with them are O-acyloxime fragments $-CO-O-N=C\diagup\diagdown$, which are distinguished by a comparatively low acylating potential.[138,139]

A study of model reactions demonstrated that the 4-phenyl-substituted 1H-2,3-benzoxazine-1-one (VI) readily reacts with aliphatic amines (*n*-butylamine and benzylamine) at 20 °C to form the corresponding adducts in quantitative yields regardless of the solvent nature (ethanol, THF, *N*-methylpyrrolidone). This azlactone does not react with aniline even under more forcing conditions (at 80 °C). In contrast with VI, its 4-methyl-substituted analogue (VII) is stable and does not react even with aliphatic amines at 80 °C.

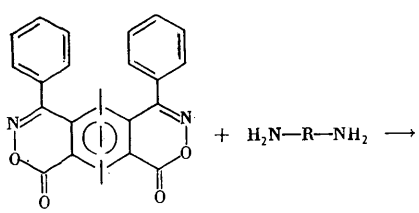


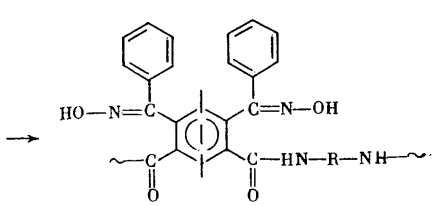
(VI)



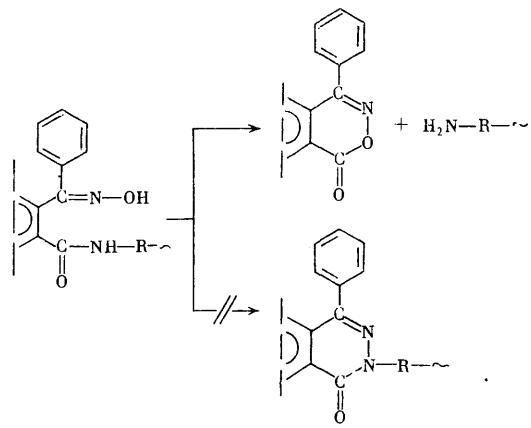
(VII)

Therefore, acyloxime benzoxazinones are much less reactive than the isoimide analogues. The higher reactivity of VI compared with its linear analogues[138,139] may be due to both strain in the ring and steric interaction between the benzene rings (shown by an arrow), which is relieved after opening of the heterocycle by aminolysis. Polycondensation of 4-phenyl-substituted benzoxazinones (Table 2, compounds Nos. 8 and 9) with aliphatic diamines in aprotic polar solvents at 20 °C is complete after 2–3 days. Polyamides are formed in quantitative yields. However, they have comparatively low viscosities (η_{inh} = 0.12–0.38 dl g^{-1}).





This and the low reactivity of the heterocycle may be due to the equilibrium nature of the reaction. This view is consistent with the ease of depolymerising the polyamide at elevated temperature (220 °C):



- - -o0o- - -

The polymer syntheses examined in the present review are stepwise polyaddition processes that obey the rules of polycondensation. A number of the reactions, for example, those involving saturated *bis*-azlactones, *bis*-isoimides and *bis*-imides, in addition to certain unsaturated *bis*-azlactones, are polyaddition processes in the pure sense. In the remaining instances, some groups or others (hydroxyls, ketones, etc.) are lost that formally can be viewed as low-molecular-weight side products. However, these do not abandon the macromolecular chains and remain bonded to them by a covalent bond. Such reactions are promising for the synthesis of various functionalised polymers including those for biomedical applications.

References

1. P W Morgan *Polymer Reviews Vol. 10, Condensation Polymers: By Interfacial and Solution Methods* (Translated into Russian), Khimiya, Leningrad, 1970, 448 pp.
2. V V Korshak, S V Vinogradova *Ravnovesnaya Polikondensatsiya* (Equilibrium Polycondensation), Nauka, Moscow, 1968, 444 pp.
3. V V Korshak, S V Vinogradova *Neravnovesnaya Polikondensatsiya* (Nonequilibrium Polycondensation), Nauka, Moscow, 1972, 696 pp.
4. L B Sokolov *Osnovy Sinteza Polimerov Metodom Polikondensatsii* (Principles of Polymer Synthesis by the Polycondensation Method), Khimiya, Moscow, 1979, 265 pp.
5. J H Saunders, K C Krisch *Polyurethans – Chemistry and Technology* (Translated into Russian), Khimiya, Moscow, 1979, Vol. 1, 470 pp.
6. R D Katsarava *Vysokomol. Soedin., Ser. A*, 1989, **31** 1555
7. V A Vasnev, A L Rusanov, M L Keshtov, et al. *Itogi Nauki i Tekhniki. Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii* (Progress in Science and Technology. Chemistry and Technology of High-Molecular-Weight Compounds), Izd. VINITI, Moscow, 1987, Vol. 23, p. 3

8. R D Katsarava *Usp. Khim.*, 1989, **58**(9) 1549 [English translation in *Russ. Chem. Rev.*, 1989(9)]
9. V V Korshak *Termostoikie Polimery* (Heat-Resistant Polymers), Nauka, Moscow, 1969, 417 pp.
10. N A Adrova, M I Bessonov, L A Laius, et al. *Pollimidy—Novyi Klass Termostoikikh Polimerov* (Polyimides—A New Class of Heat-Resistant Polymers), Nauka, Moscow, 1968, 211 pp.
11. Ya S Vygodskii, S V Vinogradova *Usp. Khim.*, 1973, **42**(7) 1225 [English translation in *Russ. Chem. Rev.*, 1973(7)]
12. I A Arkhipova, B A Zhubanov, S R Rafikov *Usp. Khim.*, 1978, **47**(4) 705 [English translation in *Russ. Chem. Rev.*, 1978(4)]
13. L G Nechitailo, A S Kalinkin, O P Stepko, et al. *Kinet. Katal.*, 1987, **28** 1322
14. A Mantecon, V Cadiz, A Serra, et al. *Angew. Makromol. Chem.*, 1988, **156** 37
15. H H Hörhold, J Opfermann, D Raabe, et al. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, 1981, 23
16. R E Gruetzner, H H Hörhold *XIII International Microsymposium "Polycondensation"*, Schwerin, DDR, April 3—7, 1989, p. 40
17. J Klee, H H Hörhold, S Varbanov, et al. *XIII International Microsymposium "Polycondensation"*, Schwerin, DDR, April 3—7, 1989, p. 77
18. Y Iwakura, M Sakamoto *J. Polym. Sci.*, 1960, **47** 227
19. V V Korshak *Dokl. Akad. Nauk SSSR*, 1982, **262** 1149
20. M Bertran, A Mantecon, V Cadiz *Angew. Makromol. Chem.*, 1989, **168** 81
21. D Gagnebien, P-J Madec, E Marechal *Eur. Polym. J.*, 1985, **21** 273
22. D Gangnebien, P-J Madec, E Marechal *Eur. Polym. J.*, 1985, **21** 289
23. G Rokicki, W Kuran *Makromol. Chem.*, 1980, **181** 985
24. P-J Madec, E Marechal *Advances in Polymer Science*, Springer—Verlag, Berlin—Heidelberg—*New York*—Tokyo, 1985, Vol. 71, p. 153
25. F La Blainvaux, P-J Madec, E Marechal *Polym. Bull.*, 1985, **13** 237
26. E Marechal *Bull. Soc. Chim. Fr.*, 1987, 713
27. A Sendijarevič, V Sendijarevič, K C Frisch, Jr., *J. Polym. Sci., Part A: Polym. Chem.*, 1987, **25** 151
28. H Sehovič, A Sendijarevič, V Sendijarevič, et al. *J. Polym. Sci., Part A: Polym. Chem.*, 1987, **25** 2729
29. L I Komarova, S N Salazkin, Ya S Vygodskii, et al. *Vysokomol. Soedin., Ser. A*, 1990, **32** 1571
30. L I Komarova, S N Salazkin, V V Korshak, et al. *Vysokomol. Soedin., Ser. B*, 1974, **16** 718
31. L I Komarova, I A Bulgakova, S N Salazkin, et al. *J. Polym. Sci., Polym. Lett.*, 1976, **14** 179
32. L I Komarova, S N Salazkin, I A Bulgakova, et al. *J. Polym. Sci., Polym. Chem. Ed.*, 1978, **16** 1643
33. T Nishikubo, E Takehada, S Saita, et al. *J. Polym. Sci., Polym. Chem. Ed.*, 1987, **25** 3049
34. T Nishikubo, S Saita, T Fujii *J. Polym. Sci., Polym. Chem. Ed.*, 1987, **25** 1339
35. Y Iwakura, M Sakamoto, Y Awata *J. Polym. Sci., Part A*, 1964, **2** 881
36. F Grundschober, J Sambeth *J. Polym. Sci., Part C*, 1967, (16) 2087
37. H E Zaugg *Organic Reactions* (Edited by R Adams), Wiley, New York, 1954, Vol. 8, p. 305
38. M Ueda, M Takahashi, Y Imai *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17** 2477
39. M Gordon, J G Miller, A R Day *J. Am. Chem. Soc.*, 1949, **71** 1946
40. E M C Arnett, J G Miller, A R Day *J. Am. Chem. Soc.*, 1950, **72** 5635
41. R Baltzly, I M Berger, A A Rothstein *J. Am. Chem. Soc.*, 1950, **72** 4149
42. J F Bunnett, G T Davis *J. Am. Chem. Soc.*, 1960, **82** 665
43. N Ogata, K Sanui, H Nakamura *Polym. J.*, 1978, **10** 499
44. M Ueda, M Yabuuchi, Y Imai *J. Polym. Sci., Polym. Chem. Ed.*, 1977, **15** 323
45. I Hayashi, S Takahashi, Y Hachihama *Kogyo Kagaku Zasshi*, 1957, **60** 646
46. M Ueda, M Yabuuchi, Y Imai *J. Polym. Sci., Polym. Chem. Ed.*, 1966, **15** 73
47. M Ueda, M Yabuuhi, Y Imai *J. Polym. Sci., Polym. Chem. Ed.*, 1977, **15** 2641
48. Y Imai, M Ueda, T Takahashi *J. Polym. Sci., Polym. Chem. Ed.*, 1976, **14** 2391
49. C G Johnson, P E Cassidy *J. Polym. Sci., Polym. Chem. Ed.*, 1989, **27** 2253
50. J M Whelan, W P Samuels, USA P. 2 935 494; *Chem. Abs.*, 1960, **54** 17961b
51. J M Whelan, R J Cotter, USA P. 3 072 613; *Chem. Abs.*, 1963, **58** 14148h
52. L Ya Rapport, G N Petrov, I I Trostyanskaya, et al. *Kauch. Rezina*, 1981, 25
53. G Rokicki *Tezisy X Meshdunarodnogo Mikrosimpoziuma po Polikondensatsii* (Abstracts of the Tenth International Microsymposium on Polycondensation), Hungary, 1985, p. 46
54. G Rokicki *Makromol. Chem.*, 1985, **186** 331
55. D R Fagerburg *J. Macromol. Sci., Chem., A*, 1987, **24** 853
56. C S Cleaver, B C Pratt *J. Am. Chem. Soc.*, 1955, **77** 1944
57. C S Cleaver, B C Pratt *J. Am. Chem. Soc.*, 1955, **77** 1541
58. E Hedaya, R L Hinmann, S Theodoropulos *J. Org. Chem.*, 1966, **31** 1311
59. Y L Fan, D F Pollart *J. Org. Chem.*, 1968, **33** 4372
60. E V Ganin, V F Makarov, B V Razynov *Zh. Org. Khim.*, 1985, **21** 2411
61. D M Brown *Adv. Org. Chem.*, 1966, **3** 79
62. B V Bocharov *Usp. Khim.*, 1965, **34**(3) 488 [English translation in *Russ. Chem. Rev.*, 1965(3)]
63. T A Khosruashvili, L I Kirmelashvili, D P Kharadze, et al. *Soobshch. Akad. Nauk Gruz. SSR*, 1989, **136** 329
64. R D Katsarava, D P Kharadze, LM Avalishvili *Pol. J. Appl. Chem.*, 1986, **30** 187
65. R D Katsarava, D P Kharadze, T M Bendiashvili, et al. *Acta Polym.*, 1988, **39** 523
66. K W Leong, V Simonte, R Langer *Macromolecules*, 1987, **20** 705
67. T M Frunze, V V Korshak, L V Kozlov *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1959, 535
68. K Hohenlohe-Ochringen, H Bretschneider *Monatsh. Chem.*, 1962, **93** 645
69. M Ueda, K Kino, K Yamaki, et al. *J. Polym. Sci., Polym. Chem. Ed.*, 1978, **16** 155
70. Y Imai *Kobunshi*, 1978, **27** 723
71. R D Katsarava, D P Kharadze, L I Kirmelashvili, et al. *Acta Polym.*, 1985, **36** 29

72. P Cefelin, B Masar, D P Kharadze, et al. *Polikondensatsionnye Protsessy* (Polycondensation Processes), Izd. Bolgarskoi Akad. Navuk, Sofiya, 1986, p. 66
73. M G Burchuladze, N A Galatenko, N N Bufius, et al. *Izv. Akad. Nauk Gruz. SSR, Ser. Biol.*, 1989, **15** 375
74. R D Katsarava, D P Kharadze, L I Kirmelashvili, et al. *VI Intern. Conf. Polym. Med. and Surgery. Leewenhorst, 12–14 April 1989*, London, 1989, P. P11/I–P11/2
75. L I Kirmelashvili, Candidate's Dissertation in Chemical Sciences, Tbilisi State University, Tbilisi, 1990, 159 pp.
76. P P Policastro, P K Hernandez *J. Polym. Sci., Polym. Chem. Ed.*, 1987, **25** 2819
77. R D Katsarava *Kompozitsionnye Polimernye Materialy* (Composite Polymer Materials), Kiev, 1986, No. 29, p. 70
78. J K Rasmussen, S M Heilmann, L R Krepski, et al. *Preprint IUPAC XXXII Int. Symp. Macromol. Kyoto*, 1988, p. 137
79. A R Katritzky, K Sakizadeh, J Swinson, et al. *J. Polym. Sci., Part A: Polym. Chem.*, 1989, **27** 1515
80. N Chau, Y Saegusa, Y Iwakura *J. Polym. Sci., Part A: Polym. Chem.*, 1982, **20** 3387
81. N Chau, Y Saegusa, Y Iwakura *Makromol. Chem., Rapid Commun.*, 1982, **3** 115
82. M Ueda, K Kino, Y Imai *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13** 659
83. J Grinshtein, M Vinits *Chemistry of Aminoacids and Peptides* (Translated into Russian), Mir, Moscow, 1965, 821 pp.
84. M Ueda, K Kino, T Hirono, et al. *J. Polym. Sci., Polym. Chem. Ed.*, 1976, **14** 931
85. Y Imai *Kobunshi* , 1977, **26** 799
86. M Ueda, M Funayama, Y Imai *J. Polym. Sci., Polym. Chem. Ed.*, 1977, **15** 1629
87. Y Imai, M Ueda *J. Synth. Org. Chem. Jpn.*, 1982, **40** 53
88. Y Imai, K Kino, M Yeda *J. Polym. Sci., Polym. Lett. Ed.*, 1975, **13** 137
89. Y Imai, M Ueda, S Kanno *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13** 1691
90. M Ueda, S Kanno, Y Imai *J. Polym. Sci., Polym. Chem. Ed.*, 1976, **14** 663
91. M S Jacovic, J Djonlagic, W J Macknight, et al. *Polym. Eng. Sci.*, 1985, **25** 751
92. M A Abishev, V A Gusinskaya, T V Sheremeteva *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 1880
93. M A Abishev, V A Gusinskaya, T V Batrakova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 2132
94. I A Arkhipova, B A Zhubanov, S R Rafikov, et al. *Dokl. Akad. Nauk SSSR*, 1973, **209** 93
95. S B Saidenova, B A Zhubanov, I A Arkhipova, et al. *Vysokomol. Soedin., Ser. A*, 1975, **17** 1441
96. T Kagiya, M Izu, T Matsuda, et al. *J. Polym. Sci., Part A-1*, 1967, **5** 15
97. T V Sheremeteva, V A Gusinskaya *Vysokomol. Soedin., Ser. A*, 1966, **8** 732
98. G S Sharifov, T V Sheremeteva, E N Zlobin, et al. *Vysokomol. Soedin, Ser. B*, 1974, **16** 651
99. T V Sheremeteva, K A Romashkova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 1474
100. M G Gherasim, I Zugravescu *Eur. Polym. J.*, 1978, **14** 985
101. R D Katsarava, D P Kharadze, L M Avalishvili *Makromol. Chem.*, 1986, **187** 2053
102. Y Imai, M Ueda, K Okuyama *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17** 1901
103. Y Imai, M Ishimori *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13** 365
104. Y Imai, M Ueda, M Ishimori *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13** 2391
105. Y Imai, M Ueda, M Ishimori *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13** 1969
106. Y Imai *J. Polym. Sci., Part B*, 1970, **8** 555
107. Y Imai *J. Polym. Sci., Part A-1*, 1972, **10** 2091
108. V V Korshak, A L Rusanov, R D Katsarava *Vysokomol. Soedin., Ser. A*, 1969, **11** 2090
109. V Korshak, E S Krongauz, A P Travnikova, et al., USSR P. 276405; *Byull. Izobret.*, 1970, (23)
110. V V Korshak, E S Krongauz, A L Rusanov, et al., USSR P. 280835; *Byull. Izobret.*, 1970, (28)
111. V V Korshak, A L Rusanov, E S Krongauz, et al. *Dokl. Akad. Nauk SSSR*, 1971, **196** 106
112. V V Korshak, A L Rusanov, R D Katsarava, et al., USSR P. 293016; *Byull. Izobret.*, 1971, (5)
113. Ts G Iremashvili, Candidate's Dissertation in Chemical Sciences, Inst. Organomet. Compounds, Moscow, 1973, 152 pp.
114. V V Korshak, A L Rusanov, et al. *Dokl. Akad. Nauk SSSR*, 1975, **221** 1334
115. S N Leont'eva, Candidate's Dissertation in Chemical Sciences, Inst. Organomet. Compounds, Moscow, 1975, 141 pp.
116. USSR P. 312857; *Byull. Izobret.*, 1971, (24)
117. USSR P. 399525; *Byull. Izobret.*, 1973, (39)
118. T Mukaiyama, T Fujisawa, H Nohira, et al. *J. Org. Chem.*, 1962, **27** 3337
119. T Mukaiyama, T Fujisawa, T Hyugaji *Bull. Chem. Soc. Jpn.*, 1962, **35** 687
120. H Inata, S Matsumura *J. Appl. Polym. Sci.*, 1987, **33** 3069
121. Y Arai, T Tanaka, USA P. 4543396; *Ref. Zh. Khim.*, 1986, 11S611P
122. Y Sano *J. Polym. Sci., Part A*, 1989, **27** 2749
123. M Suzuki, J-Ch Lim, T Saegusa *Polym. Bull.*, 1988, **19** 247
124. P A Gunatillake, G Odian *Macromolecules*, 1987, **20** 2356
125. A B Goel, O Tiba, USA P. 4746719; *Ref. Zh. Khim.*, 1989, 5S410P
126. Y Sano, USA P. 4837302; *Ref. Zh. Khim.*, 1990, 11S395P
127. A B Goel, USA P. 4698409; *Ref. Zh. Khim.*, 1988, 12S593P
128. A B Goel, Eur. P. 0297154; *Ref. Zh. Khim.*, 1989, 21S468P
129. A B Goel, T A Tufts, Eur. P. 0304507; *Ref. Zh. Khim.*, 1990, 2S302P
130. M Ueda, M Takahashi, Y Imai *Makromol. Chem.*, 1978, **179** 2783
131. M Ueda, I Imai *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17** 1163
132. H Inata, S Matsumura *J. Appl. Polym. Sci.*, 1987, **34** 2769
133. S Kubota, T Ando *J. Appl. Polym. Sci.*, 1988, **35** 695
134. V V Korshak, A L Rusanov, USSR P. 275389; *Byull. Izobret.*, 1970, (22)
135. M Soga, M Hachihama, T Shono *J. Polym. Sci., Part A-1*, 1970, **8** 2265
136. V V Korshak, et al. *Izv. Akad. Nauk Gruz. SSR, Ser. Khim.*, 1978, **4** 180
137. M Ueda, H Hazome, Y Imai *J. Polym. Sci., Polym. Chem. Ed.*, 1976, **14** 1127
138. I Hayashi, K Ogihara, K Shimizu *Bull. Chem. Soc. Jpn.*, 1983, **56** 2432
139. I Hayashi, K Shimizu *Bull. Chem. Soc. Jpn.*, 1983, **56** 3197

Translated from *Uspekhi Khimii* **61** 195–246 (1992) U.D.C. 547.567:634.813.11

Quinone methides in the chemistry of wood

S M Shevchenko, A G Apushkinskii
St Petersburg Forestry Academy

ABSTRACT. Modern ideas about the stereoelectronic structure of quinone methides and their reactivity and role as intermediates in the lignification and delignification of wood are treated systematically. A special section is devoted to the method of synthesis of model quinone methides in lignin.

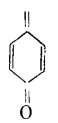
The bibliography includes 249 references.

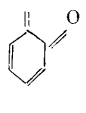
Contents

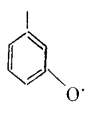
I. Introduction 105
II. Methods of synthesis 105
III. Stereoelectronic structure 108
IV. Chemical reactions 111
V. Quinone methides and the structure of lignin 118
VI. Quinone methides as intermediates in the delignification of wood 120

I. Introduction

The model quinone methods (QM) of lignin are unsaturated cyclic conjugated ketones—derivatives of alkylidenecyclohexadienones; the starting materials for their synthesis are aromatic compounds modelling various structural units of lignin. The involvement of QM in key lignification and delignification reactions is assumed to be generally recognised and this is reflected both in a special review[1] and in familiar monographs.[2–4] Stable QM which are not model compounds of lignin will be mentioned only when needed for comparisons, because the properties of these compounds have already been the subject of a recent review.[5] Endeavouring to achieve a logical description of the data, we shall begin with the properties of the simplest models and shall only then proceed directly to the chemistry of lignin. In conformity with the data accumulated in the literature at the present time, most attention will be devoted to *p*-QM (I); the less stable *o*-QM (II) have been much less investigated. Like the corresponding *m*-quinodimethanes,[6] *m*-QM (III) can apparently exist only as a biradical intermediate with negligible lifetimes. Hitherto their involvement in any kind of reactions of lignin has not been discussed.


(I)


(II)

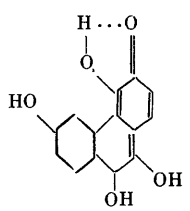

(III)

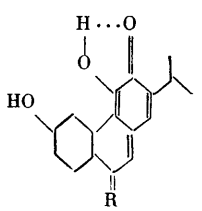
II. Methods of synthesis

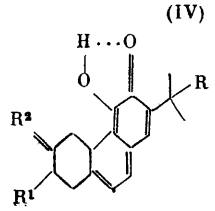
Reliable methods of synthesis of model QM of lignin, which are convenient objects for the study of the mechanisms of lignification and delignification and are synthons for model compounds of lignin, have now been developed.

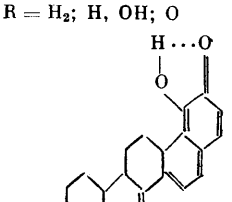
In contrast to the stable sterically hindered QM,[5,7,8] the model *p*-QM of lignin cannot be isolated in a pure form because of their low stability. They can be characterised only in solutions. The sterically hindered QM and QM fused with a benzene ring have no direct bearing on the chemistry of lignin. However, one should note that 10-methyleneanthrone has been isolated from the liquors in the anthraquinone (AQ) pulping of wood, while bianthrone has been detected among the products of the decomposition of the adduct of anthrone and model QM of lignin.[9]

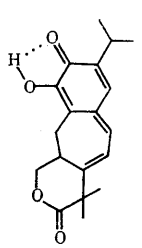
It appears useful to quote examples of stable QM isolated from plants:[10–16]


(IV)


R = H_2; H, OH; O

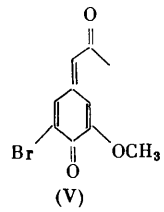

R = H, OH; R^1 = H; R^2 = H_2
R = H, R^1 = OH; R^2 = O


R = H_2, O



In these compounds, the QM system is stabilised both as a result of the lengthening of the conjugation chain and by the intramolecular hydrogen bond. Compound (IV), whose enolic form (a QM) is apparently more stable than the α-keto-isomer, is noteworthy.

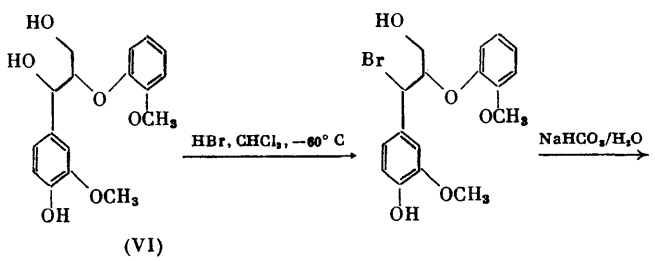
Compound (V) is a rare example of a compound close to the model QM of lignin which has been isolated in a crystalline form; however, its synthesis is poorly reproducible.[17]



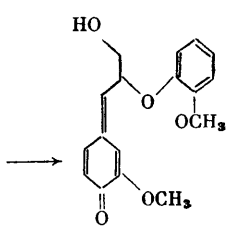
(V)

We shall emphasise two factors. Firstly, there have been numerous studies in which the formation of QM in the course of the processes investigated was postulated. Such publications must be distinguished form the few investigations whose authors dealt with QM directly and the structure of the latter was reliably demonstrated. Secondly, one should treat with caution studies where QM have been identified solely on the basis of electronic absorption spectra. The products of the degradation of these compounds are frequently coloured, which can readily lead to confusion. Thus our experience suggests that Pospisek et al.[18] and Adler and Stenemur[19] could not have obtained all the compounds which they list.

There exist two convenient routes to the synthesis of model QM of lignin: dehydrohalogenation of the corresponding *p*-hydroxybenzyl halide and oxidation of alkylphenols. For example, the method of Johansson and Miksche,[20] whereby fairly complex QM with β-aryloxide substituents have been obtained,[21] leads to success.

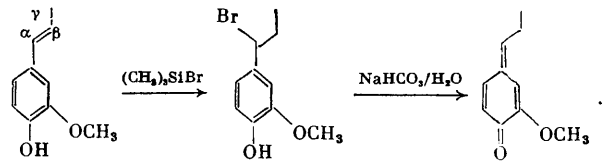


(VI)



(VII)

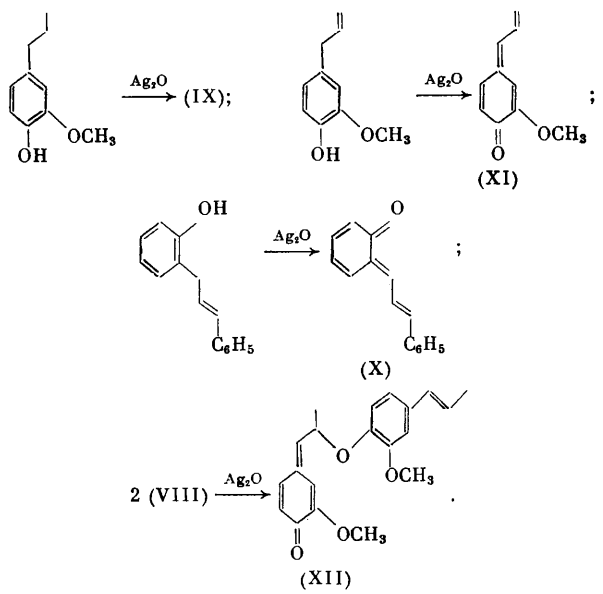
In recent years, this method has lost its importance. Its disadvantage is the use of low temperatures and a reactant such as dry hydrogen bromide, which can give rise to side reactions. In a certain sense, the method of synthesis of QM using bromotrimethylsilane (BTMS) (for its synthesis, see Andrianov[22]) proved to be ideal—this is a "test tube reaction" proceeding at room temperature with total conversion of the initial compound and as a rule an insignificant formation of side products.[23] It involves the formation of the same intermediate bromide as in the case where dry HBr is used.[248] Using bromotrimethylsilane, it is possible to obtain QM not only from *p*-hydroxybenzyl alcohols but also from α-alkenylphenols, for example isoeugenol (VIII):[147]



(VIII) (IX)

QM of the guaiacyl and syringyl series can be readily synthesised by this method; among derivatives of the *p*-hydroxyphenyl series, it has so far been possible to obtain only QM with a β-aryloxide substituent,[24,25] which apparently exerts a "through space" stabilising effect on the mechanism. There is so far no reliable evidence that QM without substituents in the α-position have been obtained.

Another common method of synthesis of QM is oxidation of alkyl- and alkenylphenols by silver oxide:[26–30]



(XII)

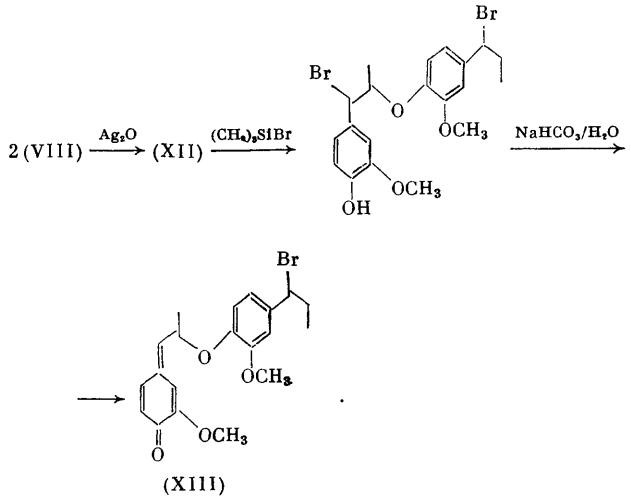
It is assumed that the mechanism of the oxidative conversion of phenols into QM includes either the disproportionation of the corresponding radicals or the formation of an intermediate quinol ether[31] (QM are probable intermediates in the rearrangement of quinol ethers to benzyl ethers[32]).

The formation of QM in the oxidation of phenols is not a "general" reaction; the result of the process depends on the type of oxidant, substrate, and conditions. Thus, contrary to expectations, homovanillic acid affords a product of a completely different type on oxidation with lead tetraacetate.[33] On the other hand, judging from the composition of the secondary products, a QM is formed on oxidation of guaiacylacetone with 2,3-dichloro-5,6-dicyanobenzoquinone.[17] In many cases, oxidation yields a broad spectrum of products.[34–36] We may note that the formation of QM in the oxidation of phenols is regarded as one of the stages of the enzymic degradation of model compounds of lignin and apparently of lignin itself.[37] It is seen from the examples presented above that, depending on the substrate, the reactions of the phenoxyl radicals generated initially may be of different kinds: in one case, they

involve the dehydrogenation of one molecule and in another dimerisation takes place. Thus each method opens up routes of QM of different types.

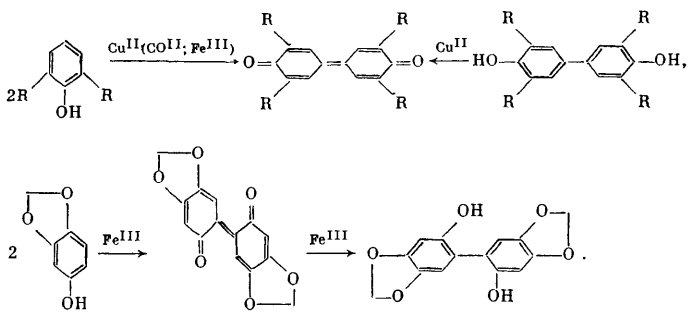
An important feature of the dimerisation reaction of the phenoxyl radicals derived from α-alkenylphenols is the retention of the steric orientation of the alkenyl substituent in the aryloxide group of the β-aryl ether type QM formed. Previously this reaction was deduced from the analysis of the secondary products formed during processes simulating the initial stages of lignification;[35] this reaction has been recently established directly for the transformation (VIII)→(XII).[38] Thus one can claim confidently that during their lifetime the alkenylphenoxyl radicals do not undergo changes in configuration. Consequently the steric structure of the unsaturated side fragments of lignin must correspond to the stereoisomeric composition of the monomeric alkenylphenols. This conclusion has definite importance for the understanding of the lignification process.

The combination of both methods of synthesis of QM opens a route to the preparation of interesting QM of the type (XIII), which contain a halogen atom in the side chain:[38]



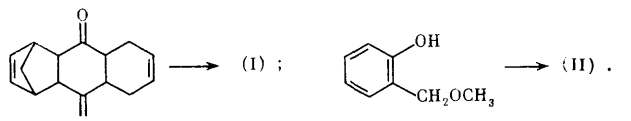
The fact that bromotrimethylsilane does not leave unaffected the multiple bonds of the molecule conjugated with the aromatic ring is used here. The same fact also precludes the employment of bromotrimethylsilane for the synthesis of QM vinylogues from compounds of the type of coniferyl alcohol (we may draw attention to an erroneous study[19] where the opposite was claimed).

The oxidative dimerisation of phenols serves as a familiar preparative method for the synthesis of substituted diphenoquinones—compounds related to QM and differing from the latter by a greater stability:[39–41]



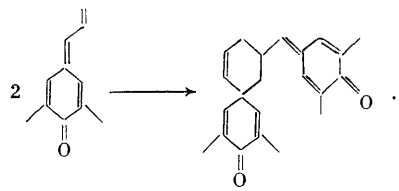
Attention should be drawn to the possibility of the formation of similar structures in lignin, for example, from fragments of the biaryl type.[42]

Individual highly reactive QM, the first members of the *p*-QM (I) [43] and *o*-QM (II) [44,45] homologous series, have been obtained by flash thermolysis:

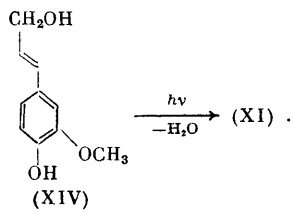


Compounds (I) and (II) remained unchanged in the solid state at a low temperature, but underwent rapid reaction on heating to room temperature or on adding nucleophiles. Flash thermolysis can hardly be used as a general preparative method. We may note that the formation of the unstable QM (II) in the gas phase was detected by photoelectron spectroscopy.[46]

In the series of sterically hindered QM, there is a method for the synthesis of stilbenenquinones by the dimerisation of QM with subsequent disproportionation.[5] In contrast to this, unhindered QM with the α-vinyl substituent are capable of dimerisation of a different type, affording an even more complex QM:[47]



Studies[48,49] in which it was possible to detect the formation of QM vinylogues [of types (XI)] in both aprotic and protic solvents (including water) in the flash photolysis of the corresponding alcohols merit mention:



In hydroxylated media, the QM obtained rapidly undergo nucleophilic addition reactions. The presence of QM was detected in this case only from electronic spectra but, together with the published results mentioned above,[48,49] the detection is convincing. It is striking that only α-vinyl-substituted QM, whose reactivity is reduced compared with the simplest representatives of the series, can be obtained by this method.

The convenient preparative methods described above lead to the formation of typical model QM of lignin in dilute solutions, but the presence of impurities is then inevitable. The target product can be purified by liquid chromatography.[28,50] Hitherto the isolation of model QM of lignin in a pure state under normal conditions has not been reported, although it is possible to concentrate a solution of a QM of the β-aryl type without degradation of the target product.[21,50]

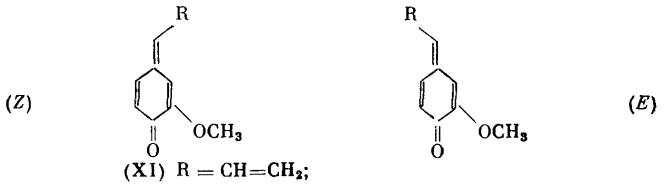
III. Stereoelectronic structure

Hitherto no data have been published on the structure of the quinone methide fragments of the polymeric lignin, but certain significant conclusions can be arrived at by investigating low-molecular-weight objects. Experimental methods, such as X-ray diffraction analysis, which yield detailed information about the molecular geometry, have been applied to certain stable crystalline QM. The introduction of aryl substituents in the α-position in the QM [compounds (XV) [51] and (XVI) [52]] or of t-butyl groups in the ring [we may draw attention to the stability of galvinoxyl (XVII) — a free radical containing a QM fragment[53]] as well as fusion with benzene rings [compound (XVIII) [54]] are methods for the stabilisation of the quinone methide system. We may note that the QM are not themselves in any way exotic compounds. It is sufficient to mention that this class includes fluoresceine and alkaline forms of phthaleine dyes.[55] On the other hand, the majority of such systems have no bearing on wood and can be in no sense regarded as model compounds of lignin. An exception is QM with an elongated conjugation chain isolated from plant raw material (see above); one of such substances [compound (XIX)] has been subjected to X-ray diffraction analysis.[11]

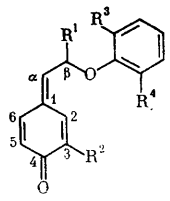
A detailed knowledge of the geometry of the skeletons of the simplest QM is important for the understanding of the physicochemical properties of compounds of this class. QM are quinone derivatives occupying in terms of many properties an intermediate position between benzoquinone (XX) and quinodimethane (XXI). The *para*-substituted compounds (I), (XX), (XXI), etc. belong to the D_{2h} symmetry group, while the corresponding *ortho*- and *meta*-substituted compounds belong to the C_{2v} group. In conformity with this, a classification of the atomic orbitals (AO) constituting the basis of the π-electron system has been put forward.[56] It is significant that, as a consequence of the different symmetries, the orbitals of the lone pairs of the oxygen atom do not mix with the π-system.

An important source of structural information is provided by calculations with optimisation of the geometry. The first attempt of this kind was apparently undertaken[57] using the MINDO/3 method for calculations relating to the simplest molecule of compound (I). In contrast to the semiempirical quantum-chemical methods, *ab initio* calculations and calculations by the empirical method of atom–atom potentials (AAP) provide more reliable predictions of the geometry. Calculations of both types have been carried out by the present authors[58] for the simplest models (XI) and (XXII). As regards molecular geometry, there is good agreement between the two methods. The distinct alternation of bonds leaves no doubt as to the quinonoid structure of QM.

An extremely interesting feature of asymmetric QM is the predominance of the (*Z*)-isomer in the vast majority of reaction mixtures obtained in the synthesis of these compounds. The (*Z*):(*E*) ratio is usually 2:1 [24,25,59,80] regardless of the mechanism of the synthesis: heterolytic cleavage of bromides or homolytic oxidation of phenol-alcohols. Calculation by the AAP methods, which are known to provide an adequate treatment of non-valence interactions, does not indicate the predominance of either the (*Z*)- or the (*E*)-isomer.[58,60,61] The same result was obtained by the semiempirical calculation using the AM1 method. On the other hand, the *ab initio* calculation in terms of the 3-21G basis set yielded a quantitative estimate of the ratio (*Z*):(*E*) which agreed fully with the experimental ratio.[58] Hence one may conclude that the stereochemistry in the series of QM is regulated not by steric but by electronic factors whose nature has not been elucidated hitherto. In combination, these data suggest that the stereoisomeric composition of QM is usually determined by thermodynamics, i.e. the corresponding synthetic reactions are subject to thermodynamic control. An exception is the case where QM is formed via the recombination of aryloxyl radicals. Such reactions lead to equal amounts of the (*Z*)- and (*E*)-isomers, maintenance of the reaction mixture at room temperature leading to a change in the ratio in the expected direction:[28,38]

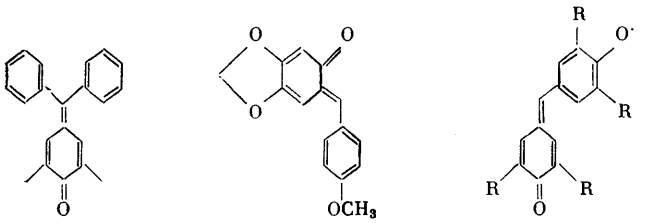


(XI) R = CH=CH$_2$;
(XXII) R = CH$_3$.

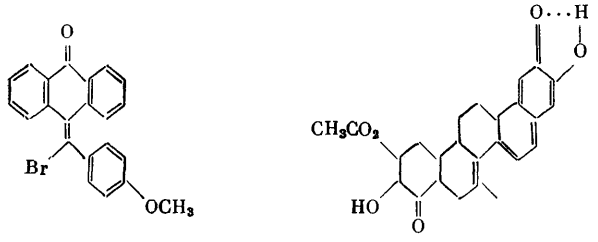


(XXII)

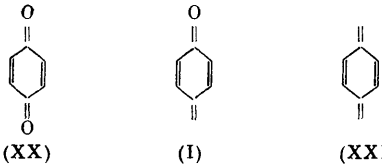
R^1 = H, CH$_3$;
R^2, R^3, R^4 = H, OCH$_3$



(XV) (XVI) (XVII), R = C(CH$_3$)$_3$



(XVIII) (XIX)



(XX) (I) (XXI)

A detailed conformational analysis of the model QM of lignin has been carried out.[58,60–63] It was established by the AAP and AMI methods that the planar conformer of compound (XI) is preferred subject to the stipulation that a second conformer with the ethenyl group displaced from the plane by ~60° should also be present in an appreciable amount.[58] On the other hand, as was to be expected, only the non-planar orientation can be achieved for the α-phenyl

substituent with the same angle of rotation.[63] The β-aryl ether QM (XXIII) have more interesting conformational features especially in connection with the elucidation of the nature of the structural reorganisation of lignin in pulping processes. Clearly, the chemically reversible transformations of the structural units (for example, the conversion of benzyl alcohol units into quinone methide units and conversely) can lead to irreversible changes in the steric structure of the polymer.

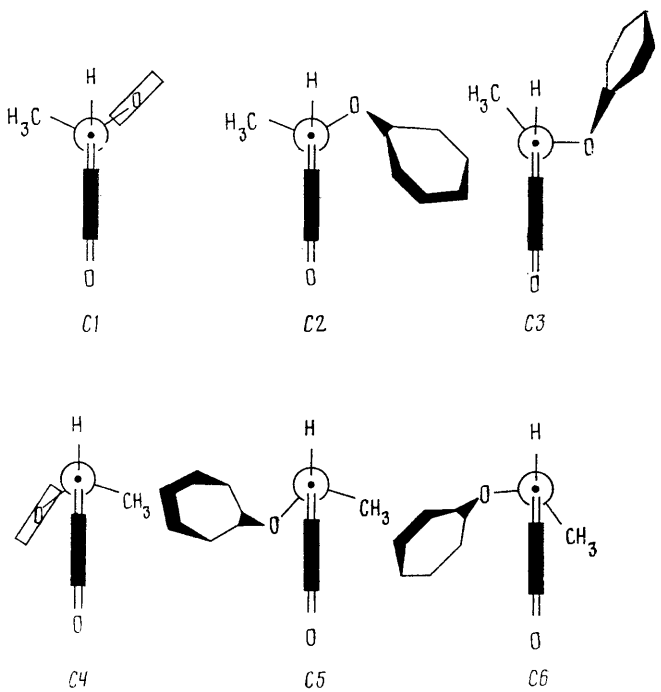
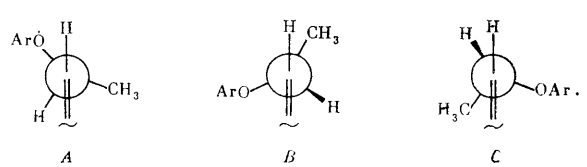


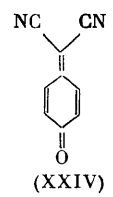
Figure 1. Conformers of the *p*-quinone methide (XXIII, $R^1 = CH_3$): the same conformers occur for other representatives of the series.[62]

Calculations by the AAP method[60–62] for compounds (XXIII) made it possible to identify the set of the possible conformers *C*1–*C*6 (Fig. 1) and to conclude that the conformational lability of the corresponding lignin units is high. The preference for the most favourable conformers *C*2 and *C*5 increases with increase in the steric hindrance of the molecule. Quantitative estimates of the relative energies of the conformers must be treated with caution, bearing in mind the data of Raos and Shevchenko.[64] However, there is no doubt that the ideas concerning the conformational composition of β-aryl ether QM developed previously[24] require revision. It was assumed[24] that three stable conformations are possible for QM (XXIII) ($R^1 = CH_3$, $R^2 = R^3 = OCH_3$): *A*, *B*, and *C*, the conformation *C* being clearly unfavourable owing to steric hindrance:



Using NMR spectroscopy combined with the nuclear Overhauser effect, the authors[24] demonstrated that the H(2) proton of the (*Z*)-isomer is close to the β-methyl group (R^1) and the H^β proton, which constitutes unambiguous demonstration of the existence in solution of the conformer *A*. Nevertheless, the conformation *A* cannot correspond to a potential energy minimum and the same experimental result would have been obtained if the given QM existed as a mixture of the conformers *C*2 (or *C*1) and *C*5 (or *C*4).[62]

The electronic structure of QM and its relation with the reactivity and chromophoric properties of these compounds have attracted attention a fairly long time ago. This was initiated by the simplest calculations using the HMO method.[65,66] Calculations within the framework of better approximations (PPP,[67] CNDO/S [8,28,68–72]) made it possible to reproduce with a high degree of accuracy the electronic absorption spectra of mononuclear QM and to assess the nature of the structural influences. The electronic spectra have long been used for the analysis of QM and large sets of data have been accumulated (for example, see Pospisek and co-workers[18,67] for special studies). However, their main importance at the present time is to serve as a control for quantum-chemical calculations[8,28] and in connection with photochemical problems.[73] The hitherto few attempts at an experimental estimation of the characteristics associated with reactivity have aroused much interest. Thus the first ionisation potentials of QM (II) and (XV), 8.80 eV [46] and 7.72 eV [70] respectively, have been determined by photoelectron spectroscopy. The proton affinity of the simplest QM (I) was found by the method of ion cyclotron resonance as 915 kJ mol^{-1}.[57] An electron affinity of 2.36 eV has been determined for the QM (XXIV) on the basis of not unduly reliable data concerning the position of the band associated with the charge transfer between the QM and hexamethylbenzene.[74] However, we were unable to detect the charge-transfer band for the QM (XI) even in a mixture with donors giving rise to characteristic bands in the presence of benzoquinone.[249] Such behaviour is consistent also with the results of quantum-chemical calculations.[72,75]


(XXIV)

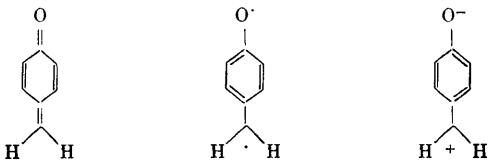
Simplest calculations by the HMO and PPP methods made it possible to establish important features of the electronic structure of QM [5,66,67,76–79] and their protonated forms.[4] The structure of QM and the associated problems of reactivity have now been analysed in fair detail on the basis of a considerable number of semiempirical (CNDO/2, CNDO/S and CNDO/S3, MNDO) [8,28,71–73,75,80–88] and non-empirical[58] calculations.

According to the results of calculations by the CNDO/S3 method,[84] the calcualted energies of the singlet–triplet excitation are too high for the corresponding structures to be regarded as the biradicals (XXV) in the ground state. Only certain excited states can have the biradical character. For planar QM, the energies of such states are unobtainable under the conditions of thermal reactions. The achievement of the biradical state is assisted by the "rotation" of the methylene group out of the plane, but such "rotation" itself requires large energies and the resulting conformation does not correspond to minima on the potential energy surface for the ground state. Thus the biradical forms of the QM (XXV) may play an

appreciable role, in our view, only in photochemical reactions (cf. Burlakov et al.[73]). The non-involvement of the QM biradicals in thermal reactions has also been confirmed by the high regioselectivity of the latter. Mentions concerning the possibility of the existence of QM in a biradical form under normal conditions, which are sometimes encountered, are based on an erroneous interpretation of EPR data during the years when the method only just began to be applied in organic chemistry. In fact solutions of pure QM are diamagnetic.[28]

As regards the zwitter-ionic structures (XXVI),[89] analysis of the bond and atomic valence indices permits the conclusion that such structures (incidentally they have a much higher energy compared with the quinonoid structures) do not correspond to a minimum on the potential energy surface for the ground state.[72,75,84] It is sufficient to say that, after the equalisation of the bond lengths in the ring (with the corresponding lengthening of the C–O and C–C$^{\alpha}$ bonds), the bond alternation does not vanish and there is no significant change in the charge on the C$^{\alpha}$ atom. The electronic[28,71] and ^{13}C NMR spectra[87,90] actually agree well with the quinonoid structures.

Like the biradical structure (XXV), the zwitter-ionic structure (XXVI) can appear only in the vicinity of the saddle point, located an extremely high energy, corresponding to the rotation of the alkylidene group. Therefore, in contrast to Zarubin and Kiryushina,[89] we do not attribute the reactivity of QM for the possibility of their existence in the zwitter-ionic form.



(I) (XXV) (XXVI)

As early as 1983,[72,81] we demonstrated that, as a consequence of the isolated nature of the energy level of the lowest unoccupied molecular orbital (LUMO), the reactions of QM with nucleophiles are usually orbital-controlled. This postulate, which is of key importance for the understanding of the reactivity of QM and which has since been justified by a whole series of empirical and non-empirical calculations,[28,58,71,75,82–87] makes it possible to account for the regioselectivity and the chemoselectivity of numerous reactions involving nucleophilic addition to QM, including those which determine the nature of the pulping processes. The regioselectivity of the orbitally controlled reactions is determined by the contributions of the atomic orbitals to the frontier molecular orbital. For all the QM examined hitherto, the atomic orbital of the C$^{\alpha}$ atom makes the dominant contribution to the LUMO. Only in the case of the QM vinylogue (XI) does another reaction centre, the C$^{\gamma}$ atom, appear with a comparable contribution of its atomic orbitals to the LUMO;[28,58] experimental kinetic data are in full agreement with this assignment.[27]

Many structural influences on the energy of the LUMO of QM have now been elucidated[8,28,71,72,75,81,83] and experimental electrochemical reduction potentials have been obtained for a series of QM in good agreement with calculated data.[28,71,79] Nucleophiles can be in their turn classified in terms of their affinity for QM in conformity with the energies of the highest occupied molecular orbitals.[81,82,89] Such classifications make it possible to estimate reliably the chemoselectivity of nucleophilic addition reactions involving QM. It must be emphasised that there is a small negative charge on the C$^{\alpha}$ reaction centre and the behaviour of QM cannot therefore be explained within the framework of charge control (only the quinonoid tautomers of α-carbonyl-containing phenols are perhaps an exception[83]).

Calculations have now been carried out by the MNDO [87] and CNDO/S3 [71] methods for fairly complex QM of the β-aryl ether type and in the latter case the effect of the conformational isomerism on the electronic structure of the molecules of (*Z*)-(XXIII) ($R^1 = CH_3$, $R^2 = R^3 = OCH_3$) has been determined. This effect is fairly weak, as is, incidentally, also the effect of the appearance of the β-aryloxide substituent itself (which verifies the applicability to lignin of the conclusions obtained from calculations for simplest models). The low-intensity band for the transition involving an intramolecular charge transfer is distinguished by a high conformational sensitivity; the energy of this transition is minimal in the *C*2 and *C*5 conformers, where the two fragments are close to one another.

A similar and more complex and perhaps more important problem is that of a theoretical assessment of the interaction of QM with phenols in neutral and ionised forms. In principle, this reaction is a typical example of the donor–acceptor interaction of a π-acid (QM) and a π-base (phenol) leading to the formation of a covalent chemical bond. Clearly, its mechanism is of interest because interactions of precisely this type determine the nature of many processes leading to the cross-linking and degradation of lignin (see below). It is important to determine whether this reaction proceeds as a classical heterolytic process or whether pre-reaction electron transfer is possible. The point is that the ways in which the heterolytic and radical-ion reactions are influenced are different. A reliable answer to this question can be obtained only by examining the "macroconformations" of the reacting system with variation of the mutual orientation of the reactants and of the distance between them, because the electronic characteristics of the electrophile and the nucleophile change as they approach one another.

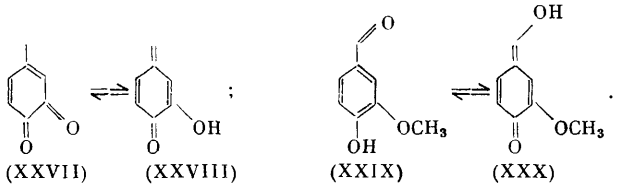
It has been shown[85,86] that the energy of the charge transfer transition in the QM–phenol and QM–phenoxide ion systems is too large for the thermal electron transfer. The addition of phenols to QM is therefore a classical polar reaction regardless of the pH. Another point is that the neighbouring location of the donor and acceptor fragments of the polymer in space makes the polymer sensitive to UV radiation, which is capable of effecting the transition of the system to the chemically excited state with charge separation. On the other hand, in the QM–9,10-anthrahydroquinone dianion (AHQ^{2-}) system the charge transfer energy is low, which indicates a high probability of electron transfer as the first stage of the dark chemical reaction. This difference between the usual phenols and 9,10-anthrahydroquinone makes it possible to explain the significant difference between the influences of the former and the latter on the pulping of wood.[86] We may note that the principal effect of the mutual approach of the reactants is an increase in the energy levels of the LUMO of the QM and that on the whole calculation for the reacting systems confirms the conclusions reached for isolated molecules.

Over short distances, electron transfer can be only a radical-ion stage of the addition reaction (it is important that the barriers to such polar reactions vary in parallel with the charge transfer energies). At the same time, one can imagine also the direct degradation of lignin by electron transfer from AHQ^{2-} or the radical-anion AHQ^{-} to the QM.[92,93] As a result of such a process, a new species is generated from the QM—the *p*-hydroxybenzyl radical-anion, which has the properties of a nucleophile and a base,

dimerising rapidly with formation of the $C^{\alpha}-C^{\alpha\prime}$ bond in the case of sterically hindered QM.[5,94] The possibility of dimerisation is explained by the fact that the negative charge in this structurally benzenoid system is located on the oxygen atom, while the spin density is concentrated on the C^{α} atom, which has a negligible charge, as in the case of the QM itself.[75] Contrary to the hypothesis of Dimmel and Shepard,[92] the direct two-electron reduction of the QM (or the one-electron reduction of the radical-anion) with formation of the corresponding dianion is virtually ruled out because of the inability of the latter to exist independently.[75]

It has been shown experimentally that the electrochemical reduction of model lignin QM of the β-aryl ether type leads to the reductive cleavage of the β-aryl ether bond.[95] The radical-anion obtained from such a QM is unstable and the principal route to its degradation is in fact the cleavage of the β-aryl ether bond. In the presence of 9,10-anthraquinone (AQ), the phenomenon of electrocatalysis is observed, i.e. electron transfer from AHQ^{-} to the QM.[95] This phenomenon is characteristic only of QM whose radical-anions are capable of rapid decomposition via the cleavage of the β-aryl ether bond: other model QM are also reduced irreversibly, but electrocatalysis in the presence of 9,10-anthraquinone does not occur.[91] An attempt has been made[88] to assess theoretically the energetics of electron transfer to QM from both reduced forms of 9,10-anthraquinone—AHQ^{2-} and AHQ^{-}. It was found that the reaction should be highly exotheric for the dianion, while for the radical-anion the difference between the energies of the initial compounds and products is low. This, however, did not enable the authors to reach a definite conclusion whether the first or second process was preferred; we may note that the very attempt at a calculation for the energetics of reactions with participation of ions without taking into account solvation is incorrect.

In conclusion we may mention that the prototropic (phenol—quinonoid) tautomerism of QM has been the subject of a theoretical study in recent years. In connection with the problem of the physiological activity of dopamine, a non-empirical calculation (STO-3G) has been carried out with complete optimisation of the geometry of the tautomers (XXVII) and (XXVIII):[96]



(XXVII) (XXVIII) (XXIX) (XXX)

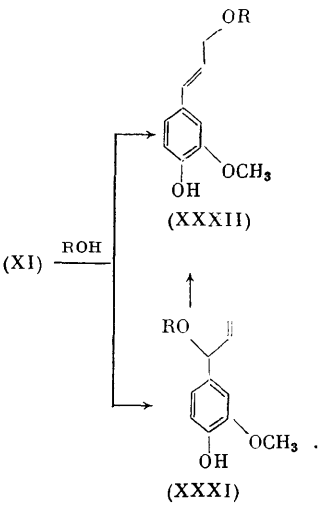
The appreciable energy difference in favour of the *o*-quinone (XXVII) and the large dipole moment of the latter, ensuring stabilisaiton in solution, led the authors to the conclusion that the fraction of the QM (XXVIII) is negligible. The situation is the same also as regards the tautomerism of *p*-hydroxycarbonyl compounds, for example (XXIX)⇌(XXX): for typical model compounds of lignin, the equilibrium is always displaced towards the phenol.[83] Nevertheless the possibility of tautomerism must be taken into account in estimating the reactivity of model compounds of lignin in conformity with the Curtin—Hammett principle.

IV. Chemical reactions

There is no doubt that in the chemistry of wood nucleophilic addition, in which these compounds play the role of substrates, is of greatest importance among the reactions of QM. The addition of water, alcohols, and phenols to QM is of interest in connection with the analysis of the lignification process and hence also of the primary structure of lignin. Another (hitherto completely undeveloped) applied aspect of this reaction is that of the chemistry of organic solvent pulping of wood in alcohols and water—alcohol mixtures.

The kinetics of the addition of hydroxylated compounds to QM have been investigated[49,97—101] using a fairly wide set of reagents but for an extremely limited number of QM. The interpretation of the results and the conclusions about the mechanism of the addition reaction reached in some of the publications[49,98,99] must be treated with caution, since the products were not identified. On the other hand, the quantitative data concerning the stability of QM in various media (in particular as a function of pH) are of undoubted interest. In aqueous solutions, the rate of reaction of the QM (XI) increases with both decrease and increase in pH, the nature of the kinetic curves agreeing with the expected change in mechanism (the primary step is the addition of a proton at low pH and the addition of a hydroxide anion at high pH; in neutral media, one can postulate a concerted nucleophilic and electrophilic attack by water molecules).[49]

Compared with the data of Hemmingson and Leary,[49] the conclusion that the reactivity of QM is low in relation to the SH^{-} and OH^{-} ions, based on the fact that solutions of QM in solvents immiscible with water are stable in contact with aqueous NaOH and Na_2S solutions, appears paradoxical.[102] In fact Ralph's interpretation[102] is erroneous; the observed behaviour apparently arises simply from the heterophase nature of the systems considered.



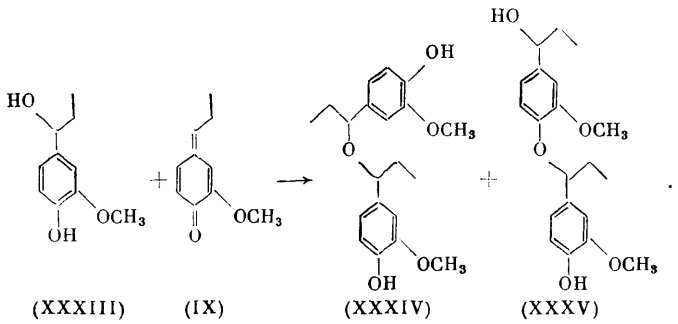
(XXXII) (XI) ROH (XXXI)

The fact that the mechanisms of the addition reactions in neutral and alkaline media are different explains also the characteristic "contradiction" between the theory and experiment in the treatment of structural influences on the reactivity of QM. It is not difficult to understand why the appearance of methoxy-groups in the ring lowers the rate of addition;[49] the reason lies in the electron-donating effect of the substituent. On the other hand, an increase in the length of the conjugation chain lowers the energy level of the LUMO, which should entail an increase in the reactivity in one-electron reduction and orbital-controlled nucleophilic addition reactions.[28] Electrochemical data have shown that such is entirely the case in the reduction reaction. As regards addition, one can confidently assume that this also applies under pulping conditions, where highly nucleophilic ions behave as active agents. On the other hand, in a neutral medium the rate of addition of hydroxylated compounds

falls sharply on passing from QM to their vinylogues.[29,100] Hence it follows that in a neutral medium the reaction mechanism involves the protonation of the carbonyl group as the first stage and not attack on the C^{α} atom. In general, one may conclude that the reactivity of QM in a neutral medium varies in opposition to their stability (an increase in stability may be achieved both by introducing electron-donating substituents and by increasing the conjugation chain length).

Analysis of the orders of the reactions of QM with various hydroxylated compounds in a neutral medium leads to the conclusion that a complex, possibly concerted addition mechanism operates,[99] but kinetic data alone are insufficient for any reliable conclusion. According to Leary et al.,[99] acids add faster than alcohols and only in the former case can one trace the parallel variation of the rate of reaction and the pK_a. In the latter case, a distinct dependence of the rate of addition on steric factors is observed (see also Apushkinskii et al.[100]). Water adds to QM fairly slowly; a sharp acceleration of the process is achieved by adding an acid catalyst.[101] The introduction of type (XI) QM vinylogues into the reaction usually leads to a mixture of 1,6- and 1,8-adducts.[27,49,97] Kinetic control of the addition reactions of both neutral hydroxy-compounds and their ionised forms (OH, OCH_3^-) leads to the preferential formation of the thermodynamically less stable product (XXXI); in an acid medium, equilibrium is readily established and the fraction of the product (XXXII) increases.[27,97] We may note that reduction by lithium tetrahydroaluminate, which in terms of its mechanism is also a nucleophilic addition reaction, affords similarly a mixture of the 1,6- and 1,8-hydrogenation products with the former predominating.[29]

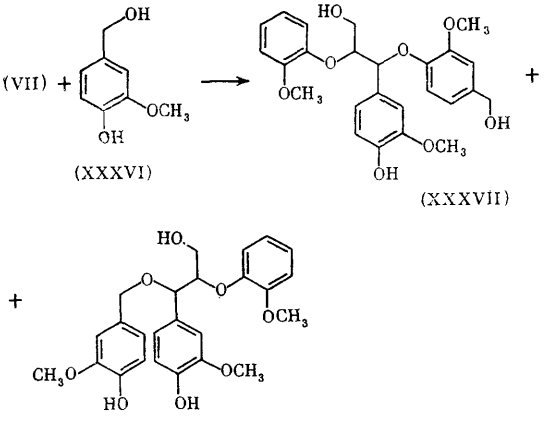
An important factor determining the results of the competitive addition of hydroxy-compounds to QM is the stability of the product. For example, under lignification conditions, the rate of hydrolysis of β-aryl ethers can exceed by a factor of 400 the rate of hydrolysis of β-alkyl ethers.[103] This is an additional factor (together with the higher rate of addition of alcohols to QM compared with phenols), which explains why the reactions of the model lignin QM with vanillyl[104] and dihydroconiferyl[103] alcohols afford dialkyl and not alkyl aryl ethers. The addition of phenols to QM in an anhydrous medium makes it possible to obtain α-aryl ethers,[100,101,105] but in aqueous solution containing an alcohol and a phenol, the alcohol addition product is formed exclusively according to Hemmingson and Leary.[104] We may note, incidentally, that the main factor is undoubtedly kinetic: according to our data, the rate of addition of alcohols to QM is much higher than that of phenols.[100] We have established by ^1H NMR spectrscopy that in an anhydrous medium guaiacylpropanol (XXXIII) adds to the corresponding QM (IX) with the preferential formation of the product (XXXIV).



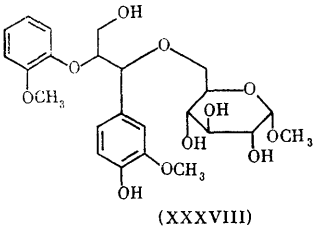
(XXXIII) (IX) (XXXIV) (XXXV)

The alternative product (XXXV) is formed in an insignificant amount, corresponding to the ratio of the rates of reaction of phenol and isopropyl alcohol with the QM (IX). Taken together, these data show that the fraction of benzyl ether linkages of the type $C^{\alpha}-O-C^{\alpha}$ and $C^{\alpha}-O-C^{\gamma}$ in native lignin must be much higher than the fraction of the α-aryl *p*-hydroxybenzyl ether fragments.[1,103]

On the other hand, according to Brunow et al.,[101] the product of the addition of vanillyl alcohol (XXXVI) to the β-aryl ether type QM (VII) is predominantly the *erythro*-benzyl aryl ether (XXXVII) in both non-aqueous and neutral aqueous organic media. Incidentally this conclusion is based on the composition of the products isolated from the reaction mixture by column chromatography in a fairly low yield.



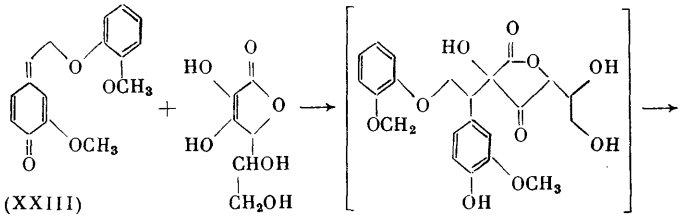
The addition of sugars and related compounds to QM has been investigated in connection with the problem of the formation of lignocarbohydrate linkages. It was shown that D-glucose, methyl α-D-glucoside, and D-glucuronic acid react with β-aryl ether type QM via the C^{α} atom with formation of the corresponding ethers and esters, for example, (XXXVIII).[106–109] It is significant that the nucleophile competing with sugars *in vivo* (water) suppresses to an appreciable extent the interaction of QM with glucose but not with glucuronic acid.



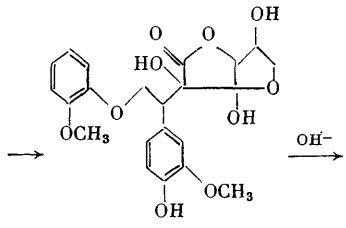
(XXXVIII)

Yet another interesting aspect of reactions of this type is associated with the delignification of wood. It has been found that reducing sugars and their derivatives are capable of cleaving β-aryl ether linkages in phenolic model compounds of lignin under the conditions of alkaline pulping.[110–112] The stability of the methylated models supports the view that this reaction proceeds via a QM intermediate, while the high reactivity of ascorbic acid and at the same time the inactivity of non-reducing sugars are evidence for the involvement of the enediol form of the cleaving agent. Indeed, under neutral conditions, the reaction of the QM (XXIII) with ascorbic acid afforded the adduct (XXXIX), which on heating in

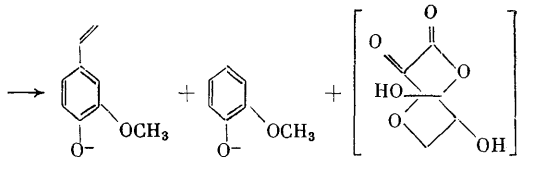
aqueous alkali gave rise to the products of the cleavage of the β-aryl ether — guaiacol and vinylguaiacol:[110]



(XXIII)

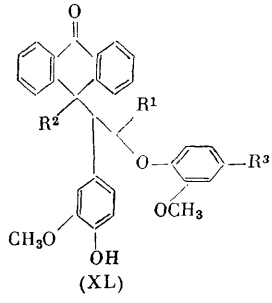


(XXXIX)



It is easy to note the close analogy between the mechanism of this reaction and the heterolytic mechanism of the action of anthrahydroquinone.[9] The difference between the structures of the adducts (XXXVIII) and (XXXIX) is noteworthy: the $C^{\alpha}(QM)-O-C$ linkage is formed in the former case and the $C^{\alpha}(QM)-C$ linkage is formed in the latter. The NMR spectra published in the literature[108,110] give rise to no doubts about the assignment of the structures, but we believe that the interpretation from a single standpoint of the mechanism of the interaction of QM with carbohydrates and related compounds requires further accumulation of experimental data. At any rate, it can now be postulated that, together with ether and ester linkages between components of the lignocarbohydrate complex (LCC), there are also carbon–carbon bonds which are readily hydrolysable in alkaline solutions.

In recent years studies on nucleophilic addition to QM received a fresh stimulus in connection with the investigation of the mechanism of the anthraquinone pulping of wood. In connection with this problem, the range of nucleophiles has expanded, which led to new fundamentally important results. The adducts (XL) of anthrahydroquinone and related compounds with model lignin QM[9,113–124] and lignin itself (under the conditions of the formation of QM *in situ* [113,125]) were obtained under mild conditions.



(XL)

$R^1 = H, CH_3, CH_2OH$; $R^2 = H, OH, CH_3\ C_6H_5$; $R^3 = H$, lignin.

Such compounds (R^2 = OH) readily undergo the Grob heterolytic fragmentation in aqueous alkali, which results in the cleavage of the β-aryl ether bond and the regeneration of anthraquinone.[9] The high regio- and stereo-selectivities of the addition are striking: in the case of model compounds, a single adduct is formed as the *threo*-isomer (R^2 = H, OH),[114,118] while for lignin the formation of the *threo*-isomer is preferred.[113] Sterically hindered derivatives of anthrone give rise to a mixture of the *threo*- and *erythro*-adducts (XL, $R^2 = CH_3, C_6H_5$), under the conditions of kinetic control the *threo*-isomer being formed preferentially; an increase in the reaction time in an aqueous alkaline solution leads to an increase in the fraction of the *erythro*-isomer, which, however, rarely reaches one half.[119,122] Such behaviour indicates the reversibility of the addition and the ease of the dissociation of the adducts in aqueous alkali. This is also indicated by other data.[126,127]

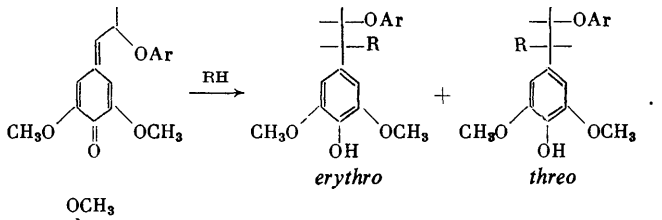
α-Aryl ethers are known to be readily converted into QM in aqueous alkali even at room temperature.[128] Therefore the introduction of dehydrodiisoeugenol and related compounds into the reaction with anthrone and anthrahydroquinone under these conditions leads to the formation of the corresponding adducts, but in the given instance with a distinct preference for the *erythro*-isomer.[115] We may note incidentally that in the case of β-aryl models containing the hydroxymethyl group the splitting off of formaldehyde is so fast that the formation of the corresponding product (stilbene) predominates over the formation of the adduct.[115]

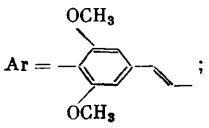
Other nucleophiles, such as amines[23] and water (in dioxane),[129] afford *threo*-adducts preferentially. Such stereoselectivity is actually the property of the QM themselves: in an acid medium, where the reaction probably proceeds via a carbonium ion, selectivity falls sharply.[23,114,129] The regioselectivity of the addition to QM can be logically accounted for within the framework of ideas about orbital control (see above) but as regards stereoselectivity the situation is more complex. In principle, in this case one might begin with modern ideas about the hindrance of reaction centres[130] and the conformational composition of the QM attributed to them by Ralph and Adams.[24] The trouble is that the ideas of Ralph and Adams (see also Chum et al.[50]) are most probably erroneous (see above). The stereochemistry of the formation of the adducts therefore still awaits its elucidation. It has been shown that the action of *erythro*-phenol-alcohols with bromotrimethylsilane[23] gives rise exclusively to the *threo*-bromo-derivative, which is converted into a 1 : 1 mixture of *erythro*- and *threo*-derivatives in 0.5 h.[102] On this basis, the author[102] put forward the hypothesis that S_N2 substitution takes place in this case. It is much more likely that the reaction proceeds via a carbonium ion.[248] The related reaction of acetyl halides with *p*-hydroxybenzyl alcohols, affording *p*-acetoxy-α-halo-derivatives in a quantitative yield under mild conditions, is known.[131] We may note that the latter derivatives are convenient synthons for the generation of QM *in situ* in an alkaline medium.[123,124,132]

General rules which would make it possible to predict the stereochemistry of the product of the addition to QM do not exist. Nevertheless, this question is important if only because of its relation with the stereoisomeric composition of the lignin chains, since the lignification process proceeds with participation of QM as intermediates. It is therefore significant that, according to Nakatusbo and Sato[21] and Dyall and Winstein,[29] the addition of water to the QM (VII) gives rise to the ratio *threo* : *erythro* = 7 : 3 in dixoane and 1 : 1 on catalysis by HCl. At the same time, carboxylic acids afford predominantly the *erythro*-diastereoisomers in their reactions with QM.[21,26,129] Kinetic data[99] make it possible to postulate a trimolecular reaction in the latter case and to relate the

anomalous stereoselectivity to the specific formation of intermolecular hydrogen bonds in a pre-reaction complex;[23,133] incidentally, such explanations have not been supported by serious evidence. The involvement of hydrogen bonds in the transition state has been discussed also in an attempt to account for the preferential formation of the *threo*-isomer in the reaction of QM with water.[21]

We may draw attention to the fact that the conclusion that one of the stereoisomers is slightly preferred is frequently reached by comparing their final yields (see, for example, Zanarotti[26]). Naturally, such results are unreliable: the correct procedure involves the analysis of spectroscopic data for the reaction mixtures. In this connection, it is not clear whether a slightly greater amount of the *erythro*-isomer is really formed in the addition of water in the presence of HCl to the β-aryl ether QM in the case of the syringyl derivatives while for guaiacyl QM the isomers are present in equal proportions.[26] The conclusion that the *erythro*-adducts of a whole series of nucleophiles are preferred under the conditions of acid and base catalysis[26] appears reliable, since the preference is fairly distinct:

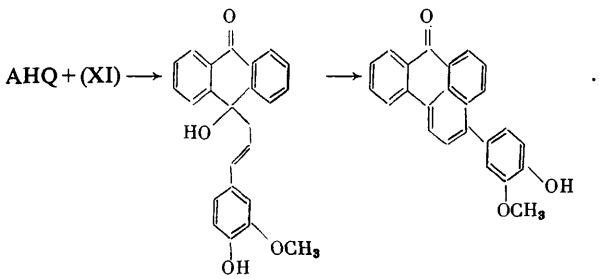




R=OCH_3, CH_3COO, C_6H_5O, $(CH_3CO_2)_2CH$, 2,4,6-$(CH_3O)_3C_6H_2$.

It may be that the discrepancy between data for the stereoisomeric composition of the products of the nucleophilic addition to QM depends on whether thermodynamic or kinetic control operates in the course of the reaction (this depends on the reactants and to a greater extent on the conditions).

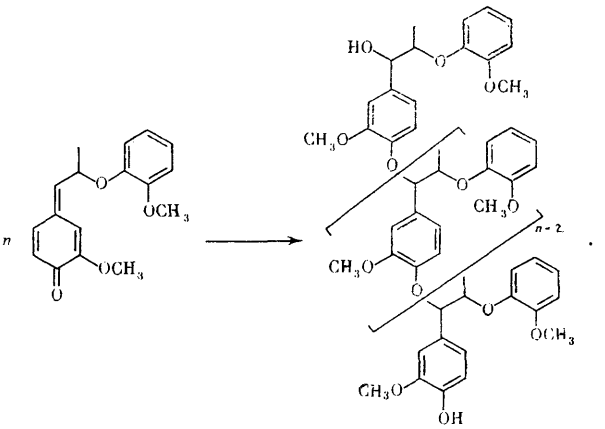
The addition of anthrone and anthrahydroquinone to QM vinylogues takes place with formation of the C(10)–C^{γ}(QM) bond;[116,125] under pulping conditions, such products are irreversibly converted into condensed systems:[9]



We may note further that in the reaction of anthrahydroquinone with QM there is a possibility of the formation also of a small amount of the product of hydroxyalkaltion in the β-position in the aromatic ring; such substances have been found also in the anthraquinone pulping liquors.[9,123]

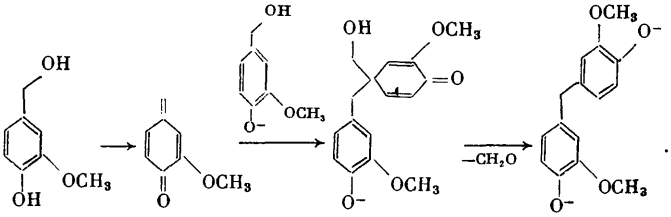
It has been recently shown in relation to the addition of primary amines that the reactivities of (*E*)- and (*Z*)-QM are different: for the (*Z*)-isomer, the addition is 1.4 times faster.[59] This observation throws new light on the significance of the studies on the stereochemistry of QM described above.

It is well known that a convenient method of modelling lignin as a polymer involves the use of a dehydropolymer, in the formation of which QM intermediates apparently play a role (see below). A different type of a model regular polymer can be obtained directly from QM by polymerisation initiated by a base or electrochemically:[50,102]



In terms of its mechanism, such polymerisation also represents nucleophilic addition. In the presence of alkali metal cations, the addition reaction is controlled kinetically and the *threo*-isomer is formed preferentially; in the presence of bulky tetraalkylammonium cations, thermodynamic control operates and preferential formation of the more stable *erthro*-product is observed (the possible explanation of this reaction is provided by the difference between the degrees of chelation of the cations).[50] A polymer, in all probability with a different structure, is formed on oxidation of guaiacylacetone derived from the corresponding QM.[17]

Under the conditions of alkaline pulping, *p*-hydroxybenzyl alcohols, which are capable of forming QM, readily undergo self-condensation with formation of oligomeric products.[104,126,134] This process, which simulates one of the possible pathways leading to the cross-linking of lignin, apparently also takes place as nucleophilic addition to QM *in situ*, for example:



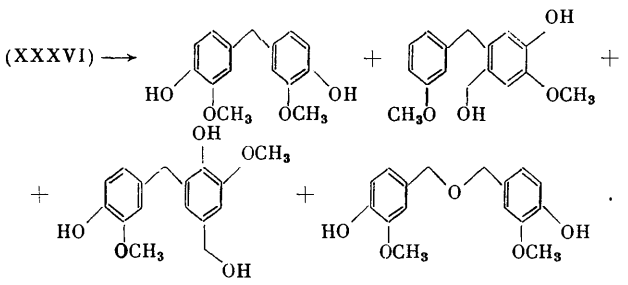
(XXXVI)

Similar reactions may be observed also in the generation of QM in another way, for example from sulphones.[135]

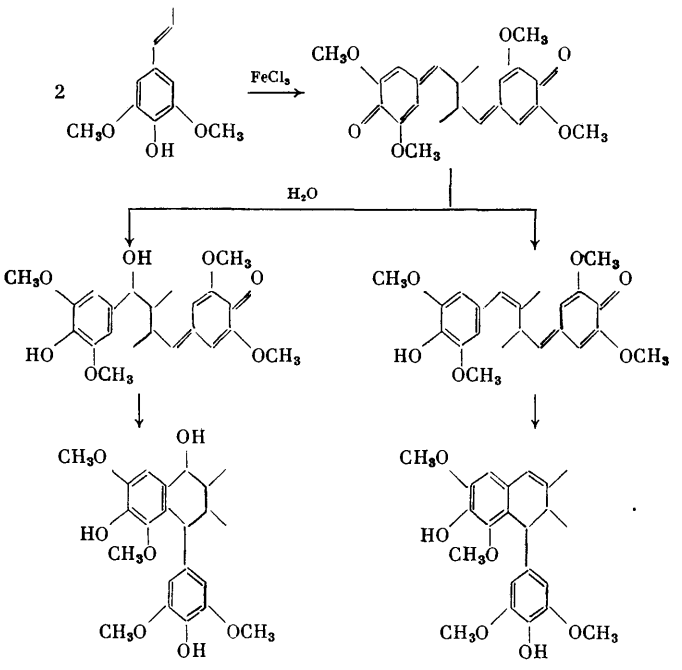
In the presence of anthrahydroquinone, this reaction is suppressed[136] and the formation of bibenzyl derivatives is observed—these may be the products of the "head to head" dimerisation of the radical-anions formed from the QM.[126]

We may draw attention to the fact that processes similar to alkaline oligomerisation take place also in neutral aqueous or

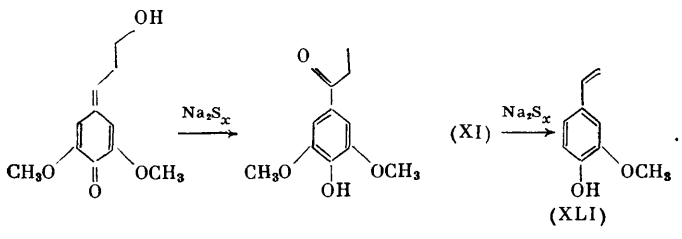
aqueous alcoholic media[104] as well as in the solid phase on silica gel[137] (simulation of the heterogeneous medium in plants), constituting therefore one of the possible lignification pathways:



An interesting example of intramolecular cross-linking has been described[34] (the reaction mechanism has not been reliably demonstrated by the hypotheses put forward are well founded):

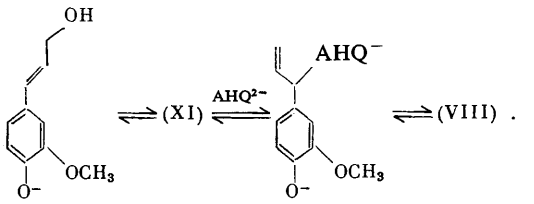


Depending on the nucleophile, the addition may be the first stage of a more complex process. Whereas sodium sulphide affords the corresponding thiol in the reaction with QM, the reaction of QM with sodium polysulphide in aqueous solution affords oxidation products even at room temperature; in the latter case the additon is merely the first undetected stage:[138]

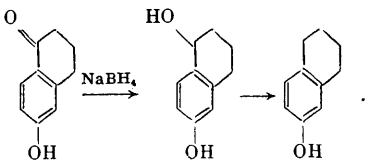


Dimethyl sulphoxide reacts similarly with QM.[132]

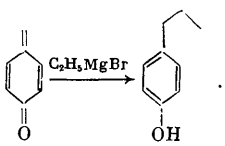
The QM reduction reactions have also been frequently discussed. On the basis of the dynamics of the accumulation of coniferyl alcohol (XIV) and isoeugenol (VIII) during anthraquinone pulping, it has been suggested that compound (VIII) is actually obtained in the pulping process from compound (XIV) by direct reduction of the latter to a QM:[139]



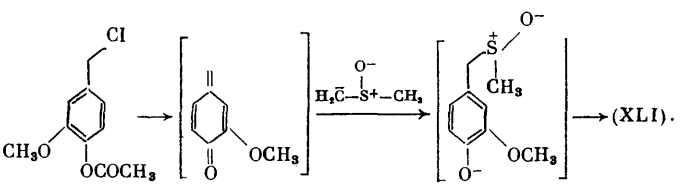
The increase of the fraction of isoeugenol among the coniferyl alcohol reaction products in aqueous alkali after the addition of anthrahydroquinone agrees in principle with this hypothesis.[140,141] However, the interaction of vanillyl alcohol (XXXVI) and apocynol (XLII) with anthrahydroquinone on heating in aqueous alkali leads not to the reduction of the corresponding QM [142] but to the formation, as shown in the first example, of adducts.[136] Apparently the hydride transfer reactions are nevertheless not characteristic of anthrahydroquinone. Reagents such as lithium tetrahydroaluminate and sodium tetrahydroborate can naturally reduce the QM directly.[26,27,29] This apparently constitutes the mechanism of the familiar reaction of alkyl hydroxyphenyl ketones with sodium tetrahydroborate:[142,143]



The use of organometallic compounds as nucleophiles makes it possible to obtain alkylphenols with a lengthened chain via QM:[43]

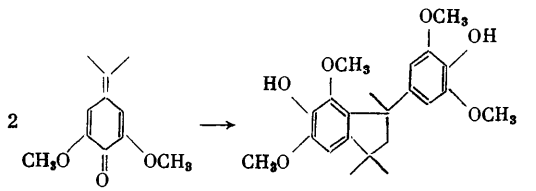


An increase in the length of the chain can be achieved also by the nucleophilic addition of the dimsyl anion (generated from dimethyl sulphoxide and sodium hydride) to QM:[132]

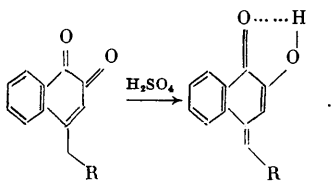


We may note that the difficulty of experiments with unstable compounds such as QM sometimes gives rise to doubts about the reliability of the results. This applies to many reports of the formation of "head to head" QM dimerisation products, for example that of Leray and Thomas.[144] The mechanism of the QM dimerisation reactions, similar to the reaction on treatment with

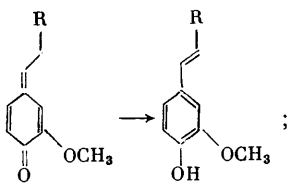
triethylammonium acetate presented below, is frequently osbscure and hardly represents the direct coupling of two QM molecules:[145]



Tautomeric transformations constitute a special type of reactions of QM. We mentioned above that the phenol–quinonoid tautomerism is usually manifested only in the case of sterically hindered compounds; for typical model compounds of lignin, aromatisation is the driving force of the rearrangement and the QM are usually transformed irreversibly into related phenols but not conversely. Condensed systems are an exception. Thus on treatment with a catalyst, 4-benzyl- and 4-alkyl-1,2-naphthoquinones are converted into QM:[146]

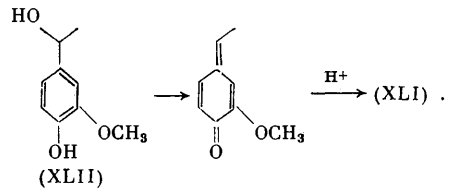


A typical rearrangement of QM is their irreversible stereoselective conversion into (*E*)-α-alkenylphenols, for example:[100,147]

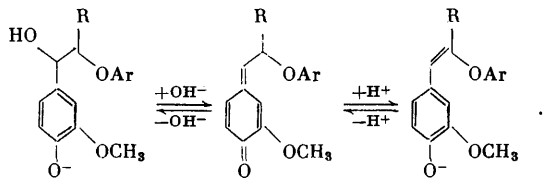


R = H, CH_3, C_6H_5, CH_2Br.

This reaction was observed previously only under the conditions of acid–base catalysis (the involvement of water was postulated at the neutral pH).[145,148,149] Thus, whereas primary and secondary amines add readily, like ammonia, to QM, treatment with tertiary amines actually leads to isomerisation.[148] Incidently, it has been found that this isomerisation also proceeds in a neutral solvent at a rate comparable to the rates of addition of alcohols and phenols (in equimolar amounts).[100,147] It is of interest to note that conversion into alkenylphenols is in essence the only pathway to the degradation of the simplest model lignin QM in the absence of other reagents.[147] Such a reaction provides a method of synthesis of stereoisomerically pure alkenylphenols, which can be in their turn quantitatively converted into the initial QM (see above). QM can isomerise also under pupling conditions. According to kinetic data, *p*-hydroxybenzyl alcohols with β-aryl ether substituents are in fact converted in this way into enol ethers.[150,151] An example of the simplest model experiment is provided by the heating of an equimolar mixture of apocynol (XLII) with anthrahydroquinone-monosulphonate in aqueous 1 M NaOH (137 °C, 1 h).[142] The expected products ethylguaiacyl (the QM reduction product) and vinylguaiacyl (XLI) (the QM isomerisation product) were isolated:



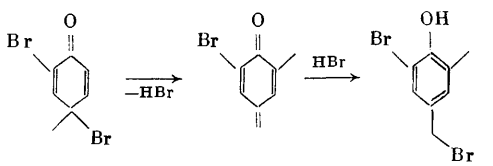
The authors[142,152] postulate the following equilibrium under pulping conditions:



This is supported by the similarity of the cleavage products in the anthraquinone pulping of phenol-alcohols and the corresponding enol ethers and also the (*E*,*Z*)-isomerisation of the latter under these conditions.

It is of interest to note that the conversion of many model compounds of lignin into isoeugenol (VIII) via a QM intermediate is achieved with formation of precisely the (*E*)-isomer;[138] the cleavage of the β-aryl ether linkage with participation of anthrahydroquinone[122] or anthrone[120] also belongs to reactions of this class. The factors which determine the stereochemistry of the product have no bearing on the stereochemistry of the intermediate adduct despite the views of the author.[122]

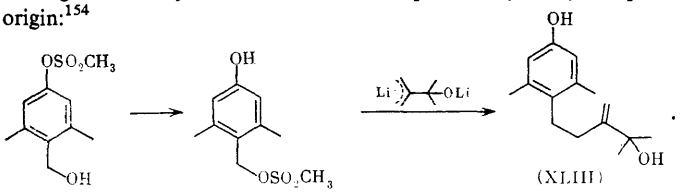
QM are capable of acting as isomerisation intermediates but this time of a completely different kind[153] (cf. Brunow and Sumelius[32]):



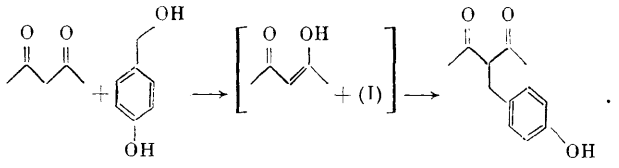
In recent years, there has been a growth of interest in organic chemistry in QM as promising synthons.[5,26,27,132,154–158] We should like to draw attention to studies unrelated to the chemistry of wood; the use of their results may lead to the discovery of new procedures for the specific transformation of lignin.

The high electron affinity of QM is responsible for the possibility of their copolymerisation with electron-donating monomers. Thus the 1,6-addition of styrene to α,α-dicyanoquinone methide takes place readily with formation of a linear regular copolymer.[74] The characteristic addition reactions make it possible to use QM in the synthesis of lignans and neolignans[26,27,159–161] and numerous compounds with *p*-hydroxybenzyl groups. It is most convenient to use QM *in situ*, whereupon *p*-hydroxybenzyl alcohols or, what is much more convenient, their derivatives, which are capable of readily affording QM under the reaction conditions, enter into the reaction directly. Such derivative may be esters,[27,162] halides,[23,123,126,132,163] methanesulphonates,[154] benzenesulphonates,[164] aminophenols,[163,165] etc.[52,166]

As an exotic example, we may quote the following reaction leading to the synthesis of a natural product (XLIII) of plant origin:[154]

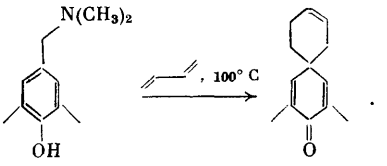


The possibility of the formation of a QM as an intermediate has been used also in the development of a method for the removal of a protecting group in the series of benzyl ethers.[131] *p*-Hydroxybenzylation of the readily enolisable 1,3-diketones takes place on heating in water (it is striking that benzyl alcohol, which is incapable of being converted into a QM, does not enter into this reaction):[155]



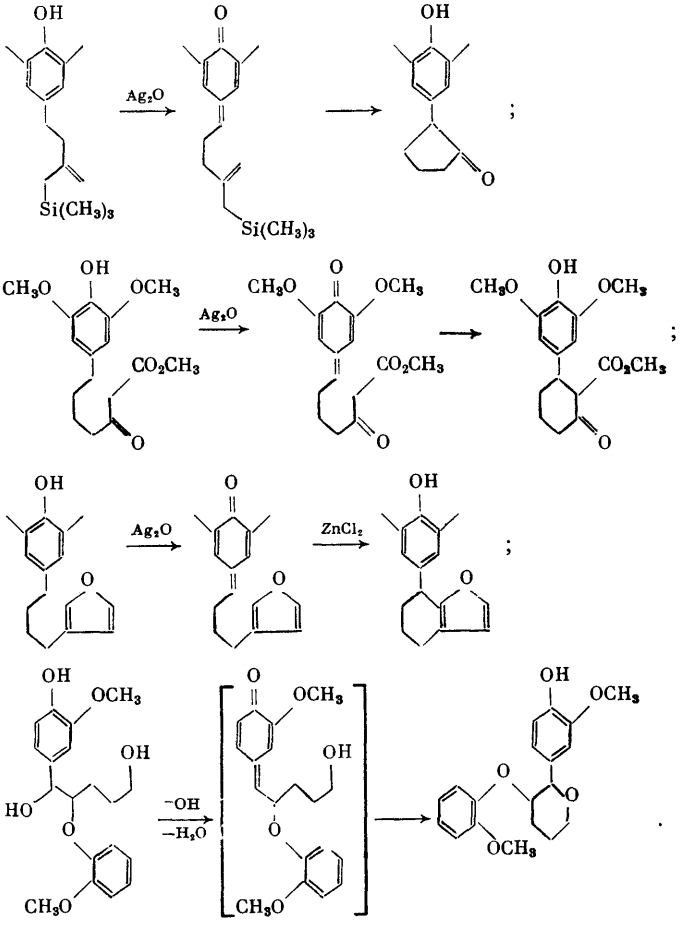
In the case of QM vinylogues, similar reactions with acetylacetone and nitroethane afford mixtures of regioisomers.[27] There is a reaction, involving intramolecular addition to the C^{α} atom, which leads to various carbocycles and heterocycles[111,167,168] (examples are given in Scheme 1).

QM can also enter into cycloaddition reactions as dienophiles and dienes. Attention should be drawn to the fact that the Diels–Alder reaction makes it possible to use specific trapping agents for QM and gives rise to prospects of obtaining unusual lignin derivatives. The following reaction may serve as an example of the use of butadiene as a trapping agent for *p*-QM formed *in situ*:[165]

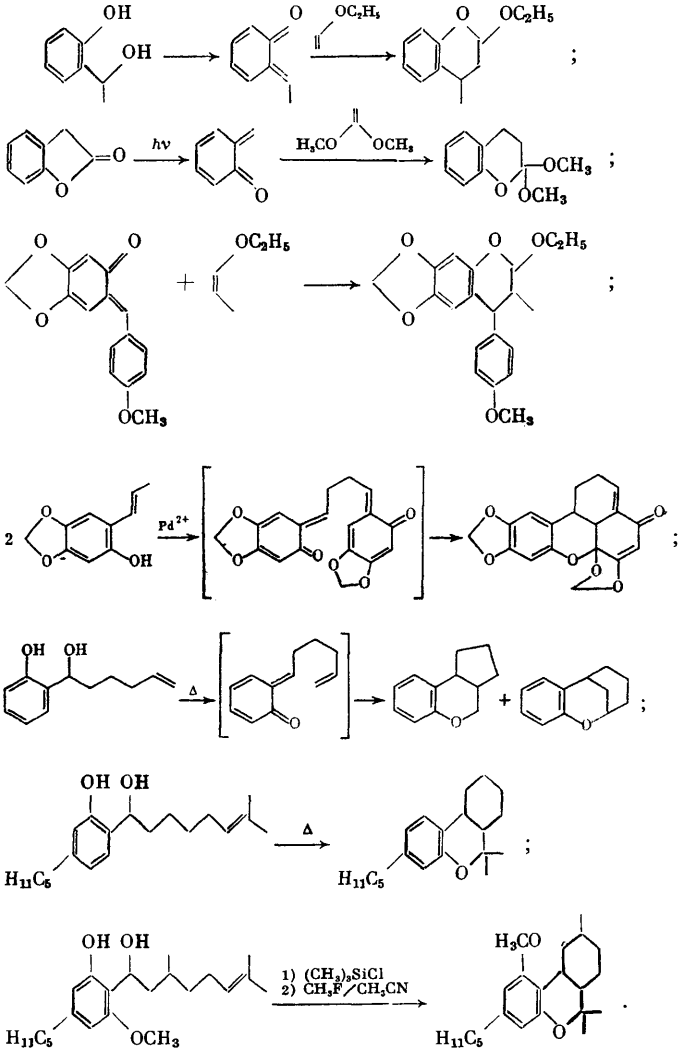


Addition to the exocyclic double bond of the QM takes place according to the idea of the orbital control of the reaction. Examples of reactions with participation of *o*-QM, also preferentially *in situ*,[30,52,166,169–175] are given in Scheme 2.

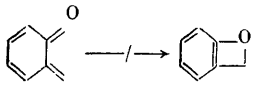
Scheme 1



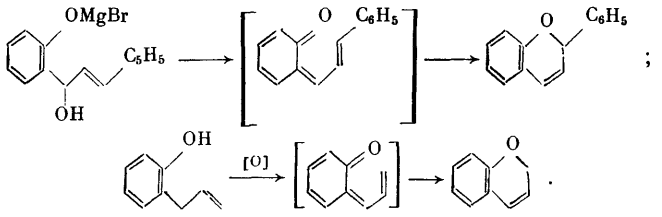
Scheme 2



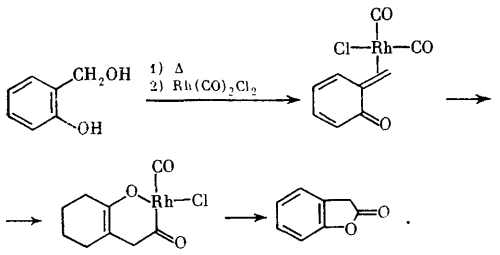
These examples refer to intramolecular cycloaddition. We may note that direct cyclisation with formation of oxetans is not characteristic of *o*-QM, in contrast to, for example, *o*-quinodimethanes:[56]



On the other hand, examples of the formation of a six-membered ring are known:[30,176]



An intermolecular cycloaddition reaction, leading to trimers, has also been noted for the simplest *o*-QM.[44,45,173,175,177] An interesting example of a reaction of QM, proceeding via an organometallic complex, which was not isolated, has been described:[178]



The properties of *o*-QM as dienes are such that the [4 + 2]-cycloaddition reaction with dienophiles having an enhanced electron density at the multiple bond, such as keten acetals and vinyl ethers, is preferred; the reactions with alkenes having weak electron-donating let alone electron-accepting substituents, do not take place quite so readily.[172]

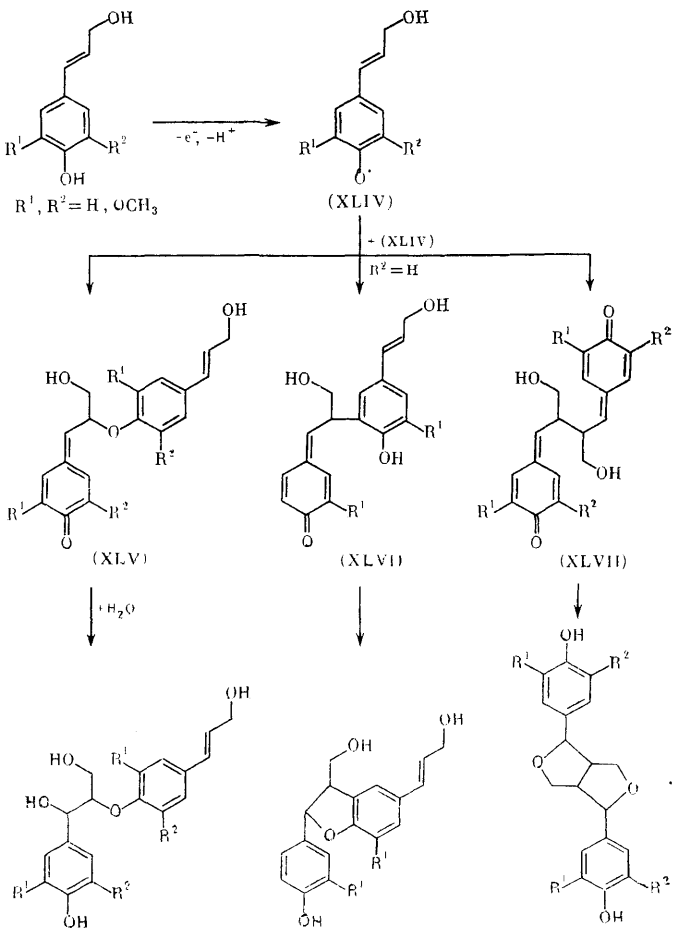
V. Quinone methides and the structure of lignin

The biosynthesis of lignin is traditionally represented as a dehydrogenation polymerisation process, during which QM, playing the role of intermediates, are formed. These views arose as a result of a considerable number of early studies and have been reflected in familiar monographs.[2,3,179] In the 1950's–1960's, it was sometimes reported that the formation of QM had been detected directly in processes modelling lignification;[1] these reports appear doubtful nowadays. The idea that QM intermediates participate in lignification processes is based mainly on the analysis of oligomeric products of model experiments on the oxidative polymerisation of compounds considered as lignin precursors.

According to Freudenberg and Neish,[179] lignin is formed via the stage involving the dehydrogenation of low-molecular-weight precursors with formation of the corresponding radicals whose dimerisation actually constitutes the first stage of the polymerisation. The rules governing the recombination of aryloxyl radicals are well known. This process leads to the formation of QM dimers, whose structure is determined by the selectivity of the dimerisation reaction. *p*-Hydroxyphenylallyl alcohols have been considered as the main lignin precursors. This agrees well not only with the available information about the structure of native lignin but also with the latest data on the ionisation potentials of the possible precursors:[180] indeed, phenols with an α-unsaturated side chain should in fact exhibit the highest reactivity in oxidation in neutral and weakly acid media; this preference is very pronounced. The regioselectivity of the dimerisation is consistent with the familiar distribution of spin density in the radicals (XLIV),[181,182] which is manifested by the formation of the dimers (VIII) and (XLV)–(XLVII) (in the form of racemic mixtures).[34,183] We should warn, incidentally, against attempts to relate directly the spin density to the fraction of particular structures in the polymer. The latter is to a large extent determined by steric factors and the relative stabilities of the products.[181]

The QM (XLV)–(XLVII) are converted into phenolic dilignols as a result of a nucleophilic addition reaction (the reaction with water affords β-aryl ether structures; an intramolecular reaction gives rise to cyclic systems). Examples of the possible processes are given in Scheme 3.[1,184,185]

Scheme 3



Subsequent growth of the macromolecule involves the oxidation of the dilignols to the corresponding radicals and the reactions of the latter with one another and with other radicals. This can also result in the formation of QM.[183] According to Forss and Fremer,[184] the

macromolecule is formed from the dilignols via the following stages (only the stages with participation of QM are listed):

dehydrogenation of oligolignols, which subsequently react with one another and with monolignols, affording biaryl derivatives, diaryl ethers, and QM;

the addition of phenols to QM, in which oligomeric lignols participate without losing a hydrogen atom;

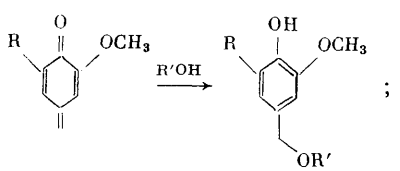
addition of carbohydrates to QM, which results in the formation of lignocarbohydrate linkages;

polymerisation of QM leading to linear aryl benzyl ethers.

Two mutually complementing models of lignification exist—bulk and endwise models; the true process can be only of a mixed kind.[184]

We emphasise that the existing ideas about lignification should be regarded merely as a hypothesis but a hypothesis which is fairly logical and which works well. Within its framework, QM play an unusually great role as intermediates. Thus about 70% of the interunit bonds in conifer lignin are formed as a result of β-coupling[185] and any radical reaction involving the β-position yields an intermediate QM which is subsequently converted into a more stable system. Among the characteristics of the reactions of QM, nucleophilic addition to the C^{α} atom is the most important reaction (if not the only one) for lignification.[1] Plant tissues contain simultaneously a multiplicity of compounds capable of acting as nucleophiles (water, carbohydrates, uronic acids, and alcoholic and phenolic groups of the lignin being formed). Nucleophilic addition ensures the formation of typical lignin structures: *p*-hydroxybenzyl alcohols, ethers, and esters. Therefore studies on the kinetics and mechanisms of the above reaction are of primary importance for the understanding of the structure of wood: thus whatever nucleophile adds preferentially to the QM, it determines the frequency of various types of benzyl structures in the final polymer.

The situation as regards the relative nucleophilicities of the solution components in the wood cell is fairly complex. We have already mentioned the mixed order of the addition reaction, indicating its complex mechanism. The dependence of the rate of reaction on the pK_a of the hydroxy-compound[179] seemingly shows that the addition of acids should proceed more readily and hence that one should expect a higher content of ester linkages in the lignocarbohydrate complex compared with ether linkages.[2] At the same time, it has been noted[186] that without a catalyst coumaric and ferulic acids react fairly slowly with QM (in the presence of tetrabutylammonium hydroxide, esters are formed instantaneously and quantitatively). The experiments on the competitive addition of nucleophiles such as ethanol, water, and acetic acid[98] showed that the reaction of a model QM with their isoequimolar mixture afford predominantly benzyl ethyl ether:

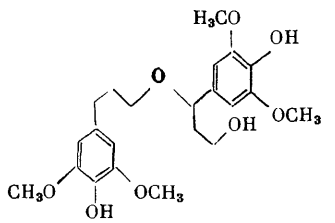


;

R = $C(CH_3)_3$, R′ = H, C_2H_5, CH_3CO.

At a higher pH (4–6), the concentration of the more nucleophilic CH_3COO^- ion increases and benzyl acetate becomes the main product, although benzyl ethyl ether is formed in appreciable amounts. In an alkaline medium, the presence of the strong nucleophiles HO^- and $C_2H_5O^-$ again leads to a low yield of the ester. One may conclude that in the neutral or weakly acid medium, characteristic of plant tissues, ester type lignocarbohydrate linkages are formed most readily, although a considerable proportion of ether linkages should be present together with the latter. It is significant that, by virtue of its weaker nucleophilic properties, water does not interfere with the formation of the lignocarbohydrate complex. However, an excess of water in the presence of a deficiency of other nucleophiles makes the formation of linear chains with α-alcoholic groups the main reaction pathway of primary QM; we may note that similar structures arise also in the hydrolysis of benzyl ether linkages, which takes place readily.[179]

The nucleophilic addition of lignin fragments to QM with participation of alcoholic, phenolic, and carboxylic acid groups of the former should be regarded as one of the important routes to the formation of lignin.[1,101,183] Unfortunately, the instability of the $C^{\alpha}-O-C^{\gamma}$ and $C^{\alpha}-O-C(4)$ bonds formed gives rise to serious difficulties in securing evidence for their presence in the native polymer; early studies devoted to the formation of such bonds require additional tests. However, the isolation of the dimer (XLVIII) from the products of the hydrogenolysis of lignin[1] appears to constitute convincing evidence for this; the presence of bonds of this kind agrees also with the familiar results of computer simulation of the biosynthesis lignin.[187]

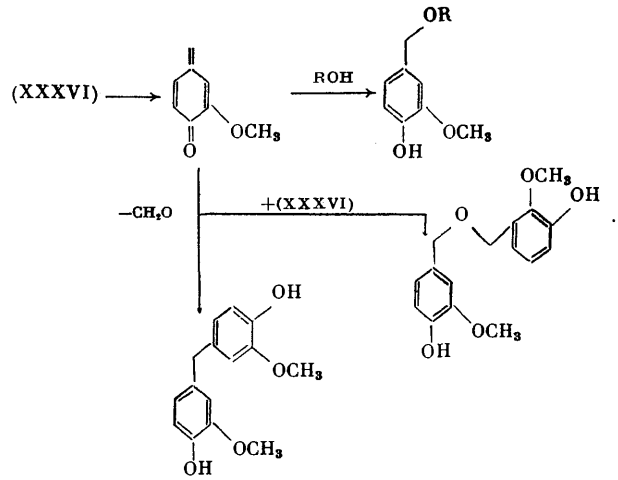


(XLVIII)

Model QM combine with glucuronic acid[107] and glucose[107,183] (see above). This reaction proceeds also in the presence of water. Such processes can be regarded as simulation of the formation of the lignocarbohydrate complex. However, bearing in mind the competition by water and other nucleophiles, the formation of an appreciable amount of the lignocarbohydrate linkages in this way requires a fairly high concentration of carbohydrates near the QM at the instant of their formation or the fixation of the quinone methide structure in the vicinity of the carbohydrates of the cell wall. The latter is fairly probable since it is believed that the dehydrogenation polymerisation of monolignols takes place in the outer cell membrane in the vicinity of the carbohydrates of the cell wall, which contains in addition a relatively small amount of free water.[183]

The view that the reactions of QM during lignification are irreversible and that the structure of native lignin is therefore directly determined by the nature of the reactions of the primary QM was widely held previously.[2,179,185] Hence follows, for example, the misunderstanding arising on comparing the frequency of the lignocarbohydrate linkages and the number of carbon fragments capable of reacting with QM. It was found later that not only under severe pulping conditions but also directly in plant tissues there is a possibility of the formation of "secondary" QM.[188,189] If this is so, then the autodegradation and secondary structure formation processes can lead in the course of time to appreciable changes in the frequency with which interunit bonds of different types are encountered (we have in mind both the ways in which the lignin subunits are joined together and the lignocarbohydrate linkages).

This possibility is supported by convincing experiments on model compounds. Thus in neutral and weakly acid aqueous media, vanillyl alcohol (XXXVI) forms α-ether linkages with aliphatic alcohols and glucose (the half-reaction time for 10% ethanol is 2.7 years).[188] The involvement of QM in this process is confirmed if only by the fact that veratryl alcohol is converted into an ether much more slowly under the same conditions. The self-condensation of vanillyl alcohol can serve as the simplest model of the secondary cross-linking of lignin. Under lignification conditions, this process also takes place[1] with the exclusive formation of dibenzyl and not aryl benzyl ether. Further self-condensation of lignin over a period of time with formation of diarylmethane structures is also possible.



Model studies together with the analysis of the composition of the lignins and dehydropolymers isolated suggests the important role of QM both in the initial stage of lignification and in the course of the wood ageing processes.[1] In the early stage, the competition by the nucleophile for the "primary" QM determines the ratio of the structural units with a free and etherified α-hydroxyls. It has been suggested that, owing to the presence of a large amount of water during lignification, the "primary" lignin contains many benzyl alcohol groups and resembles Feudenberg's dehydropolymers.[1] After a time, re-etherification and the formation of stable *p*-hydroxybenzyl ether structures (the lignocarbohydrate linkages and the $C^{\alpha}-O-C^{\gamma}$ linkage) take place. Such development of the lignification process agrees with the model[187] proposed as a result of computer simulation using data for the compositions of the lignins isolated.

The question of the relation between the colour of lignins and the presence of quinone methide structures in them is interesting and hitherto has been little elucidated. Its practical importance is evident, since a correct answer to it may lead to novel procedures for combating the yellowing of cellulose.

It is believed that, together with qinonoid structures, stilbenequinones, conjugated bis-*p*-quinone methides, and hydroxyaryl-substituted QM are included among the chromophoric systems of the residual lignin.[190−192] It must be emphasised that these are only hypotheses based on the results of model experiments and not on the analysis of the lignins themselves after chemical processing of wood (the assignment of the structures in the latter case is not unambiguous). The formation of stable QM structures in the self-condensation and subsequent oxidation in air of a number of model compounds of lignins has been postulated[193−195] on the basis of the spectroscopic characteristics of the products. Even these data, obtained on simple models, do not appear to be reliable. On the other hand, the presence of such systems both in the bulk of cellulose and in treated liquors is fairly likely. The conjugated and shielded QM are stable and are usually brightly coloured—both as a result of conjugation and as a consequence of the possibility of intramolecular charge transfer in systems of this kind.[63,68,196] The latter effect should be manifested particularly strikingly in the presence of alkali when the electron-donating phenolic groups are ionised.

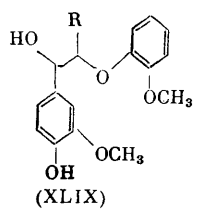
VI. Quinone methides as intermediates in the delignification of wood

Although it has not so far been possible to detect the presence of quinone methide structures under the conditions of the pulping of wood, nevertheless this does not by itself justify a sceptical attitude to the proposed mechanisms of the pulping reactions with participation of QM. In principle, such a situation arises for the majority of intermediates: if they are indeed highly reactive, then their stationary concentration is low; the study of intermediates always requires special methods and conditions different from those which obtain when the relevant reactions are carried out.

It is remarkable that QM give rise to identical problems in the chemistry of wood and in bioorganic chemistry. Thus hypotheses that many biological processes take place with participation of these intermediates and that one is dealing with compounds very similar to model QM of lignin have long been put forward.[17,197−204] It has been suggested that the formation of QM can explain the reactivity of many flavonoids.[205]

The conclusion that many key pulping reactions take place via QM is based on numerous experiments performed on model compounds. As early as the beginning of the 1960's, the results of kinetic studies on the hydrosulphide and hydrosulphite treatment of vanillyl alcohol (XXXVI) suggested that these processes proceed via a QM intermediate whose formation is the rate-limiting stage; this has received additional confirmation from the marked retardation of the reaction in alkaline and neutral media on alkylation of the phenolic hydroxyl.[206,207] It was also established that the formation of QM determines the rate of degradation of the benzyl ether linkages[208] (the blocking of the phenolic hydroxyl stabilises such linkages, in particular the lignocarbohydrate linkages[106]).

Subsequently these views were confirmed by kinetic experiments on more complex models[111,209−212] and it is at present regarded as established for example, that the stage determining the rate of the alkaline degradation of β-aryl ethers (XLIX) is the formation of QM. The situation is similar also as regards the corresponding syringyl analogues but with the difference that the presence of two electron-donating methoxy-groups (incidentally such groups stabilise the QM) promotes a faster elimination of the α-hydroxy-group.[212]



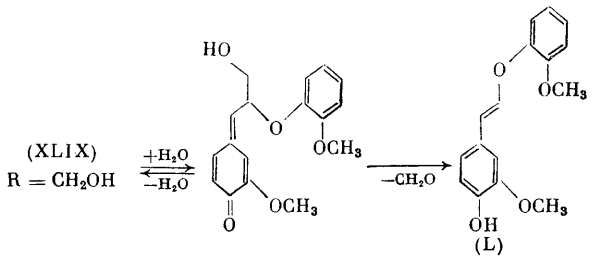
(XLIX)

R = H, CH_3, CH_2OH.

In experiments on model compounds, it was shown that the conversion of the initial *p*-hydroxybenzyl alcohol into a QM is the rate-limiting stage both in the cleavage of β-aryl ethers under the conditions of sulphate pulping and in condensation processes.[210,213] This is why the given reaction is of first order with respect to the initial alcohol and its rate is independent of the concentration of the OH^- and SH^- ions (at pH ⩾ 12 when the phenolic groups are fully ionised and at a SH^- concentration sufficient to capture all the QM intermediates). These data are part of the experimental evidence for the quinone methide mechanism of the cleavage of β-aryl ether linkages. An additional confirmation of this mechanism comes from the fact that β-aryl ethers without a free phenolic hydroxyl are cleaved more slowly.[214–216] However, the mechanism of degradation in the case of models containing two syringyl nuclei has not been ultimately elucidated and is apparently more complex than in the case of the guaiacyl–guaiacyl and syringyl–guaiacyl models; it is sufficient to say that the transition from the β-guaiacoxide to the β-syringoxide substituent accelerates the cleavage[212] (cf. Miksche[209]).

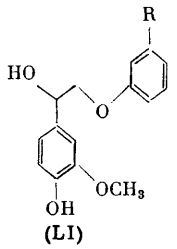
The most important experiment demonstrating the formation of QM during pulping was carried out by Miksche and co-workers.[20,213] They kept the stereoisomerically pure model (XLIX, R = CH_3) in 0.1 M aqueous NaOH at 100–120 °C for several hours. A considerble proportion of the initial compound was then recovered from the reaction without change in its chemical structure but in the form of a 1 : 1 mixture of the *threo*- and *erythro*-stereoisomers. Only the reversible formation of a planar intermediate could lead to such a result. Bearing in mind that the reaction proceeds in alkali and the formation of a carbonium ion is therefore ruled out, one can assume that under the conditions specified *p*-hydroxybenzyl alcohol give rise to QM at an appreciable rate and the latter combine in their turn with a OH^- anion to reform the initial compound; thus a stationary concentration of QM exists in the solution.[128]

These data have been confirmed in principle also in another study,[102] where the behaviour of the more representative model (XLIX, R = CH_2OH) was investgiated and 79% of the initial compound in the form of an *erthro*:*threo* = 3:1 mixture was recovered from the pure *erythro*-isomer. It was found that, under similar conditions (125 °C, 1.5 h), both in the presence of pure NaOH and in the presence of Na_2S the starting material is recovered to the extent of 50–60% having isomerised to the extent of 5–10%; the vinyl ether (L) is then formed as a reaction product in an appreciable amount (15–30%). Hence follows the following reactivity sequence: (HO^- > HS^-) ≃ retroaldol condensation (i.e. the elimination of formaldehyde).[102]



In our view, the results of these experiments (if they are confirmed) indicate something else, namely that, under the conditions of alkaline pulping, the conversion of the β-aryl ether structures of the type considered into vinyl ether structures is the main reaction pathway. However, one should refrain in this case from making assessments of the reactivity of the kind which refer in principle to chemical reaction kinetics: it is extremely likely that the process is thermodynamically controlled. A strikingly low degree of isomerisation has been quoted by Ralph:[102] it can be either a result of the virtually complete conversion of the QM formed into a vinyl ether or can be eividence of a low degree of conversion of the initial β-aryl ether into the QM. Overall, these results conflict with modern ideas and clearly require additional tests.

Whereas the hypothesis that the pulping reactions of *p*-hydroxybenzyl alcohol groups proceed via QM itself belongs to the class of generally accepted ideas, makes it possible to explain the entire set of experimental data, and is hardly criticised, the answer to the question of the rate-limiting stage in the cleavage of β-aryl ether structures is far from being unambiguous. In the study of the cleavage of the model (LI) under the conditions of alkaline pulping, a distinct dependence of the rate of the process on the substituent R was obtained.[217] This is possible only when the slow stage in the overall mechanism is the direct decomposition of the β-aryl ether linkage. On the other hand, in the formation of vinyl ethers from similar models the rate-limiting stage is in fact the formation of the QM.[217]



(LI)

The rapid and slow stages can apparently change depending on the models and the types of pulping. Thus under the conditions of sulphate and anthraquinone pulping of wood, the influence of the substituent R is no longer felt but a distinct dependence of the rate of cleavage on the substituent in the phenolic ring (QM precursor) is observed.[218] Here the slow stage is clearly the formation of the QM; the reason for the change in the rate-limiting stage is clear from Fig. 2.

Yet another question is important: how many QM precursor structures are present in native lignin and is their number sufficient for QM to play the appreciable role attributed to them? A large proportion of the phenolic hydroxyls in structures of the arylglycerol–β-aryl ether type have been converted into ether groups.[138,185] The fraction of *p*-hydroxybenzyl alcohol groups in the lignin of ground pine wood is estimated as 0.06 per methoxy-group[3] (p. 167, see also Veeramani[219]), but it is difficult to estimate the reliability of these data. However, we may note that *p*-hydroxybenzyl ethers, which can be readily converted into QM, may also serve as QM precursors[138,150] and the rupture of only a small number of weak bonds may be sufficient for the degradation of the polymer, facilitating its dissolution. Furthermore, the fraction of QM precursor structures increases during pulping as the α- and β-aryl ether linkages are cleaved and phenolic hydoxyls are thereby liberated. The new phenolic units are capable in their turn of being cleaved via the quinone methide mechanism and such cleavage of units can proceed until a subunit of a different type is encountered (lignin piling[216]). Gierer[220] noted that the delignification in the course of traditional pulping of wood proceeds exclusively via nucleophilic reactions, while in the bleaching of bulk cellulose electrophilic reactions take place initially and may then be

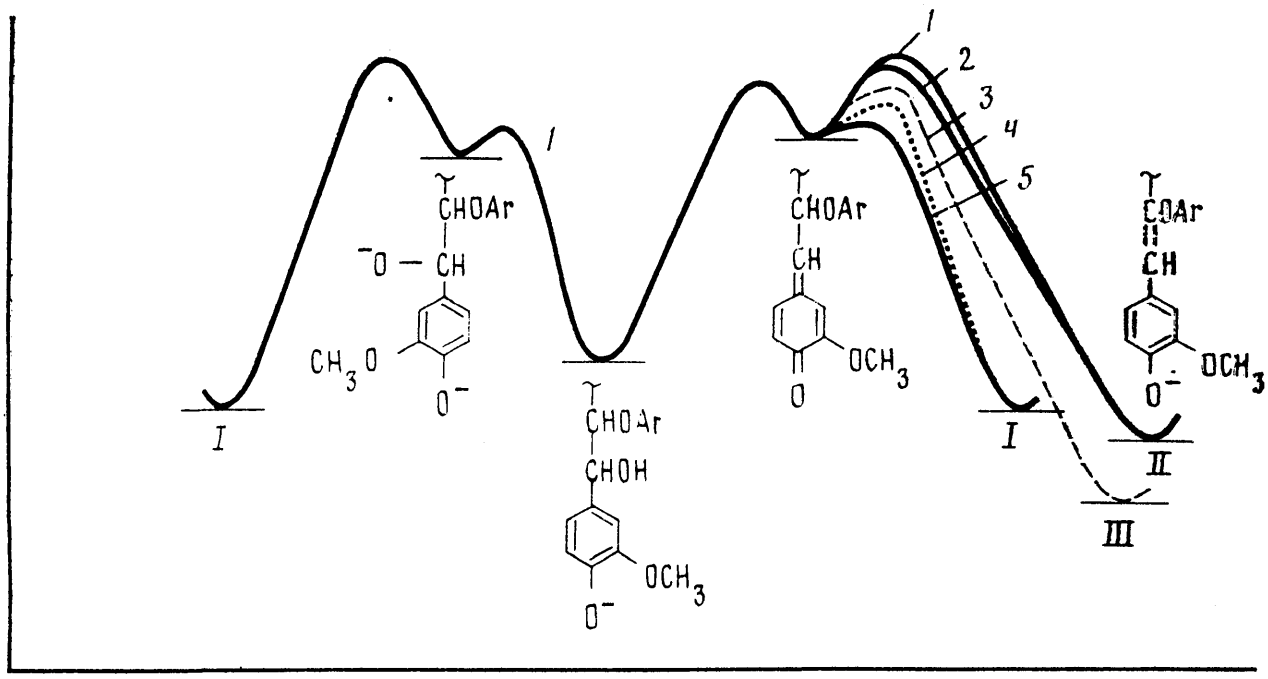
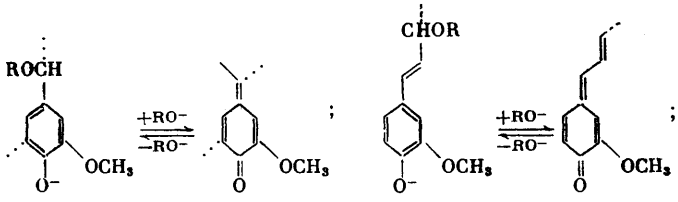


Figure 2. Proposed energy diagram for the reaction of terminal phenolic units of lignin:[218] (I) fragments (dissociation of the β-ether linkage); (II) vinyl ether; (III) condensation products; (*1*) OH^-; (*2*) terminal CH_2OH group, elimination of CH_2O; (*3*) ArO^-; (*4*) SH^-; (*5*) AHQ^{2-}.

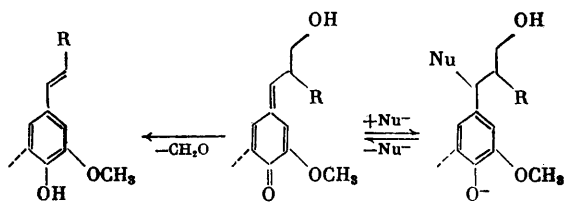
followed by nucleophilic processes. The active agent in pulping consists of nucleophiles (SO_2 and OH^-, SH^-, HSO_3^-, SO_3^{2-}, AHQ^{2-}, and AHQ^-). According to current ideas, these agents do not destructure lignin via direct substitution reactions. In the first stage, they react with electrophilic substrates, which also include QM. The latter are known to be formed via the elimination of an α-substituent or, in the case of conjugated systems, a γ-substituent. This process may proceed at any pH. A reaction of this kind at high pH is illustrated by the following scheme:



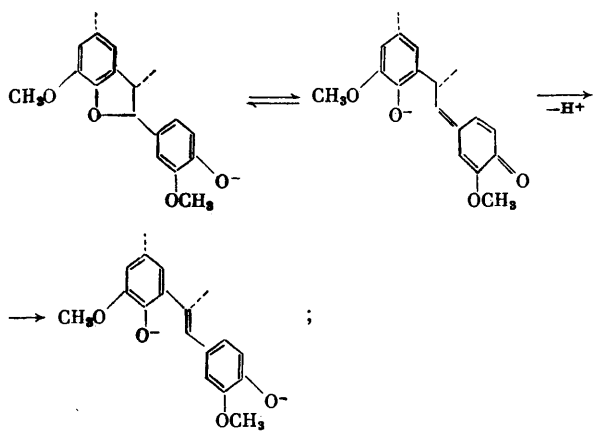
R = H, Alk, Ar.

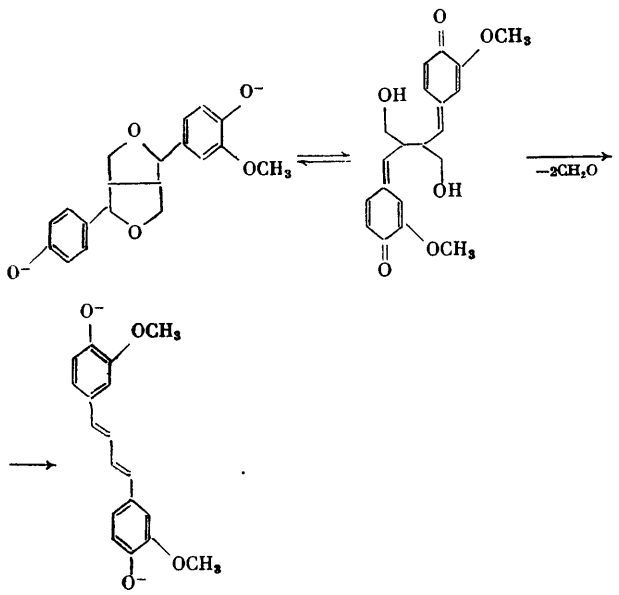
In a familiar review,[220] similar schemes refer also to the reactions of lignin in acid media; this is erroneous, since in the latter case one should refer to the formation of the corresponding α-carbonium ions.

When several nucleophiles are present in solution, they compete with one another, attacking the substrate, and the nature of the reaction of lignin in different types of pulping is determined to a large extent by the relative nucleophilicities of the components of the liquor, their concentration, and also the properties of the corresponding α-substituents as leaving groups (we recall that the formation of the QM is reversible). Another competing reaction leading to aromatisation is the elimination of formaldehyde with formation of the more stable styryl structures.[111,141,221,222]



The stilbene and diarylbutadiene structures are formed from coumaran and pinoresinol lignin fragments:

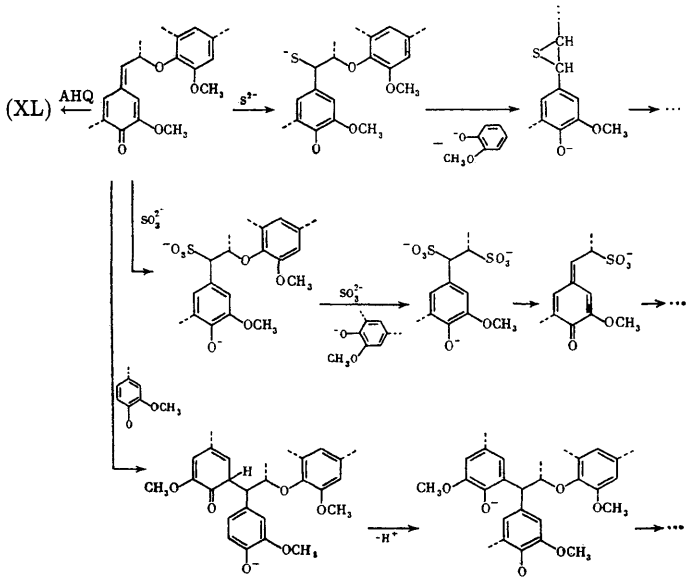




Since similar processes are inhibited on blocking the phenolic hydroxyl, one may conclude that the formation of the QM intermediate is essential for the reaction of the given type;[223,224] it is probably in fact the rate-limiting stage in the formation of vinyl ethers.[111]

According to existing ideas, the pulping reagents are strong nucleophiles which effectively capture the QM with formation of adducts, which rapidly and irreversibly decompose with the dissociation of β-aryl ether linkages. Such cleavage represents in essence a redox process. In broad outline, the mechanism of the heterolytic addition–cleavage is the same for sulphate,[140,216,225] sulphite,[226–228] and anthraquinone[9,229] pulping as well as the pulping in the presence of low-molecular-weight phenols[230,231] (Scheme 4).

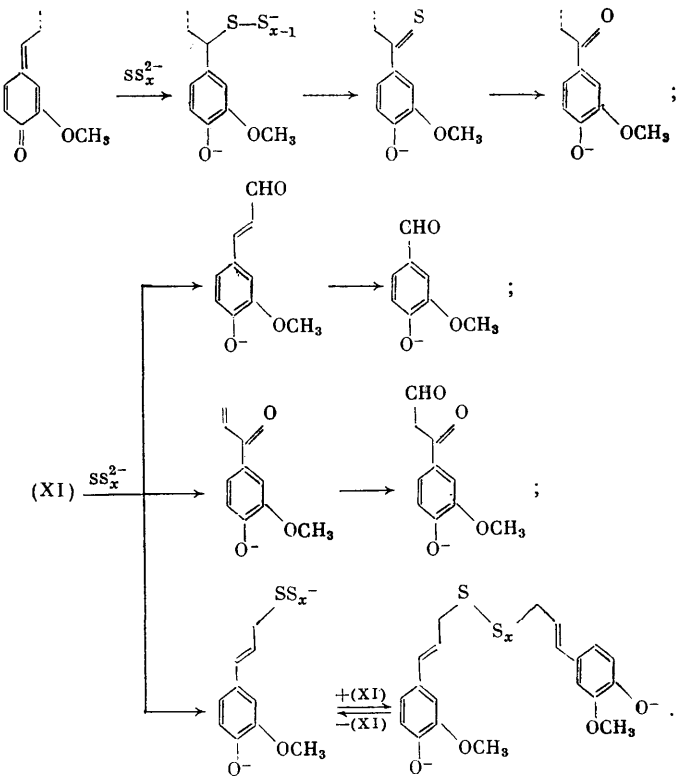
Scheme 4



We may note that similar products of the addition to *o*-QM under pulping conditions are formed also from *o*-hydroxybenzyl alcohol structures.[232] The cleavage of the β-aryl ethers via intramolecular attack on the ionised α-substituent is in principle possible both in the case of α-alcohols and α-thiols. However, the p*K* values for the ionisation of benzyl alcohols are much higher than for thiols. Therefore it appears that the fragmentation of the phenol-alcohol units is more effective in the sulphate pulping than in the soda pulping.[121]

Other complex processes also take place at the same time. Thus the formation of a number of products from model compounds of lignin under the conditions of sulphate pulping has been explained by the mechanisms presented in Scheme 5, which apparently operate in the course of the reactions of wood itself.[138,141]

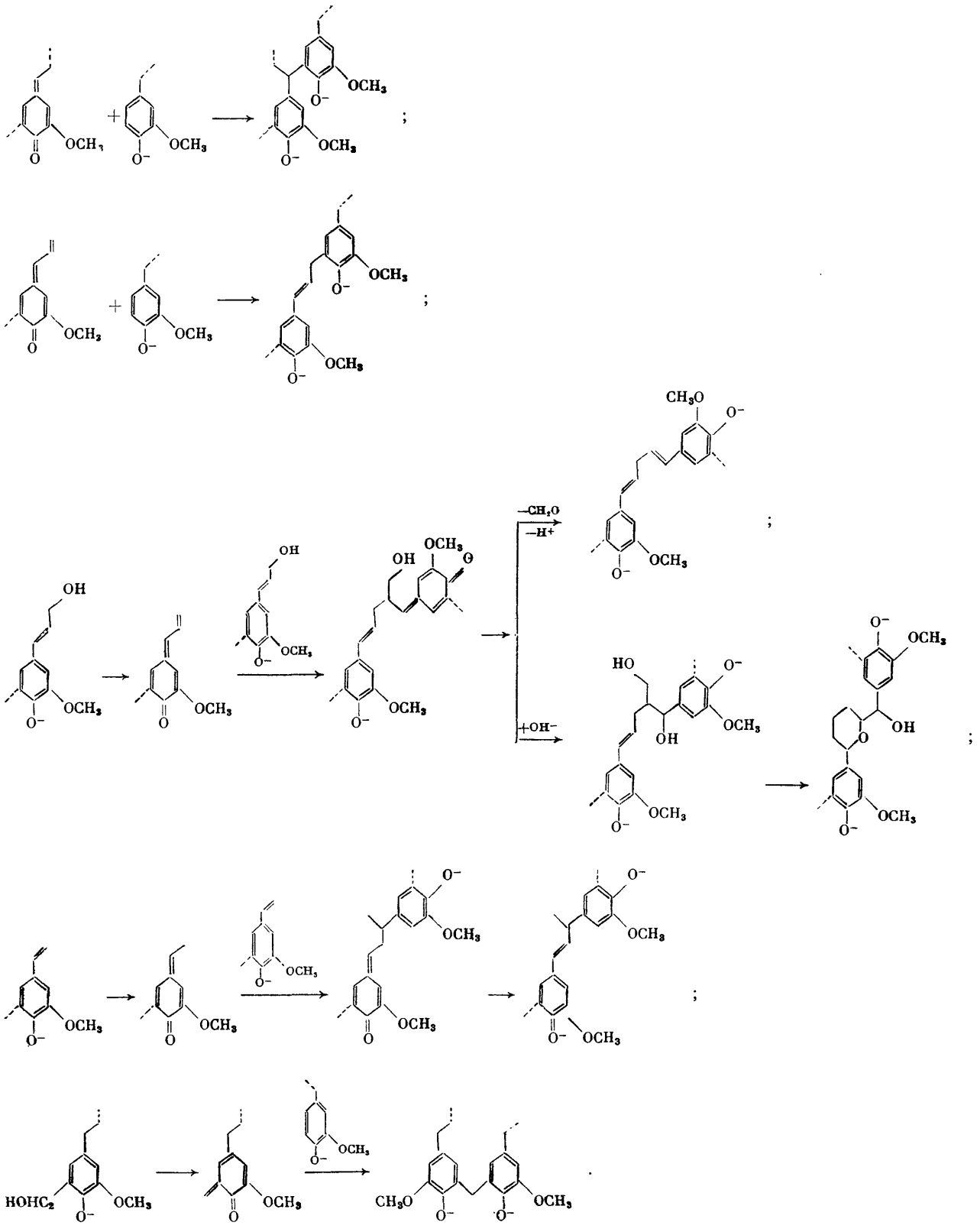
Scheme 5



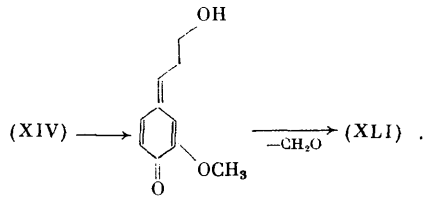
These reactions constitute polysulphide oxidation and in the case of the QM (XI) the initial stage is 1,6- or 1,8-addition. Clearly in polysulphide pulping their role should increase.

In the absence of strong nucleophiles (soda pulping), the elimination of terminal hydroxymethyl groups with conversion of the native β-aryl ether structures into the β-aryloxystyryl structures (more stable in alkali) predominates.[216] This reaction naturally does not belong to the class of fragmentation reactions. On the contrary, it produces formaldehyde, which is in principle capable of cross-linking phenols. The elimination of formaldehyde from various fragments of lignin represents generally speaking a process which can be fairly readily achieved and the formation of QM as intermediates

Scheme 6



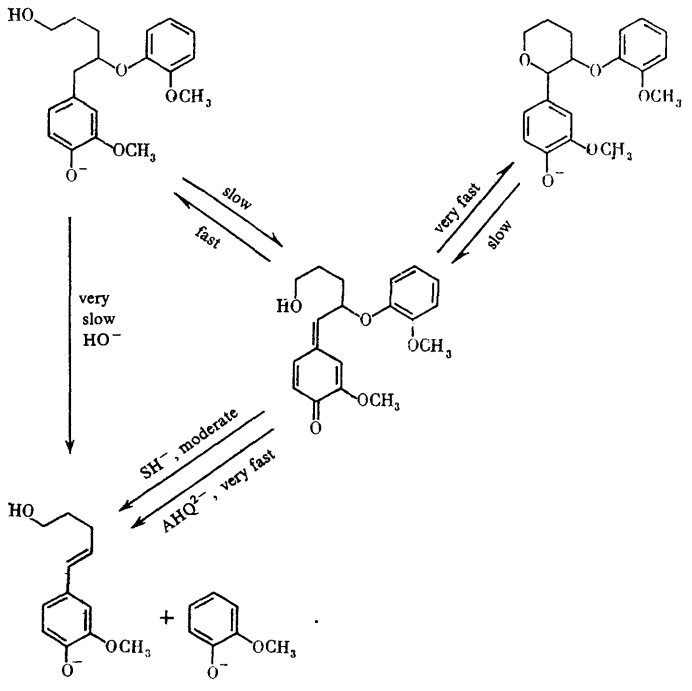
actually facilitates it. Thus the following mechanism has been postulated for the simple coniferyl alcohol (XIV) model:[141,233]



The relative importance of various routes to the rearomatisation of the QM is determined by the basicity and nucleophilicity of the reagents. Competitive experiments made it possible to establish the following series based on the rates of the reactions considered: the formation of QM $\ll$ elimination of CH_2O < addition of carbanions to QM < addition of SH^- to QM.[210]

When the structure of the lignin fragment does not lead to the chain degradation pathway, the addition of a low-molecular-weight nucleophile nevertheless assists the delignification process, retarding (although not blocking completely) the condensation of lignin and preventing the formation of stable styrene structures.[216,234] One of the important routes to such condensation involves the addition of phenolic fragments of lignin to QM, which takes place readily in an alkaline medium[104,138,141,216,220,232,233,235,236] (Scheme 6).

A remarkable example of a model system of competing pulping reactions has been described:[111]



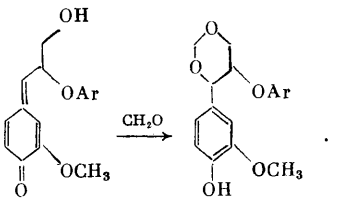
In the case represented, the nucleophilic addition of pulping agents competes with intramolecular addition and the efficiency of the suppression of the latter by the introduction of anthrahydroquinone demonstrates the unique properties of this nucleophile. Striking examples of the suppression of the self-condensation of *p*-hydroxybenzyl alcohols and dioxane-lignin by this reagent as well as other strong nucleophiles as reductants are also known.[126,135,237]

We may note that the corresponding bibenzyls have been detected among the products of the self-condensation of model alcohols in the presence of anthrahydroquinone.[126] In principle, these compounds can be the products of the dimerisation of the radical-anions produced by electron transfer to the QM,[238] but an unambiguous conclusion concerning their origin is so far impossible. Bearing in mind the theoretical considerations described above, the hypothesis[238,239] of the possibility of electron transfer to the QM from arylate anions or carbohydrates under the pulping conditions appears unconvincing.

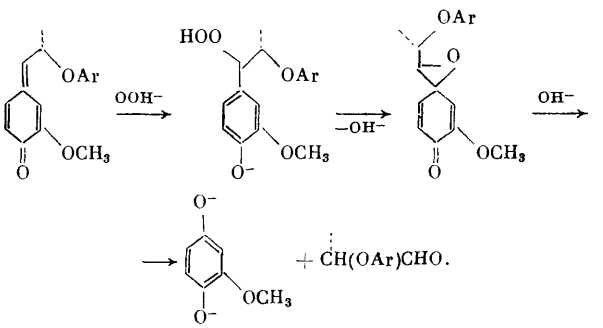
It is of interest to note that heating of *p*-hydroxybenzyl alcohols in aqueous alcoholic mixtures affords, together with their self-condensation products, also etherification products which are most probably produced via QM.[104,188] It appears that such processes can occur in the course of organic solvent pulping.

Evidently the influence of phenols on the pulping process should depend on their molecular weight: the interaction of lignin QM with low-molecular-weight phenols leads to cross-linking accompanied by the rupture of the chain (the overall effect is positive), while the addition of high-molecular-weight fragments of lignin prevents the delignification process. Low-molecular-weight phenols, for example coniferyl alcohol (XIV), which can themselves be readily converted into QM condensing with lignin under pulping conditions, are an exception. As already mentioned, the presence of powerful nucleophiles (for example, SH^- and AHQ^{2-}) in the pulping liquor hinders condensation processes of different types.[136,237,240] We emphasise that the final result of the "fight for QM" depends not only on the nucleophilicity of the reagents but also on the rates of the subsequent irreversible reactions—cleavage or condensation.

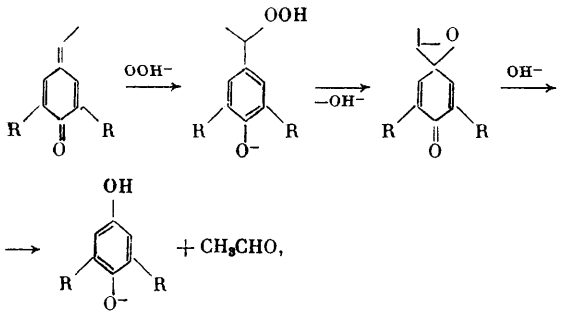
We may also note the following reaction as an interesting example of condensation with participation of QM and low-molecular-weight lignin degradation products:[241]



Unusual reactions with participation of QM may occur in oxidative delignification, where both electrophiles (for example, O_2) and nucleophiles (for example, OOH^-) function as active agents. The addition of the peroxide ion can lead to the rupture of the lignin chain:[233,241]

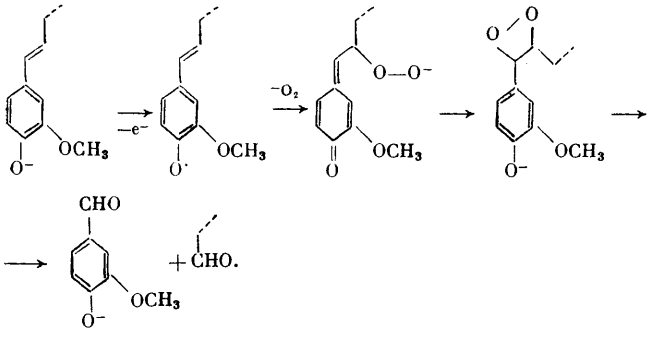


The following reactions were observed in a model experiment:[241,242]



R = C(CH$_3$).

The oxidation of conjugated phenols leads to the dissociation of the $C^{\alpha}-C^{\beta}$ bond, the intramolecular nucleophilic addition to QM being an important stage of the process:[233,241–243]

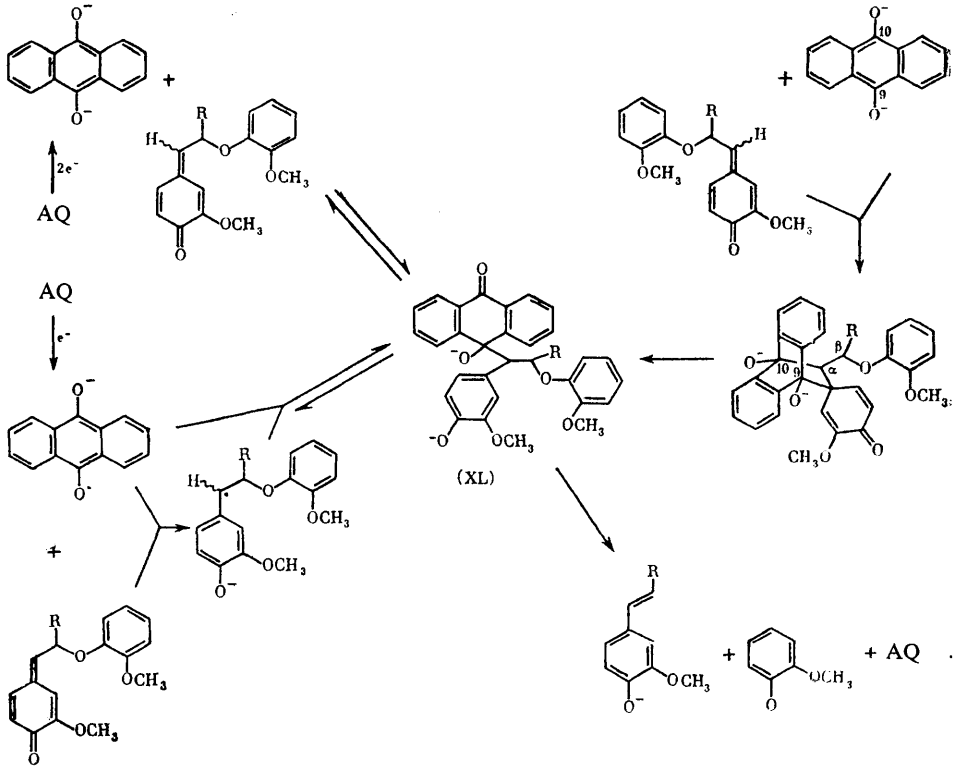


We have already noted that there is a close similarlity between the mechanisms of pulping involving strong nucleophiles (the fact that the addition of anthraquinone exerts a greater effect on the soda pulping of wood than on the sulphate pulping has in fact been explained by the competition between the related reagents[9]). The results of studies of the anthraquinone pulping carried out in recent years are therefore of special interest. Together with the observation of the characteristic features of the process involving anthraquinone as such, they made it possible to re-examine the properties of lignin and its reactivities in various technological processes.[9]

Above we discussed in detail various aspects of the reactions of model lignin QM with derivatives of anthracene such as anthrahydroquinone and anthrone. The "classical" mechanism of the cleavage of phenolic β-aryl ether subunits of lignin in the course of pulping involves the formation of the adduct (XL), which then undergoes Grob fragmentation. Such ideas are based on the isolation of the adduct under mild conditions; the adduct decomposes via the postulated mechanism on heating in aqueous alkali. However, this does not yet rule out the possibility of other reaction pathways.

Anthranol and anthrahydroquinone may be regarded as effective trapping agents for QM. The reasons for their high affinity for QM and the associated ability of these compounds to cleave the β-aryl ether linkages of lignin have been interpreted within the framework of different theories. The interaction of the above reagents with QM can be quite logically explained within the framework of the theory of hard and soft acids and bases:[9,89] in this approach, the anions behave as nucleophiles attacking the electrophilic substrate and the key stage of the process is the formation of an adduct of the type (XL) (Scheme 7).

Scheme 7



It has been suggested[142] that the oxidation-reduction interaction of anthrahydroquinone with QM can proceed via the formation of a charge-transfer π-complex and that the anthraquinone–AHQ^{2-} system as it were "creeps" along the surface of the gel-like lignin polymers and hemicelluloses supplying or abstracting electrons. Dimmel and co-workers[92,93,95,111,238,239,244] proposed a likely one-electron transfer theory in which the key stage ensuring cleavage is electron transfer to QM.

Finally, Ralph[102] recently put forward the hypothesis (with a reference to a private communication by Suckling) that the primary stage of the reaction of the reduced form of the catalyst with the lignin QM may be the Diels–Alder reaction. This hypothesis is least well founded. However, it is significant that all three mechanisms can involve the formation of the "key" adduct (XL), admittedly via different pathways, so that it is so far not clear whether we are justified in regarding all the above pathways as alternative pathways. On the other hand, it is useful to formulate a fundamental question the answer to which would make it possible to understand whether there is any point in considering a charge-transfer mechanism as an alternative to the "classical" mechanisms. This question refers precisely to the properties of QM and can be written as follows: what is faster under the pulping conditions—the decomposition of the corresponding radical-anion or the coupling of the latter to anthrahydroquinone? Only in the former case can the specific features of the one-electron reactions be manifested significantly (although, as we have already mentioned, in the latter case also the demonstration of the existence of a one-electron stage might affect the choice of procedures for intensifying the catalytic process).

Dimmel et al.[95] drew attention to the fact that the reductive cleavage of β-aryl ether QM with participation of the reduced forms of anthraquinone, but without the formation of an adduct, is observed in electrochemical experiments. However, it is not clear how likely in general the formation of an adduct is under the conditions of the electrochemical carried out by Dimmel et al.[95] Furthermore, as a consequence of the dependence of the rates of formation of the adduct and of the electron transfer on the temperature and the solvent, the legitimacy of the extrapolation of the results of Dimmel et al.[95] to the pulping process is not evident. We may note that experiments do not provide an answer to the following question either: is the dianion AHQ^{2-} or the radical-anion $AHQ^{\cdot-}$ more likely as the electron donor? The rapid disproportionation of $AHQ^{\cdot-}$ usually leads to the simultaneous formation of AHQ^{2-} and Dimmel et al.[95] dealt with a mixture of reduced forms of anthraquinone at least in preparative experiments (cf. Shevchenko et al.[127]).

In our view, the mechanism of electron transfer catalysis is quite likely, but it is very difficult to demonstrate it reliably and so far there is no such evidence. This is a fairly common situation; electron transfer processes do not constitute any kind of exception but the assignment of any reactions to the given class is based on a set of indirect evidence and is frequently liable to be controversial. Apparently in the given case one should use photostimulation, but so far such experiments have not been carried out. The hypothesis is supported by the catalytic activity of bulky organometallic complexes.[245]

One should not imagine that the situation is one where the operation of an electron transfer mechanism necessarily implies that the reduced form of the catalyst is able to "bombard" lignin readily with electrons from a large distance. Outer-sphere electron transfer is known to constitute the least favourable pathway in the reaction between two compounds: the two reagents should react regardless of any advantages which the electronic interaction between them could afford. Polar and inner-sphere processes are in most cases preferable as regards energy.[246] The phenomenon of autocatalysis observed by Dimmel et al.[95] does not in any way conflict with this: it nevertheless implies that the electron transfer to QM in solution takes place more readily than from the electrode surface. This does not imply that the mutual approach of the reactants is not necessary for the process to occur. Naturaly tunnelling over a large distance is possible,[247] but, for reasons already stated, its probability must be much lower than the probability of more complex mechanisms involving, for example, the formation of pre-reaction charge-transfer complexes. Such mechanisms with chemical stages are characteristic of electron transfer reactions.[246]

References

1. G Leary *Wood Sci. and Technol.*, 1980, **14**(1) 21
2. K V Sarkanen, C H Ludwig (Editors) *Lignins* (Translated into Russian), Lesnaya, Prom., Moscow, 1975
3. S P Grushnikov, V V Elkin *Dostizheniya i Problemy Khimii Lignina* (Advances and Problems in the Chemistry of Lignin), Nauka, Moscow, 1973
4. N N Shorygina, V M Reznikov, V V Elkin *Reaktsionnaya Sposobnost' Lignina* (Reactivity of Lignin), Nauka, Moscow, 1976
5. A A Volod'kin, V V Ershov *Usp. Khim.*, 1988, **57**(4) 595 [English translation in *Russ. Chem. Rev.*, 1988(4)]
6. J L Goodman, J A Berson *J. Am. Chem. Soc.*, 1984, **106**(6) 1867
7. V V Ershov, G A Nikiforov, A A Volod'kin *Prostranstvenno-Zatrudnennye Fenoly* (Sterically Hindered Phenols), Khimiya, Moscow, 1972
8. S G Semenov, S M Shevchenko *Zh. Org. Khim.*, 1985, **21**(2) 368
9. S M Shevchenko, I P Deineko *Khimiya Drevesiny*, 1983, (6) 3
10. A G Gonzalez, Z E Aguilar, J G Luis, et al. *Phytochemistry*, 1988, **27**(6) 1777
11. A G Gonzales, B M Fraga, C M Gonzales, et al. *Tetrahedron Lett.*, 1983, **84**(29) 3033
12. A V B Sankaram, M Murthi Martanda, K Bhaskaraiah, et al. *Tetrahedron Lett.*, 1988, **29**(2) 245
13. H C Fernando, A A L Gunatilaka, V Kumar, et al. *Tetrahedron Lett.*, 1988, **29**(3) 387
14. F Simoes, A Michavila, B Rodriguez, et al. *Phytochemistry*, 1986, **25**(3) 755
15. D Karanatsios, J S Scarpa, C H Eugster *Helv. Chim. Acta*, 1966, **49**(3) 1151
16. A V Sankaram, K Bhaskariah, M Marthandamurthi, et al. *Tetrahedron Lett.*, 1989, **30**(7) 867
17. G M Buchan, A B Turner *J. Chem. Soc., Perkin Trans. 1*, 1979, (5) 1326
18. J Pospisek, M Pisova, M Soucek *Collect. Czech. Chem. Commun.*, 1975, **40**(1) 142
19. W Alder, B Stenemur *Chem. Ber.*, 1956, **89**(2) 291
20. B Johansson, G E Miksche *Acta Chem. Scand.*, 1972, **26**(1) 289
21. F Nakatsubo, K Sato, T Higuchi *Mokuzai Gakkaishi*, 1976, **22**(1) 29
22. K A Andrianov *Kremniiorganicheskie Soedineniya* (Organosilicon Compounds), Goskhimizdat, Moscow, 1955

23. J Ralph, R A Young *J. Wood Chem. and Technol.*, 1983, **3**(2) 161
24. J Ralph, B R Adams *J. Wood Chem. and Technol.*, 1983, **3**(2) 183
25. S M Shevchenko, A G Apushkinskii, V A Gindin, M Ya Zarubin *Zh. Org. Khim.*, 1990, **26**(5) 1069
26. A Zanarotti *J. Chem. Res. (S)*, 1983, 306; *J. Chem. Res. (M)*, 1983, 2625
27. A Zanarotti *J. Org. Chem.*, 1985, **50**(7) 941
28. S M Shevchenko, S G Semenov, E I Evstigneev, et al. *Zh. Org. Khim.*, 1987, **23**(9) 1891
29. L K Dyall, S Winstein *J. Am. Chem. Soc.*, 1972, **94**(7) 2106
30. L Jurd *Tetrahedron*, 1973, **33**(2) 163
31. R D Parnell, K E Russell *J. Chem. Soc., Perkin Trans. 2*, 1974, (2) 161
32. G Brunow, S Sumelius *Acta Chem. Scand., Ser B*, 1975, **29**(4) 499
33. N R Hunter, G Plourde *Synth. Commun.*, 1986, **16**(10) 1233
34. A F A Wallis *Aust. J. Chem.*, 1973, **26**(3) 585
35. K V Sarkanen, A F A Wallis *J. Chem. Soc., Perkin Trans. 1*, 1973, (18) 1869
36. K V Sarkanen, A F A Wallis *J. Chem. Soc., Perkin Trans. 1*, 1973, (18) 1878
37. E S Caldwell, C Steelink *Biochem. Biophys. Acta*, 1969, **184**(2) 420
38. S M Shevchenko, A G Apushkinskii, V A Gindin, M Ya Zarubin *Khimiya Drevesiny*, 1990, (4) 112
39. S Tsuruya, Y Kishikaa, R Tanaka, T Kuse *J. Catal.*, 1977, **49**(3) 254
40. F R Hewgill *Tetrahedron*, 1978, **34**(10) 1595
41. A McKillop, S J Ray *Synthesis*, 1977, (12) 847
42. W J Connors, J S Ayers, K V Sarkanen, J S Gratzl *TAPPI J.*, 1972, **26**(1) 289
43. M S Lasne, J L Ripoll, J M Denis *Tetrahedron*, 1981, **37**(3) 503
44. P D Gardner, H Sarratisadeh, R L Brandon *J. Am. Chem. Soc.*, 1959, **81**(20) 5515
45. B L McIntosh, O L Chapman *J. Chem. Soc., Chem. Commun.*, 1977, (14) 771
46. V Eck, A Schweig, H Vermeer *Tetrahedron Lett.*, 1978, (27) 2433
47. J A Hemmingson *Tetrahdron Lett.*, 1977, (34) 2967
48. G Leary *J. Chem. Soc., Perkin Trans. 2*, 1972, (5) 640
49. J A Hemmingson, G Leary *J. Chem. Soc., Perkin Trans. 2*, 1975, (7) 1584
50. H L Chum, D K Johnson, P D Palasz, et al. *Macromolecules*, 1987, **20**(11) 2698
51. T L Lewis, I C Paul, D Y Curtin *Acta Crystallogr., Sect. B*, 1980, **36**(1) 70
52. A Arduini, A Pochini, R Ungaro, P Dimiano *J. Chem. Soc., Perkin Trans. 1*, 1986, (8) 1391
53. D E Williams *Mol. Phys.*, 1969, **16**(2) 145
54. M Kaftory, Y Apeloig, Z Rappoport *J. Chem. Soc., Perkin Trans. 2*, 1985, (1) 29
55. V I Stepanov *Vvedenie v Khimiyu i Tekhnologiyu Organicheskikh Krasitelei* (Introduction to the Chemistry and Technology of Organic Dyes), Khimiya, Moscow, 1984
56. A Skancke, P N Skancke *Chemistry of Quinonoid Compounds, Vol. 2* (Edited by S Patai, Z Rappoport), Wiley, New York, etc., 1988
57. H Dits, N M M Nibbering, J W Verhoeven *Chem. Phys. Lett.*, 1977, **51**(1) 95
58. H Konschin, J Jakobsons, S M Shevchenko *J. Mol. Struct. (Theochem.)*, 1990, **238** 231
59. R M Ede, J Ralph, L Main *Proceedings of the IVth International Symposium on Wood and Pulping Chemistry, Paris*, 1987, Vol. 2, p. 171
60. S M Shevchenko, J Jakobsons, V A Gindin *Tezisy Dokladov VII Vsesoyuznoi Konferentsii po Khimii i Ispol'zovaniyu Lignina, Riga* (Abstracts of Reports at the VIIth All-Union Conference on the Chemistry and Utilisation of Lignin, Riga), Riga, 1987, p. 24
61. S M Shevchenko, J Jakobsons *Izv. Rad. IV Jugoslov. Simpoz. Org. Hemiji. Beograd*, 1987, p. 82
62. J Jakobsons, S M Shevchenko *Izv. Akad. Nauk Latv. Ser. Khim.*, 1990, (2) 186
63. S M Shevchenko, M Ya Zarubin *Zh. Strukt. Khim.*, 1986, **27**(5) 25
64. N Raos, S M Shevchenko *J. Mol. Struct. (Theochem.)*, 1988, **164**(3–4) 407
65. G M Coppinger, R H Bauer *J. Phys. Chem.*, 1963, **67**(12) 2846
66. H-U Wagner, R Gompper *The Chemistry of Quinonoid Compounds* (Edited by S Patai), London, 1974, Vol. 2, p. 1145
67. L Musil, M Pisova, J Pospisek, M Soucek *Collect. Czech. Chem. Commun.*, 1976, **41**(8) 2238
68. M Remko, J Polcin *Z. Phys. Chem.*, 1978, **258**(2) 219
69. M Remko, J Polcin *Monatsh. Chem.*, 1977, **108**(6) 1313
70. L Musil, B Koutek, J Velek, et al., *Collect. Czech. Chem. Commun.*, 1983, **48**(10) 2825
71. S M Shevchenko, S G Semenov, A G Apushkinskii, et al. *Zh. Org. Khim.*, 1990, **26**(9) 1839
72. S G Semenov, S M Shevchenko *Zh. Strukt. Khim.*, 1983, **24**(5) 25
73. V M Burlakov, E I Chupka, L B Maksimova, et al. *Khim. Prir. Soedin.*, 1988, (6) 858
74. S Iwatsuki, T Itoh, K Ishiguro *Macromolecules*, 1987, **20**(5) 939
75. S G Semenov, S M Shevchenko *Khimiya Drevesiny*, 1986, (3) 61
76. K A Savov, M F Kiryushina, M Ya Zarubin, V V Dzherikhov *Khimicheskaya i Mekhanicheskaya Pererabotka Drevesiny i Drevesnykh Otkhodov* (Chemical and Mechanical Treatment of Wood and Wood Waste), Leningrad, 1980, No. 6, p. 60
77. K A Savov, M F Kiryushina, M Ya Zaruvin *Khimiya Drevesiny*, 1984, (2) 19
78. M Pisova, L Musil, B Koutek, et al. *Collect. Czech. Chem. Commun.*, 1976, **41**(10) 2919
79. L Musil, B Koutek, M Pisova, M Soucek *Collect. Czech. Commun.*, 1981, **46**(5) 1148
80. K Takahashi, N Namekata, K Takase *Tetrahedron Lett.*, 1986, **27**(45) 5515
81. S G Semenov, S M Shevchenko *Zh. Org. Khim.*, 1983, **19**(5) 1084
82. S M Shevchenko, S G Semenov, I P Deineko *Khimiya Drevesiny*, 1984, (6) 63
83. S G Semenov, S M Shevchenko *Khimiya Drevesiny*, 1987, (1) 86
84. S G Semenov, S M Shevchenko *Croat. Chem. Acta*, 1987, **60**(4) 605
85. S G Semenov, S M Shevchenko *Croat. Chem. Acta*, 1988, **61**(1) 113
86. S G Semenov, Yu F Sigolaev, S M Shevchenko *Croat. Chem. Acta*, 1988, **61**(1) 73

87. T J Elder, M L McKee, W D Worley *Holzforschung*, 1988, **42**(4) 233
88. T J Elder, D J Gardner, M L McKee, S D Worley *J. Wood Chem. Technol.*, 1989, **9**(3) 277
89. M Ya Zarubin, M F Kiryushina *Proceedings of the IVth International Symposium on Wood and Pulping Chemistry, Paris*, 1987, Vol. 1, p. 407
90. J Ralph, R M Ede *Holzforschung*, 1988, **42**(5) 337
91. E I Evstigneev, S M Shevchenko *Khimiya Drevesiny*, 1990, (5) 102
92. D R Dimmel, D Shepard *Canad. Wood Chem. Sympos., Niagara Falls*, 1982, p. 1
93. D R Dimmel *J. Wood Chem. and Technol.*, 1985, **5**(1) 1
94. M O F Goulart, H P Utley *J. Org. Chem.*, 1988, **53**(11) 2520
95. D R Dimmel, L F Perry, P D Palasz, H L Chum *J. Wood Chem. and Technol.*, 1985, **5**(1) 15
96. H-J Hofmann, R Cimiraglia, L Tomasi *Pharmazie*, 1986, **41**(7) 518
97. J A Hemmingson *J. Chem. Soc., Perkin Trans. 2*, 1976, (5) 616
98. G Leary, W Thomas *Tetrahedron Lett.*, 1975, (42) 3631
99. G Leary, I J Miller, W Thomas, A D Woolhouse *J. Chem. Soc., Perkin Trans. 2*, 1977, (13) 1737
100. A G Apushkinskii, S M Shevchenko, M Ya Zarubin, V A Gindin *Khimiya i Tekhnologiya Voloknistykh Polufabrikatov Razlichnogo Naznacheniya, Mezhvuzovskii Sbornik Trudov* (The Chemistry and Technology of Fibrous Semi-finished Products for Different Purposes: Intercollegiate Collection of Reports), 1990, p. 38
101. G Brunow, J Sipilä, T Mäkelä *Holzforschung*, 1989, **43**(1) 55; J Sipilä *Ann. Acad. Sci. Fenn. Ser. A, II, Chemica*, 1990, **226** 1
102. J Ralph *1989 International Symposium on Wood and Pulping Chemistry, Raleigh, N. C., USA*, 1989, Vol. 1, p. 61
103. G J Leary, D A Sawtell *Holzforschung*, 1984, **38**(1) 53
104. J A Hemmingson, G Leary *Aust. J. Chem.*, 1980, **33**(4) 917
105. H Nimz, H D Ludemann *Makromol. Chem.*, 1974, **175**(9) 2577
106. H Taneda, S Hosoya, J Nakano, H-M Chang *ISF-85 Proc. Intern. Sympos. on Fibre Sci. and Technol., Barking*, 1986, p. 320
107. K Tanaka, F Nakatsubo, T Higuchi *Mokazai Gakkaishi*, 1976, **22**(10) 589
108. K Tanaka, F Nakatsubo, T Higuchi *Mokazai Gakkaishi*, 1979, **25**(10) 653
109. S Chara, S Hosoya, J Nakano *Mikazai Gakkaishi*, 1980, **26**(6) 408
110. T J Fullerton, A L Wilkins *J. Wood Chem. and Technol.*, 1985, **5**(2) 189
111. D R Dimmel, L F Schuller *J. Wood Chem. and Technol.*, 1987, **7**(1) 97
112. J Janson, T J Fullerton *Holzforschung*, 1987, **41**(6) 359
113. J Ralph, L L Landucci *J. Wood Chem. and Technol.*, 1986, **6**(1) 73
114. J Ralph, L L Landucci *J. Org. Chem.*, 1983, **48**(22) 3884
115. J Ralph, R M Ede, N P Robinson, L Main *J. Wood Chem. and Technol.*, 1987, **7**(2) 133
116. L L Landucci, J Ralph *J. Org. Chem.*, 1982, **47**(18) 3486
117. L L Landucci *TAPPI J.*, 1980, **63**(7) 95
118. J Ralph, L L Landucci *J. Org. Chem.*, 1983, **48**(3) 372
119. K Poppius *Acta Chem. Scand., Ser. B*, 1985, **39**(10) 861
120. K Poppius *Acta Chem. Scand., Ser. B*, 1984, **38**(7) 611
121. J Gierer, O Lindeberg, I Noren *Canadian Wood Chem. Symposium., Niagara Falls*, 1982, p. 23
122. K Poppius *Enhanced β-Aryl Ether Cleavage in Lignin Model Compounds Caused by Reduced Species of Anthraquinone Under Alkaline Pulping Conditions*, Ph.D. Thesis, Helsinki, 1985
123. D R Dimmel, D Shepard *J. Org. Chem.*, 1982, **47**(1) 22
124. S M Shevchenko, V A Gindin, M R Ryblova *Zh. Org. Khim.*, 1985, **21**(10) 2231
125. L L Landucci *J. Wood Chem. and Technol.*, 1981, **1**(1) 61
126. D R Dimmel, D Shepard *J. Wood Chem. and Technol.*, 1981, **1**(2) 147
127. S M Shevchenko, V E Zubarev, A P Rudenko *Croat. Chem. Acta*, 1988, **61**(4) 763
128. G E Miksche *Chemistry of Delignification with Oxygen, Ozone and Peroxides*, Tokyo, 1980, p. 103
129. F Nakatsubo *Wood Research*, 1981, (67) 59
130. S M Shevchenko, M A Kuznetsov *Zh. Org. Khim.*, 1986, **22**(4) 688
131. L D Taylor, J M Grasshof, M Pluhar *J. Org. Chem.*, 1978, **43**(6) 1197
132. D R Dimmel, D Shepard, L F Perry, et al. *J. Wood Chem. and Technol.*, 1985, **5**(2) 229
133. J Ralph, L L Landucci, R A Young *Canadian Wood Chemistry Symposium, Niagara Falls*, 1982, p. 153
134. B-H Yoon, M Okada, S Yasuda, N Terashima *Mokuzai Gakkaishi*, 1979, **25**(4) 302
135. L Pavlickova, B Koutek, K Ubik, M Soucek *Collect. Cezch. Chem. Commun.*, 1976, **41**(1) 299
136. S M Shevchenko, I P Deineko, V A Gindin, M Ya Zarubin *Khimiya Drevesiny*, 1984, (1) 66
137. Ph Girard, P Yianni, J-P Desvergne, et al. *J. Chem. Res. (S)*, 1985, (11) 358
138. G Brunow, G E Miksche *J. Appl. Polym. Sci., Appl. Polym. Sympos.*, 1976, (28) 1155
139. D K Seyler *Delignification Mechanisms in Alkaline Anthraquinone Pulping*, Ph.D. Thesis, Raleigh, N.C., USA, 1985
140. R D Mortimer *J. Wood Chem. and Technol.*, 1982, **2**(4) 383
141. O Lindeberg *Chem. Commun. Univ. Stockholm*, 1979, (6) 1
142. D H Hawes *A Mechanistic Interpretation of the Effects of Anthraquinone on Lignin Model Compounds*, Ph.D. Thesis, Raleigh, N.C., USA, 1985
143. L F Fieser, M Fieser *Reagents for Organic Synthesis* (Translated into Russian), Mir, Moscow, 1970, Vol. 3, p. 86
144. G Leray, W Thomas *Aust. J. Chem.*, 1977, **30**(10) 2323
145. M Pisova, J Pospisek, M Soucek *Collect. Czech. Chem. Commun.*, 1975, **40**(7) 1768
146. A Takuwa, I Hidetoshi, S Osamu, M Kazuhiro *J. Chem. Soc., Perkin Trans. 1*, 1986, (9) 1627
147. S M Shevchenko, A G Apushkinskii, V A Gindin, M Ya Zarubin *Khimiya Drevesiny*, 1990, (4) 111
148. J Pospisek, M Pisova, M Soucek, O Exner *Collect. Czech. Chem. Commun.*, 1975, **40**(7) 2093
149. J Velek, B Koutek, M Soucek *Collect. Czech. Chem. Commun.*, 1979, **44**(1) 110
150. G E Miksche *Lignin Reactions in Alkaline Pulping Process*, Lund (Sweden), 1974
151. M C Schroeter *Hydrolysis of Models Featuring β-Ether Structures of Lignin in Alkali and Sodium Anthraquinone Monosulphonate*, Ph.D. Thesis, Raleigh, N.C., USA, 1980

152. R G Hise *Delignification Mechanisms in Kraft-AQ and Soda-AQ Pulping: The Role of Oxidative Hydrolytic Processes in the Cleavage of C—C Bonds*, Ph.D, Thesis, Raleigh, N. C., USA, 1984
153. J Vicens *Tetrahdedron*, 1987, **43**(7) 1361
154. J N Marx, Q-R Bih *J. Org. Chem.*, 1987, **52**(3) 336
155. A J Poss, R K Belter *J. Org. Chem.*, 1988, **53**(4) 891
156. A J Poss, R K Belter *Tetrahedron Lett.*, 1987, **28**(23) 2555
157. D C Thompson, Y N Cha, M A Thrush *J. Biol. Chem.*, 1989, **264**(7) 3957
158. M Wakselman *Nouv. J. Chim.*, 1983, **7**(7) 439
159. R S Ward *Chem. Soc. Rev.*, 1982, **11**(2) 75
160. O L Chapman, M R Engel, J P Springer, J C Clardy *J. Am. Chem. Soc.*, 1971, **93**(24) 6696
161. J Schizuri *Yuki Gosei Kagaku Kyukaishi*, 1984, **42**(10) 889
162. B Loubinouz, J Maiazimbakana, P Gerardin *Tetrahedron Lett.*, 1989, **30**(15) 1939
163. G Decodts, M Wakselman, M Vilkas *Tetrahedron*, 1970, **36**(13) 3313
164. B Koutek, L Pavlickova, M Soucek *Synth. Commun.*, 1976, **6**(4) 305
165. J M Roper, C R Everly *J. Org. Chem.*, 1988, **53**(11) 2639
166. T Inoue, S Inoue, K Sato *Chem. Lett.*, 1989, (4) 653
167. S R Angle, K D Turnbull *J. Am. Chem. Soc.*, 1989, **111**(3) 1136
168. S R Angle, M S Louie, H L Mattson, W Yang *Tetrahedron Lett.*, 1989, **30**(10) 1193
169. A Arduini, A Bosi, A Pochini, R Ungaro *Tetrahedron*, 1985, **41**(15) 3095
170. M A Chauncey, M F Grundon, M J Rutherford *J. Chem. Soc., Chem. Commun.*, 1988, (8) 527
171. J J Talley *J. Org. Chem.*, 1985, **50**(10) 1695
172. R Hug, H J Hansen, H Schmid *Helv. Chim. Acta*, 1972, **55**(5) 1675
173. Y L Mao, V Boeckelheide *Proc. Natl. Acad. Sci. USA*, 1980, **77**(1) 1732
174. J P Marino, S L Dax *J. Org. Chem.*, 1984, **49**(19) 3671
175. D A Bolon *J. Org. Chem.*, 1970, **35**(11) 3666
176. G Casnati, A Pochini, M G Terenghi, R Ungaro *J. Org. Chem.*, 1983, **48**(21) 3783
177. S B Cavitt, R Sarrafizadeh, P D Gardner *J. Org. Chem.*, 1962, **27**(4) 1211
178. R F Heldweg, H Hogeween *J. Am. Chem. Soc.*, 1976, **98**(19) 6040
179. K Freudenberg, A C Neish *Constitution and Biosynthesis of Lignin*, Springer-Verlag, Berlin, etc., 1968
180. S M Shevchenko, M Ya Zaruvin, B Kovac, et al. *TAPPI J.*, 1989, **72**(5) 228
181. T J Elder, S D Worley *Wood Sci. and Technol.*, 1984, **18**(4) 307
182. O Martensson, G Karlsson *Arkiv Kemi*, 1968, **31**(2) 5
183. T Higuchi *Wood Research*, 1980, (66) 1
184. K Forss, K-E Fremer *J. Appl. Polym. Sci., Appl. Polym. Sympos.*, 1983, (37) 531
185. E Adler *Wood Sci. and Technol.*, 1977, **11**(3) 169
186. A Scalbet, B Monties, C Rolando, A Siera-Escudero *Holzforschung*, 1986, **40**(3) 191
187. W G Glasser, H R Glasser *Paperi ja Puu*, 1981, **63**(2) 71, 77, 82
188. J A Hemmingson *Aust. J. Chem.*, 1979, **32**(1) 225
189. J A Hemmingson, G J Leary, I J Miller, et al. *J. Chem. Soc., Chem. Commun.*, 1978, (3) 92
190. C I Simonescu, G Rozmarin, V I Popa *Holzforschung und Holzverwertung*, 1987, **39**(5) 112
191. M I Chudakov *Khimiya Drevesiny*, 1978, (2) 3
192. S Yasuda *Kagaku to Seibutsu (Chem. and Biol.)*, 1980, **18**(1) 30
193. S Yasuda, K Fuji, B-H Yoon, N Terashima *Mokuzai Gakkaishi*, 1979, **25**(6) 431
194. S Yasuda, B-H Yoon, N Terashima *Mokuzai Gakkaishi*, 1979, **25**(12) 771
195. S Yasuda, B-H Yoon, N Terashima *Mokuzai Gakkaishi*, 1980, **26**(6) 421
196. S M Shevchenko, S G Semenov *Zh. Strukt. Khim.*, 1990, **31**(2) 40
197. H-J Hofmann, R Cimiraglia, R Bonaccorsi, et al. *Eur. J. Med. Chem.*, 1989, **41**(7)
198. A A Larsen *Nature*, 1969, **224**(5214) 25
199. M Sugumaran *Biorg. Chem.*, 1987, **15**(2) 194
200. M Sugumaran *Sympos. Molec. Cell. Biol., New Ser. (Molec. Entomol.)*, 1987, **49** 357
201. M Sugumaran *Archives Insect Biochem. and Physiol.*, 1988, **9**(2) 73
202. M Sugumaran, S J Saul, V Semenski *Archives Insect Biochem. and Physiol.*, 1988, **9**(4) 269
203. K Ramakrishnan, J Fisher *J. Med. Chem.*, 1986, **29**(7) 1215
204. O Takahachi *Biochem. Pharmacol.*, 1988, **37**(14) 2857
205. M R Attwood, B R Brown, S G Lisseter, et al. *J. Chem. Soc., Chem. Commun.*, 1984, (3) 177
206. L Ivnas, B Lindberg *Acta Chem. Scand.*, 1961, **15**(5) 1081
207. K Hästbacka *Soc. Sci. Fennica. Commun. Phys.-Math.*, 1963, **26**(4) 1
208. S Larsson, B Lindberg *Acta Chem. Scand.*, 1962, **16**(7) 1757
209. G E Miksche *Acta Chem. Scand.*, 1973, **27**(4) 1355
210. J Gierer, S Ljunggren *Svensk Papperstidn*, 1979, **82**(17) 503
211. J R Obst *Holzforschung*, 1983, **37**(1) 23
212. R Kondo, Y Tsutsumi, H Imamura *Holzforschung*, 1987, **41**(2) 83
213. G E Miksche *Acta Chem. Scand.*, 1972, **26**(10) 4137
214. G E Miksche *Acta Chem. Scand.*, 1972, **26**(8) 3275
215. J Gierer, S Ljunggren *Svensk Papperstidn*, 1979, **82**(3) 71
216. J Gierer *Wood Sci. and Technol.*, 1980, **14**(4) 241
217. D R Dimmel, L F Schuller *J. Wood Chem. and Technol.*, 1986, **6**(4) 535
218. D R Dimmel, L F Schuller *J. Wood Chem. and Technol.*, 1986, **6**(4) 565
219. H Veeramani, G A Wani *Chem. Ind. Development*, 1977, **11**(12) 13
220. J Gierer *Holzforschung*, 1982, **36**(1) 43
221. G E Miksche *Acta Chem. Scand.*, 1972, **26**(8) 3269
222. J Gierer, J Lenic, I Noren, I Szabo-Lin *Acta Chem. Scand., Ser. B*, 1974, **28**(7) 717
223. J Gierer, I Noren *Acta Chem. Scand.*, 1962, **16**(7) 1713
224. K Lundquist, K Hedlund *Acta Chem. Scand.*, 1967, **21**(7) 1750
225. G Brunow, G E Miksche *Acta Chem. Scand.*, 1972, **26**(3) 1123
226. G Gellerstedt, J Gierer *Acta Chem. Scand.*, 1972, **26**(2) 701
227. G Gellerstedt, J Gierer *Acta Chem. Scand., Ser. B*, 1975, **29**(5) 561
228. G Gellerstedt, J Gierer *Acta Chem. Scand., Ser. B*, 1977, **31**(8) 729
229. R D Mortimer *J. Wood Sci. and Technol.*, 1985, **5**(3) 347
230. J Gierer, I Petterson *Can. J. Chem.*, 1977, **55**(4) 593
231. J Gierer, O Lindberg *Acta Chem. Scand., Ser. B*, 1979, **33**(8) 580

232. T J Fullerton *J. Wood Chem. and Technol.*, 1987, 7(4) 441
233. F Imsgard *Autoxidation in Alkaline Media of Phenolic Compounds Related to Lignin*, Ph.D. Thesis, Stockholm, 1976
234. J Gierer, O Lindberg *Acta Chem. Scand., Ser. B*, 1978, **32**(8) 577
235. J Gierer, F Imsgard, I Petterson *J. Appl. Polym. Sci., Appl. Polym. Sympos.*, 1976, (28) 1195
236. H Aminoff, G Brunow, K Falck, G E Miksche *Acta Chem. Scand., Ser. B*, 1974, **28**(3) 373
237. D R Dimmel, D Shepard, T A Brown *J. Wood Chem. and Technol.*, 1981, **1**(2) 123
238. D R Dimmel, L F Perry *International Symposium on Wood and Pulping Chemistry (Technical Papers)*, Vancouver, Canada, 1985, p. 177
239. D A Smith, D R Dimmel *International Symposium on Wood and Pulping Chemistry (Posters)*, Vancouver, Canada, 1985, p. 39
240. R Kondo, J L McCarthy *J. Wood Chem. and Technol.*, 1985, **5**(1) 37
241. J Gierer, F Imsgard, I Noren *Acta Chem. Scand., Ser. B*, 1977, **31**(7) 561
242. J Gierer, F Imsgard *Svensk Papperstidn*, 1977, **80**(16) 510
243. J Gierer *Holzforschung*, 1982, **36**(2) 55
244. D R Dimmel, L F Schuller *J. Wood Chem. and Technol.*, 1986, **6**(3) 345
245. L J Wright, T J Fullerton *J. Wood Chem. and Technol.*, 1984, **4**(1) 61
246. L Eberson *Electron Transfer Reactions in Organic Chemistry*, Springer-Verlag, Berlin, etc., 1987, p.234
247. S V Stovbun, A I Mikhailov, V I Goldanskii *Proceedings of the IV International Symposium on Wood and Pulping Chemistry, Paris*, 1987, Vol. 2, p. 179
248. S M Shevchenko, L G Akim, A G Apushkinsky, V A Gindin *Chem. Papers (Chem. Zvesti, Bratislava)*, 1991, **45**(1) 109
249. A G Apushkinskii *Candidate's Thesis in Chemical Sciences, Leningrad Forestry Academy*, Leningrad, 1987

Translated from *Uspekhi Khimii* **61** 257–292 (1992) U.D.C. 541.64:66.097+661.8

Specific characteristics of catalysis by polymer-immobilised complexes†

A D Pomogailo
Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka

ABSTRACT. The most important factors which affect to different extents the activity and selectivity of immobilised complexes in numerous processes have been examined. Attention has focussed particularly on a discussion of the factors responsible for the increase in cooperative stabilisation of active centres in such systems in comparison with homogeneous systems. The basic facts about polyfunctional catalysis based on immobilised complexes are presented. Certain questions and the potential for further advancement in this direction are discussed.

Bibliography, 107 references.

Contents

I.	Introduction	133
II.	Ligand exchange in metallo-polymeric systems	134
III.	Characteristics of electron transfer reactions in metallo-polymeric systems	135
IV.	Protective functions of the macroligand	136
V.	Local concentration effects in metallo-polymeric catalysis	137
VI.	Problems of homogeneity and evolution of active centres in the immobilised systems	138
VII.	The effect of the surface density of immobilised metallo-complexes on their catalytic activity	140
VIII.	Characteristics of the effect of temperature on the catalytic properties of immobilised complexes	141
IX.	The contribution of energy of non-equilibrium configurations of the chain to catalysis	144
X.	Cooperative stabilisation of active centres in the immobilised systems	145
XI.	The selectivity of immobilised catalysts	148
XII.	The problem of polyfunctional catalysis	148
XIII.	Conclusion	150

I. Introduction

A simple and promising idea, based on the knowledge of the chemical or physical forces which bind metallo-complexes (MX_n) with an organic or inorganic microligand, has promoted the development of many catalytic processes and has become the main factor for subsequent convergence of homogeneous and heterogeneous catalysis. The relevance of the concept itself and the intensity of the investigations have led to the creation of an essentially new avenue of catalysis with its own constructive principles and techniques.

There are two main objectives in the immobilisation of metallo-complexes. The first is the creation of stable catalysts with high activity, selectivity and reproducibility (as in homogeneous systems) and moreover readily separable from the reaction products and recoverable (as in heterogeneous contacts). Thus it was suggested initially that from the practical standpoint such systems should combine the advantages and eliminate the disadvantages of traditional catalysts.

In scientific terms the second objective is no less important, i.e. to construct catalysts possessing a high concentration of active centres with known structures which are also suitable for the analysis of their evolutionary transformations during the catalysed reaction. By resolving this question it would be possible to move towards a scientifically founded selection of catalysts and to predict their catalytic action.

It is necessary immediately to make the proviso that, despite significant advances in this field, it has been found much more difficult than anticipated to resolve the tasks set. Firstly, it was found that it is not easy to obtain isostructural metallo-complexes which can be firmly retained on the surface under the conditions of a catalysis. Secondly, along this route a multitude of specific difficulties arise which are associated with the behaviour of immobilised complexes in heterostructural catalytic reactions. The causes of the increase in rate of certain processes concomitantly may be the causes of the decrease in rate of other processes. Thirdly the nature of such systems which is determined by many factors hinders the prediction of the behaviour of system MX_n, the polymeric support during the catalytic reaction, and the preliminary assessment of the effect of the conditions under which this reaction takes place on all possible transformations of the components. Macromolecular effects including the effect of the microenvironment (local polarity, the neighbour effect, the effect of the size of the polymeric globule, the degree of substitution of the functional groups L, etc.) the electrostatic properties of the ionic groups bound with the polymeric chain (polyelectrolyte catalysis), isolation of active centres (dilution effect), local concentration effects (functional groups during the spherical binding of the chains on one side and the substrate close to the polymeric globule on the other), and the effect of polydentaticity, etc. play a particularly important role. When insoluble polymers are used as supports, it is necessary to take into account the biographic heterogeneity of the surface, and the swelling and migration of the attached complexes in the course of the reaction, etc. The situation becomes much more complicated if the attached complex undergoes partial dissociation during the reaction and if catalysis is achieved simultaneously with mobile and immobile particles.

The author considers that the present review summarises the most important features of catalysis by immobilised complexes, the synthesis and structures of the latter having been the subject of a large number of reviews and monographs.[1–5]

† The first five articles are a continuation of No. 12 in 1990 concerning problems of catalysis.

II. Ligand exchange in metallo-polymeric systems

Almost all studies have shown that immobilised systems have higher stability than normal catalysts even under conditions which are comparatively severe for metallo-complex catalysts (increase in temperature and pressure, highly polar solvents, active substrates). Since the metallo-polymers are formed in an enclosed microvolume in which quite a large number of macromolecules, functional groups, and different types of particles (MX_n, electrons, protons, radicals, oligomers, etc.) is involved, on the whole the state of the metallo-polymeric system is characterised by a combination of concentrations of free functional groups, and also complexes, which may contain different numbers of ligands of each type which may occupy various positions in the macromolecule.

The two main reasons leading to a decrease in the cooperative stabilisation and even to the disruption of the immobilised complexes during catalysis are their instability:

$$\widetilde{L}\text{—}MX_n \overset{K'}{\rightleftharpoons} \widetilde{L} + MX_n, \quad \widetilde{L}\text{—}MX_n + S \overset{K''}{\rightleftharpoons} \widetilde{L} + MX_nS$$

(S is the solvent, substrate, co-catalyst, or specially introduced additive). The overall contribution of these processes is reflected in the decrease in content of the metal on the support or in the concentration of the metal passing into solution. The specific contribution of the chemical instability of macrocomplexes is usually higher than thermodynamic instability. In systems which are used to polymerise olefines,

$$MX_n \cdot D \overset{K'}{\rightleftharpoons} MX_n + D$$

$$MX_n \cdot D + AlR_xCl_{3-x} \overset{K}{\rightleftharpoons} MX_n + D \cdot AlR_xCl_{3-x}$$

when $MX_n = VCl_4$, D = MMA or $AlR_xCl_{3-x} = AlEt_3$ in benzene at 293 K, $K' = 1.8 \times 10^{-3}$ mol l^{-1}, while $K = 8.7 \times 10^2$.[6] Replacement of the ligand environment by the polymeric environment leads to an increase in both the thermodynamic and chemical stability of the complexes. Thus by using the stopped-flow technique the kinetics of the pseudo-first order exchange reaction (pH 9.3–11.0; 298 K; excess of EDTA) was studied,[7]

$$Cu(2+)\text{-PVC} + EDTA \rightarrow Cu(2+)\text{-EDTA} + PVC$$

the kinetic equation of which has the following form:

$$-\frac{d[Cu(2+) - PVC]}{dt} = k_1 \frac{[Cu(2+) - PVC]}{[PVC]} = k_2 \frac{[Cu(2+) - H - PVC]}{[PVC]},$$

and $k_1 = 3.62 \times 10^{-3}$ mol sec^{-1}, $k_2 = 3.68 \times 10^4$ mol sec^{-1}. The ligand exchange occurs by two mechanisms, either by H^+ attack (from EDTA) with the formation of the intermediate complex Cu(2+)-H-PVC and its subsequent dissociation, or by solvolysis involving water.

One of the characteristic examples of exchange reactions involving low- and macromolecular ligands is the exchange of the axial ligand in benzylcobaloxime and in cobaloxime $Co(DH)_2$ covalently linked with chloromethylated polystyrene (PS):[8]

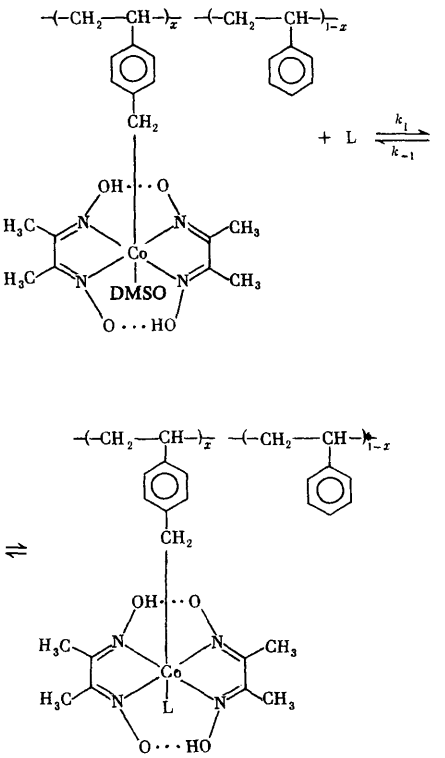


Table 1. Rate constants of ligand exchange in $RCo(DH)_2DMSO$.[8]

R	L	k_1, $l\,mol^{-1}\,sec^{-1}$	k_{-1}, $l\,mol^{-1}\,sec^{-1}$	$K \cdot 10^{-2}$
Polymer	SCN^-	$1 \cdot 10^3$	4.8	2.1
Benzyl	SCN^-	$1.2 \cdot 10^3$	15	0.8
Polymer	Py	23.6	$2 \cdot 10^{-3}$	118
Benzyl	Py	16.5	$1.7 \cdot 10^{-2}$	9.8

Although the Co(3+) complexes are comparatively resistant to substitution, the presence of the macromolecular ligand promotes a more rapid substitution of the axial ligand in the *trans*-position (solvent was DMSO or DMSO + benzene). It is apparent from Table 1 that the rate constants of the forward reaction in the systems compared are similar, although the constants of the reverse reaction for the dissociation of the complex which contains the low molecular weight *trans*-ligand is approximately 3 ($L = SCN^-$) and 9 (L = Py) times higher.

Thus the higher values of the equilibrium constants of ligand exchange in the metallo-polymer systems in comparison with the low molecular weight benzyl complexes may be attributed to the smaller

values of the rate constants for the reverse reactions. This may be associated both with the higher local concentration of cobaloxime in the polymer matrix in comparison with its concentration in the volume of the DMSO solvent and also with steric hindrances which create a macrochain, hampering ligand transport from the polymeric "cells" and promoting its recombination. In the DMSO-benzene mixed solvent with increase in the latter the polymeric globule expands, as a result of which the effect of these factors decreases. Increase in this characteristic viscosity is accompanied by a decrease in the rate constant of the forward reaction and an increase in the rate constant of the reverse reaction (Fig. 1). The higher rate constant of the ligand exchange (L = Py) in polymer-bound cobaloxime (in DMSO) was due to great changes in entropy.

R	ΔF, k J mol^{-1}	ΔH, k J mol^{-1}	ΔS, a.u.
Polymer	−17.6	−38.6	−16
Benzyl	−16.4	−67.2	−40

Similar results have been obtained in studies of other systems. One should note that the calculation of the standard potentials and observed rate constants of outer-sphere exchange involving Co(2+) and Fe(3+) ions taking into account the change in structural parameters of the macrocomplexes indicates that the systems examined are in many ways similar to metallo-protein complex systems.[9]

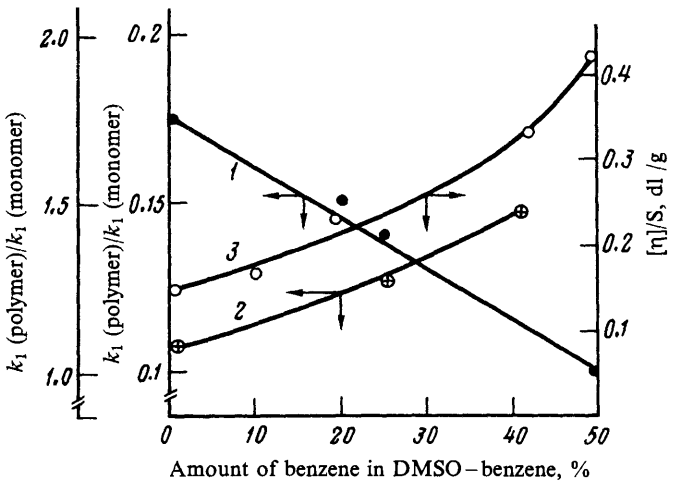


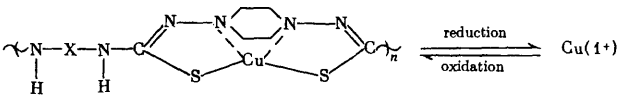
Figure 1. Variation in the relative rate constants of the coordination of pyridine with cobaloxime k_1 (*1*) and k_{-1} (*2*) and the characteristic viscosity of the macrocomplex (3) as a function of the composition of the DMSO-benzene mixture.[8]

Hence the replacement of a low molecular weight ligand environment by a polymeric environment hinders the entry of the reagents into the coordination sphere of the transition metal and causes its additional polarisation in the heterogeneous electrostatic field of the ligands, which also confers increased stability upon the macrocomplex. The ability of the coordinatively saturated metal atom in the macrocomplex to form coordination vacancies should have significant value for ligand exchange. They may arise at the immobilisation stage owing to the prevention of dimerisation of the metallo-complexes or on account of the easy disruption of M–M bonds, as a result of the reduction of the transition metal, the effective adsorption of excess of ligand by the matrix, etc.

III. Characteristics of electron transfer reactions in metallo-polymeric systems

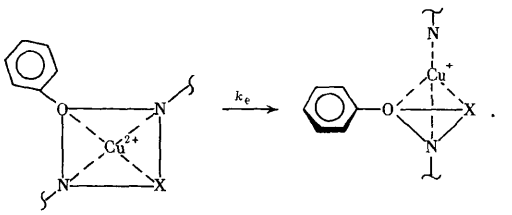
Electron transport in metallo-polymeric systems determines the rate of many processes, and is almost always the slowest stage of the catalytic act. Such an intramolecular process is very sensitive to the active centre environment, i.e. the nature of the ligand, the solvent, the ionic strength, pH, etc. It is accompanied by a rearrangement of the complex and by conformational changes in the polymer.

The primary structure of the support, the distribution of the redox-centres, the charge density, and the polarity of the polymer domains have a strong effect on electron transport in macromolecular formations. The most frequent redox transformations occur in the immobilised systems Fe(2+) ⇄ Fe(3+), Cu(1+) ⇄ Cu(2+), Co(2+) ⇄ Co(3+), and Mo(5+) ⇄ Mo(6+) and certain others. The redox processes sometimes occur even at the metallo-complex immobilisation stage,[5] and they most often occur in oxidation reactions. Thus the chelate complexes of Cu(2+) catalyse the oxidation of aldehydes to acids or cyclohexanol to cyclohexanone. In this case Cu(2+) is reduced to Cu(1+).[10]



In turn the Cu(1+) ion in the polymeric complex is oxidised to Cu(2+) in the reduction reactions of nitrobenzene to azoxybenzene, nitrocyclohexane to cyclohexanoxime, 1,4-benzoquinone to hydroquinone, and $KMnO_4$ and MnO_2. Such a conjugated process is named the "ping-pong" mechanism.

To determine the specific characteristics of the polymeric environment, the oxidation of Cu(1+) complexes with polyvinylimidazoles (PVI) by molecular oxygen was compared with their imidazole analogue.[11] The study was conducted using the stopped-flow technique in buffer systems (Table 2). A higher enthalpy and a lower entropic factor is typical of the oxidation of polymer complexes. The differences in the kinetic and activation parameters are associated with conformational transformations of the macroligand in the course of the redox reaction which lead to a change in bond lengths and the angles between them in the Cu(1+) and Cu(2+) complexes:



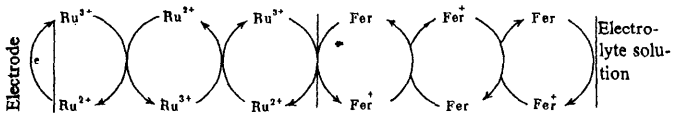
The occurrence of conformational transformations during the oxidation were demonstrated by viscosimetric measurements.

Similar patterns are also found in the redox cycles Co(3+) ⇄ Co(2+). For example the outer-sphere reactions of Co(3+) macrocomplexes with poly-4-vinylpyridine (P4VP), polyethylenimine (PEI), polyvinylimidazole (PVI) and Fe(2+) complexes with electron transport occur at lower rates than the reactions of Co(3+) complexes with low molecular weight ligand-analogues.[12,13] The opposite situation is found, when hydrophobic interactions occur between the polymer ligand and Fe(2+). This is associated with an increase in the local concentration of the reducing agent in the macrocomplex (see Chapter V). Thus addition of styrene sulphonate increases the rate of reduction of Co(3+) in the P4VP-complex 10–30-fold in comparison with the pyridine complex.

Table 2. Kinetic and activation parameters of the oxidation of Cu(1+) complexes at 298 K.[11]

Ligand	pH	$k_{eff} \times 10^2$, l mol^{-1} sec^{-1}	$\Delta F^{\neq}$, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1}, deg^{-1}
Poly-1-vinylimidazole	4.7	2.7	61.3	48.3	−44.1
	4.3	14.0	57.1	29.4	−92.4
Poly-4(5)-vinylimidazole	6.0	0.10	66.0	61.8	−14.4
	4.7	0.26	64.7	57.5	−24.0
Imidazole	8.0	4.9	60.5	13.4	−154.6

Metallo-complexes bonded to the polymers are quite extensively used in electrocatalytic redox processes. With this objective, by immobilising metallo-polymers on electrodes, chemically modified electrodes and also bilayer polymeric electrodes incorporating two types of electroactive films are obtained. In such composites the outer layer is subjected to the action of the substrate, while the inner layer is in direct contact with the surface of the electrode. The scheme for such a bilayer electrode is shown below:[14]



At a particular electrode potential the outer film of poly-[Ru(Dipy)$_3^{2+}$-vinylpyridine] participates in the redox reaction with polyvinylferrocene (PVFer):

$$\text{Poly[Ru(Dipy)}_3]^{2+} + \text{PVFer} \rightarrow \text{poly[Ru(Dipy)}_3]^{+} + \text{PVFer}^{+}.$$

At high potentials the reduction of the outer and oxidation of the inner films occur.

It will be shown below (see Section VI) that the extent of chain loading (the extent of coordination of functional groups f) is found to have a significant effect on the specific catalytic activity (SCA) of the macrocomplexes. The extent of chain loading also affects the activation parameters of the electron transfer reaction (Table 3). With increase in f the values of $\Delta F^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ decrease, which may be associated with the state of the polymer chain, and particularly with its elongation (as indicated by the increase in the characteristic viscosity) and hence with a change in the charge density on the polymer chain.[13] The reverse oxidation reaction Co(2+) → Co(3+) may be both more rapid and also slower than with the low molecular weight reagents.

Table 3. Activation parameters of the electron transfer reaction and the change in viscosity in the Co(3+).PVI–Fe(EDTA)$^{2-}$ system at pH 5 and 303 K.[13]

f	[η], dl mmol^{-1}	$\Delta F^{\neq}$, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, e. e.
0.10	2.26	51.7	144.5	72.8
0.12	2.33	50.4	136.1	67.4
0.15	2.86	49.1	106.3	45.0
0.25	3.25	46.6	97.4	39.3
0.32	3.34	45.3	94.5	30.3
N-vinyl-2-methylimidazole	–	52.0	31.9	15.6

Of the other comparatively numerous examples confirming the concepts being developed, redox-reactions involving molybdenum macrocomplexes should be mentioned, i.e. cyclic redox-processes of peptide Mo(5+) complexes immobilised as a chloromethylated copolymer of styrene with divinylbenzene (CSDVB) (a reductase or oxidase analogue),[15] and also redox reactions of cystein thiolato dioxomolybdenum(6+) centres attached to polyethyleneglycol (molybdo-oxidase model).[16]

It is important that repetition of electron transport acts does not cause changes in the multinuclear state of Cu, Co, and Mo complexes, etc., whereas the macroligand reorganisation relates to certain of the most important factors influencing the reaction with electron transfer in the polymer matrices.[17]

IV. Protective functions of the macroligand

One of the protective functions of the macroligand is the creation of diffusion barriers, which impede the deactivation of the active centres or interaction of the substrates with reactive reagents or microadditives in the reaction medium (for example H_2O, O_2, etc.). Thus to protect high-spin Fe(2+)-porphyrin complexes, which are oxidised in solution to low-spin Fe(3+)-complexes and which thereby bind O_2, their combinations with polymeric ligands in aqueous solution are used (polymers and copolymers based on 1-vinylimidazole, 1-vinyl-2-methylimidazole, 1-vinylpyrrolidone, water-soluble copolymers based on quaternised 4-vinylpyridine, etc.).[18] Such an approach is more effective than the creation of steric hindrances around the active centres, and the use of low temperature, etc.

There have been successful attempts to construct on this basis synthetic O_2 carriers for reverse oxidation in water and other proton media. With this objective the metalloporphyrins are bonded to the hydrophobic regions of water-soluble polymers (oxygen protection).

The spatial stabilisation of active centres also plays an important role. The presence of a hydrophobic environment around them reduces or even excludes the possibility that oxodimers are formed in the presence of O_2 and in the subsequent irreversible oxidation of M^{n+}.[19]

The protective function of the macroligand which is realised for example in the oxidation of phenols by molecular O_2 ensures the protection of the catalytically active binuclear Cu(2+) complex.[20,21] A similar stabilising effect is directed against the so-called substrate inhibition. The mechanism of the reaction incorporating the transfer of two electrons from the substrate to oxygen in the molecular orbital system of the metal is more easily achieved in immobilised binuclear Cu(2+) complexes.

We shall examine certain other variants in which the protective function of the macroligand is exerted. A major defect of traditional heterogeneous catalysts for the isotopic exchange of hydrogen in the liquid phase is their extreme instability caused by the capillary condensation of water and by blocking of the catalyst. To prevent such phenomena different variants of its hydrophobisation have been elaborated, including the use of polymers. Such an approach may be regarded as the microencapsulation of the catalyst in the polymer. Thus, the T−H-exchange catalyst was obtained by immobilising MX_n on CSDVB, and polytetrafluoroethylene (PTFE) is most often used for this purpose.[22] Regeneration involves heating the catalyst to remove water droplets from the pores. The polymer matrix plays such a role by ensuring the protection of diazo-complexes from the action of moisture thereby increasing their life-time even at room temperature.[23]

An unusual hydrophobic protection was used in relation to unstable Mo(5+) complexes. Being immobilised on chloromethylated CSDVB modified with peptide groups, they become stable within several days in the presence of H_2O and O_2.

Another mechanism of the protective action of water and even of the increase in rate of catalytic processes for the water is realised when the water is bound by hydrophilic polymers.[24] For example, on account of the solvate effect observed in the presence of polymers (polyethyleneimine propionate, poly-4-vinyl-N-ethylpyridinium bromide, etc.) there is a 10^5-fold increase in the rate of polyelectrolytic catalytic hydration of *tris*-(oxalato)cobalt in binary mixtures of water with DMSO or DMF. This is associated with the selective adsorption of H_2O from a mixture of solvents. The preferred hydration of the complex close to the polymer on the one hand leads to the localisation of anionic reagents around this polymer, and on the other hand leads to repulsion of H_3O^+.

Hydrophobic protection plays a major role in reactions catalysed by metallo-organic compounds (or by organometal intermediates formed). Polar media are also used for these purposes. This is possible because in many reactions the globules of the functionalised macromolecules with attached catalytic centres surrounded by solvents fulfil the function of isolated microreactors.[25,26]

V. Local concentration effects in metallo-polymeric catalysis

The increased activity of immobilised catalysts may be caused both by an increase in the local concentration of substrate and active forms in such microreactors, despite possible steric hindrances as the reagent approaches the catalyst and during the transport of the reaction products. The super-equilibrium substrate concentration in domains situated adjacent to the active centres is achieved by electrostatic, donor-acceptor, and π-interactions involving active regions and functional groups (L) of the polymers. There are numerous examples of such effects. Thus on hydrogenation of styrene in the presence of Pd(0) bonded to functionalised CSDVB (4−6% DVB) the rate of the reaction increases, if the L group promoted the formation of π-complexes with the substrate.[27] The activity of allylacrylate correlated with the π-acceptor and polar properties of L. The $-NO_2$ and $-OMe$ groups promote the formation of molecular associates with the substrates, while $-OH$, $-NH_2$, $-NR_3$, and $-CH_2OCH_2$ groups react with the substrate owing to polar effects. Polymers with a hydrophobic surface retard the rate of hydrogenation of nonpolar substrates. The introduction of 2,4-dinitrophenyl groups even at a level of 7% causes a marked reduction in the rate of hydrogenation of 4-vinylcyclohexane. The high activity of Rh(1+) on phosphinated CSDVB in hydrogenation reactions of polynuclear heteroatomic compounds is associated with an increased substrate concentration close to the metallo-centre.[28]

Differences in the polarity of the polymer and solvent lead to an increase in substrate concentration in the polymer in comparison with the reaction volume. When a more polar solvent is used, the nonpolar substrate is able to penetrate more readily into the polymer phase owing to the polarity gradient. Transport of the polar substrate into the nonpolar sphere is made difficult, which is reflected in the decrease in rate of the reaction. The form of the catalyst particles (granules, powder, film, fibre) also has an influence.

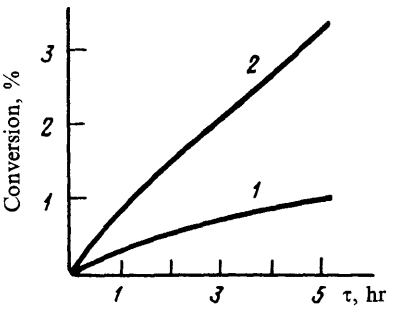


Figure 2. Kinetic curves of the oxidation of ethylbenzene in the presence of macrocomplexes not built (*1*) and built (*2*) on ethylbenzene.[30]

The functional groups may be involved not only in the binding of MX_n but also in the catalytic process itself by protecting the active centre from microadditives and catalyst poisons or by promoting secondary reactions. In principle the interaction of L with the substrate may be accompanied by more profound transformations such as protonation, ionisation, and alkylation, and sometimes also by quaternisation and oxidation in reduction reactions. Such processes apparently play a particularly significant role with metallo-complexes immobilised on strongly cross-linked polymers in which the proportion of the vacant L is comparatively high. However they may occur also in reactions in which grafted macroligands are involved. Thus from a kinetic study of the oxidation of cyclohexene by molecular O_2 in the presence of Co(2+), bonded to PE-grafted-poly(acrylic acid) (PE-pr-PAA) it was concluded that a high

concentration of the peroxide being formed is created close to the surface of the heterogeneous catalyst, and that peroxide decomposition provides the major contribution to the initiation of chains in the developing process. Close to the catalytic centres, the cobalt ions on the polymer, there are vacant carboxylic groups which, owing to the formation of hydrogen bonds, are able to adsorb ROOH molecules, thereby creating their high local concentration. Apparently by regulating the concentration of the vacant L, it is possible to control the course of the reaction, i.e. in the immobilised systems one more control level appears which has no analogues in homogeneous or heterogeneous catalysis.

A new phenomenon of structural adjustment of the active centres on the substrate has been observed in the liquid-phase oxidation of ethylbenzene and xylols by molecular oxygen.[30,31] This process involves the formation of soluble Co(2+) complexes, for example with the copolymer of the diethyl ester of vinylphosphonic acid and AK in the presence of the substrate (ethylbenzene) or α-phenylethylhydroperoxide. The specific structural adjustment for the reacting substances is then fixed by intermolecular cross-linking of the polymer support by *N,N'*-methylene bis-acrylamide with subsequent removal of the template substrates from the cross-linked formations. Such an adjustment markedly increases the activity and selectivity of the catalyst (Fig. 2).

Cases are known in which a "hyperequilibrium" concentration of the product forming in metallo-polymeric particles is attained. Thus on polymerisation of ethylene by gel-immobilised systems,[32] after contact with monomer the catalyst particles swollen in the solvent undergo further swelling and PE accumulates within each particle. The "hyperequilibrium" swelling of cross-linked catalyst particles is caused by the accumulation of polymer within the previously created three-dimensional network of the polymeric support. The energy of extending such particles by the value ΔV (additional increase in volume owing to the "hyperequilibrium" swelling of the three-dimensional structure of the original gel) is equal to

$$A = \int_{V_p}^{V_{ст}} P(V)\mathrm{d}V,$$

where P is the swelling pressure, V_{st} is the particle volume in the stationary working state, V_p is the volume of the particle stably swollen in the pure solvent, and $\Delta V = V_{st} - V_p$. This work is accomplished owing to the free energy of ethylene polymerisation and causes additional stress to the elastic network of the support. Apparently in such systems a specific mechanism also operates to limit material chains. The swelling pressure acting on the growing macromolecules strives to "force" it out on the catalyst granule† (mechanical activation of the elementary act).

Thus the nature of the macrocomplexes is such that they behave as a special phase in which the concentration of reagents is higher than in the volume of the solution (or in the gas phase in the case of gas phase processes).

† It is assumed that a certain prolonged stress arises also at the "growing point" of the macromolcule, i.e. at the metal–carbon bond. It may be the source of the increase in probability of chain restriction.

VI. Problems of homogeneity and evolution of active centres in immobilised systems

The frequently higher specific catalytic activity of the immobilised complexes may be attributed to structural defects in the coordination centres and to unsaturation, which promotes coordination of the substrate, and also to cooperative effects. Many of these factors may be taken into account during the construction of the immobilised catalysts. For example the composition of bonded complexes may be controlled to a certain extent by selecting the L:M ratio. In most reactions between the macroligand and MX_n the equilibrium is established almost immediately after the components are mixed, but sometimes a prolonged period is required for this to be attained, particularly if the macroligand is polyfunctional. In certain cases the total rearrangement of the complex occurs more slowly than the catalysed reaction. Since the structural homogeneity of the complex is important for ensuring high and stable activity, it becomes essential to take into account the rate of such a rearrangement.

The formation of the required structure determined by the electronic configuration of the transition metal ion is also dependent on the conformational exchange in the macroligand which leads to the creation of the appropriate orientation. Such an exchange is associated with energy losses which are greater the more the chain conformation differs from the required conformation. In this sense the "pliability" of the macromolecule is important, and therefore the macroligand cannot be regarded as a certain set of independent functional groups.

Furthermore the polymeric matrix may bind and stabilise coordinatively unsaturated metallo-complexes.[33] The rate of rearrangement (relaxation) of the active centre is low because of the large size of such formations, especially in the case of strongly cross-linked matrices. These processes become complicated in the transition from homogeneous to heterogeneous and especially to enzyme-mediated catalysis.[34] Therefore in a catalysable reaction a nonequilibrium configuration of active centres (and their hyperequilibrium concentration) becomes possible. In heterogeneous catalysis in this case nonequilibrium phases may arise.

During catalysis by immobilised complexes not only the total content (concentration) of the attached MX_n but also its distribution profile in the polymeric matrix (topography) is of great importance. Numerous observations indicate the static distribution of the transition metal on the support. Analysis and calculation of the topography of immobilised complexes opens one of the avenues for increasing the efficiency of the catalysts. Optimisation is achieved by moving the active centres on to the surface (or on to the thin layer adjacent to the surface layer) of the polymeric support.[35] When such catalysts are constructed their main role is attributed to the topography of the functional groups of the macroligand and its accessibility. The latter is determined by the contribution of the polymer chain during a change in the microenvironment of functional groups, viscosity and density of the cross-linkages in gel and microgel particles and by the thermodynamic compatibility of the polymer matrix and reaction medium and by the polymeric support pore structure and their size distribution (including in the swollen state). On account of a certain mobility of the polymeric chains on the surface and at the boundary of the section of the polymer-medium phases, reorientation and rearrangement of the macromolecular fragments occur,[36] as a result of which the polar groups are found to be turned to the side of the polar phases or vice versa. Moreover the nature of the distribution may also affect even

the properties of the functional groups. For example the surface sulpho-groups possess lower acidity than groups situated within the polymer mass.[37] The interaction between adjacent dicarboxylic groups (a copolymer of maleic acid and methylvinyl ether) leads to the emergence of alternating singly and doubly charged dicarboxylic groups, etc.[38]

When coordinatively unsaturated Rh(3+) complexes situated within the polymeric globules are reduced, they form multinuclear associates, which are active centres for photoinduced catalytic evolution of H_2 from H_2O (the rate of the process reaches 640 mol H_2/g-atom PRh. h^{-1}) and there is no reduction in activity after 6000 cycles).[39]

The nature and topography of the functional groups have a significant effect on the migration processes. We shall follow this process using two examples.[40] Active centres of ethylene dimerisation with homogeneous "nickel" systems are formed from Ni(2+) compounds via a series of transformations:

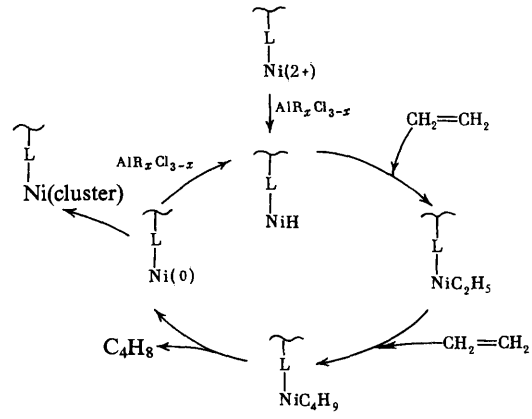
$$\begin{array}{c} Ni(2+)+AlR_xCl_{3-x}\rightarrow Ni(1+)+Ni(0)\rightarrow(\text{colloidal}) \\ \downarrow {\scriptstyle AlR_xCl_{3-x}} \\ Ni(2+)+Ni(0)\ \text{etc.} \end{array} \qquad (1)$$

The average productivity of the active complex ("chain length") is $(2-3)\times 10^3$ moles of monomer per mole of σ-alkyl (or hydride) Ni(2+) complex. It is important that regeneration of the active centres is ensured through the presence of Ni(0) complexes into the redox ring (1). However in homogeneous systems even at 333–343 K the system is essentially totally deactivated within only 1–2 h. The role of the polymeric support in the Ni-immobilised catalysts is reduced to the stabilisation of active centres and to the prevention of the association of Ni(0) in the course of the reaction.[41] In fact the magnetic susceptibility of the isolated products is dependent on the intensity of the magnetic field apparently because of the presence in them of ferromagnetic nickel in addition to the paramagnetic ions.

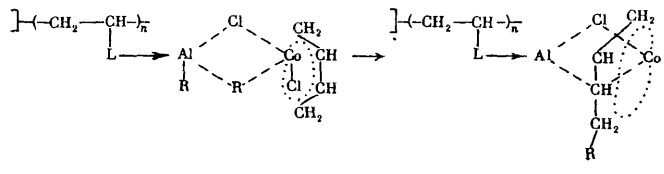
Table 4. Content of ferromagnetic nickel (%) in products of the interaction of $Ni(CH_3COO)_2$ with PE-pr-PAK (A) and Ni(naphthenate)$_2$ (B) with $Al(C_2H_5)_xXCl_{3-x}$.[41]

System	Measurement temperature, K		
	293	80	4.2
(A)+$Al(C_2H_5)_3$	0.34	0.56	2.4
(A)+$Al(C_2H_5)_3$+C_2H_4	0.48	0.50	1.4
(Б)+$Al(C_2H_5)_3$	1.2	2.1	
(A)+$Al(C_2H_5)_2Cl$	0.55	1.2	6.3
(Б)+$Al(C_2H_5)_2Cl$	27	34	37.5
(Б)+$Al(C_2H_5)_2Cl$+C_2H_4	34	53	
(A)+$Al(C_2H_5)Cl_2$	0.34	0.31	
(Б)+$Al(C_2H_5)Cl_2$	31.2	31.6	51.4
(Б)+$Al(C_2H_5)Cl_2$+C_2H_4	14.5	17.6	43.8

The proportion of the latter increases significantly with decrease in the temperature of the measurement, which can be attributed to the presence of finely dispersed superparamagnetic particles of smaller size (10–100 Å)[42] among the products of the reduction in addition to the large ferromagnetic particles (> 100 Å). On dimerisation of the ethylene by homogeneous systems (B) within only 0.5 h ca. 30% of the Ni(2+) ions are converted into finely dispersed metallic nickel, which is unable to undergo reoxidation (Table 4).[41] Under these conditions the content of metallic nickel in immobilised system (A) is only a fraction of a percentage. In the attached complexes constituting a magnetically diluted system, aggregations of Ni(0) particles should precede their migration over the surface of the support. The functional surface coat apparently prevents such a migration as a result of which during the formation of active centres isolated Ni(0) complexes are formed which have the ability to become involved once more in the redox-cycle even in the absence of substrate (ethylene):



When this is absent in the PE-pr-P4VP.$CoCl_2$–$Al(C_2H_5)_2Cl$ system, the presence of the substrate (on polymerisation of butadiene or isoprene) significantly affects the formation of ferromagnetic cobalt.[43] A quantitative calculation of the cobalt content in the different magnetic states, ferro-[Co(0)]-, dia[Co(1+)], and the Co(2+)-paramagnetic states showed that the fraction of ferromagnetic cobalt is equal to ca. 50%, the same level as in diamagnetic cobalt.[43] The interaction between components of the "cobalt" systems in the absence of monomer leads to the reduction of a significant part (up to 50%) of Co(2+) to the metallic state. At least 90% of the total ferromagnetic cobalt is concentrated in relatively large (> 100 Å) particles. The formation of such associates is the main reason for the fall in activity of "cobalt" systems on ageing in the absence of monomer. When the catalysed reaction takes place, only 6–8% ferromagnetic cobalt is found in the transformation products, and most is present in the diamagnetic state, Co(1+). This is probably attributable to its stabilisation *in statu nascendi* by the monomer as a result of the formation of the π-complex active in the polymerisation:



A similar transformation was observed also in immobilised systems based on Mo(5+),[44] V(4+),[45] etc. complexes.

VII. The effect of surface density of immobilised metallo-complexes on their catalytic activity

The well-known effect of "chain loading" or surface density (ρ_s) on the specific catalytic activity of heterogeneous immobilised systems may be linked with the association of the metal on the support.

Catalysts, the active particles of which are accessible to the substrate, usually possess maximum specific catalytic activity. For example if the Kramer complex $Rh_2Cl_4(C_2H_4)_4$ on phosphinated CSDVB containing different quantities of cross-linking agent (2–60%) are obtained under conditions which essentially exclude polymer matrix swelling (and penetration of the metallo-complex into it), its activity in the hydrogenation of hexene-1 is found to be 1.5–4-fold greater than that in analogues synthesised under conditions in which the polymer becomes greatly swollen (Table 5).[46] Aggregation efficiency is also dependent on the nature of the functional groups. Amino groups usually hinder aggregation more markedly than phosphine groups.[47]

Table 5. Hydrogenation of hexene-1 in the presence of the immobilised Kramer complex.[46]

Divinylbenzene (DVB) content, %	P/Rh in the catalyst		Activity *, sec^{-1}	
	Non-swollen	Swollen	Non-swollen	Swollen
2	25	6.5	2.35	0.49
25	5.6	3	1.02	0.60
60	2	3	0.66	0.40

* Product yield in moles per mole of Rh.

The dependence of the specific catalytic activity on ρ_s is usually a complex relationship. Most often with increase in ρ_s the specific catalytic activity increases, reaches a maximum value, and then decreases. Experiments have shown that such patterns exist for the hydrogenation (Fig. 3),[48,49] oxidation,[50] dimerisation,[51] and polymerisation of ethylene, etc.[52] Maximum specific activity of the PE-pr-P4VP.VCl_4–$AlEt_2Cl$ system during ethylene polymerisation is attained for example at a bonded vanadium content of 0.6 mass% (18 atoms/100 Å^2).

Such patterns are undoubtedly the consequence of the distribution characteristics of the active component. It has been quite reliably established that metal ions are distributed on the support both as isolated complexes and as cluster formations with a high local concentration of attached complexes.[5] With change in ρ_s the ratio between them also changes. There is a general tendency that with decrease in phosphorus content of the phosphinated macroligand and also with decrease in P/Rh the Rh particle size increases and gradually approaches the particle size in the polymer containing no functional groups.[53] An increase in the phosphorus content decreases the rate of decomposition of rhodium complexes to the metal. When P/Rh = 40, crystallites are not found even after heating to 398 K for several days.

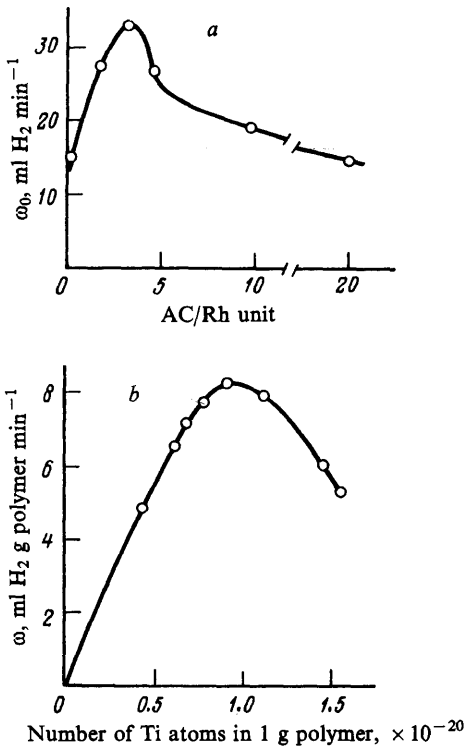


Figure 3. The variation in reaction rate as a function of the quantity of bonded metal in the macrocomplex: *a*, hydrogenation of furfurol in the presence of Rh on PAA;[49] *b*, hydrogenation of hexene-1 in the presence of titanocene bonded to CSDVB modified with cyclopentadienyl groups.[48]

However one cannot associate the observed nature of the dependence of the specific catalytic activity on ρ_s with either the concentration of isolated ions or with the concentration of associates. At the same time it is evident that, on increase in ρ_s, the concentration of associates consisting of a small number of particles, for example dimers or trimers, should pass through a maximum. The suggestion that active particles in the immobilised systems are formed from isolated transition metal ions stabilised by cluster formations is justified. Their content should also be markedly dependent on the surface density. In fact an analysis of the magnetic susceptibility of different spin states of "nickel" systems confirms that with increase in the surface density of Ni(2+) during the formation of active centres the dimensions of the clusters increase and the relative content of the boundary nickel atoms stabilised by the electron system of the entire cluster passes through a maximum.[41] In other words the dome-shaped plot representing the dependence of the specific catalytic activity on ρ_s correlates with the distribution function of the clusters with respect to size. One should note that in certain systems the dependences of the specific catalytic activity on ρ_s are different. For example the rate of H_2O_2 decomposition in the presence of Cu(2+) complexes with a polyampholite (copolymer of 2-methyl-5-vinylpyridine and AK)‡ is

‡ (Owing to the strong dependence on pH this reaction closely resembles enzyme-mediated processes.)

determined by the formation of complexes with different compositions.[54] A correlation is found between the catalytic activity and the content of diamagnetic Cu(2+) complexes, when the latter may include binuclear complexes§ (similar to the active centres of haemocyanin) with a strong antiferromagnetic interaction.

The presence of the ascending branch of the dependence of the specific catalytic activity on ρ_s may be attributed to the collective interaction of immobilised vanadium atoms.[56] A decrease in the activity of the attached $TiCl_4$ complexes during the polymerisation of ethylene continues until each active centre becomes adequately separated from the other.[57]

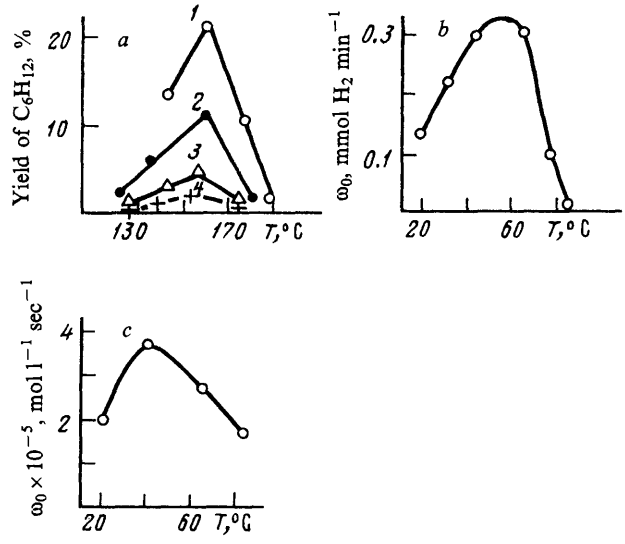


Figure 4. The effect of temperature on the rate of hydrogenation in the presence of the immobilised complexes. *a*, Hydrogenation of benzene with the use of Pt–nylon-66 (*1*), Rh–nylon-66 (*2*), Ir–nylon-66 (*3*) and Pd–nylon-66 (*4*) systems;[59] *b*, hydrogenation amination of 2-methylpropanol in the presence of Pd on polytrimethylolmelamine;[61] *c*, hydrogenation of allylbenzene on the $Ni(acac)_2$–copolymer of butylacrylate, acrylonitrile, acrylic acid and methylolacrylamide–$Al(C_2H_5)_2Cl$.[60]

Thus one of the principal transformations of the immobilised complexes may be associated with the evolutionary transformations accompanied by an increase (more rarely a decrease) in nuclearity. The following sequence of such transformations is observed: immobilised monomer complex → formation of small (bi-, tri- etc.) particles (clusters) → formation of multinuclear associates (diameter 10–20 Å or more) → appearance of metal phase. Small sized particles interact very intensively with the polymer matrices. sized particles interact very intensively with the polymer matrices. Usually as a result of an electronic transition at the metal atoms a positive charge arises promoting coordination of substrate molecules which also affects the activity of the catalyst. The deep interaction of such particles with the support facilitates the conservation in them of a developed π-electron system.[58] The situation becomes complicated because the systems examined are dynamic formations. The concentration and structure of the metallo-complexes may be altered in the course of the catalytic reaction as a consequence of cluster formation, aggregation, crystallisation, and displacement of the metal on to the surface from the body of the matrix, which are especially intensive at the stage of activtion of the attached complex.

VIII. Characteristics of the effects of temperature on the catalytic properties of immobilised complexes

When the catalytic systems under the examination are used one should remember that the temperature usually affects the rate of the reaction in a complicated manner. Since the MX_n-macroligand system itself undergoes certain transformations, the dependence of the reaction rate on temperature often has a bell-shaped relationship. Such dependences are found particularly during the hydrogenation of benzene in the presence of the platinic group of metals on nylon-66 (Fig. 4),[59] hydrogenation of allylbenzene by gel-immobilised nickel complexes,[60] hydrogenised amination of 2-methylpropane by nitrobenzene on Pd-polytrimethylolmelamine,[61] and oxidation of ethylbenzene on Co(2+) macrocomplexes (Fig. 5), etc.[50]

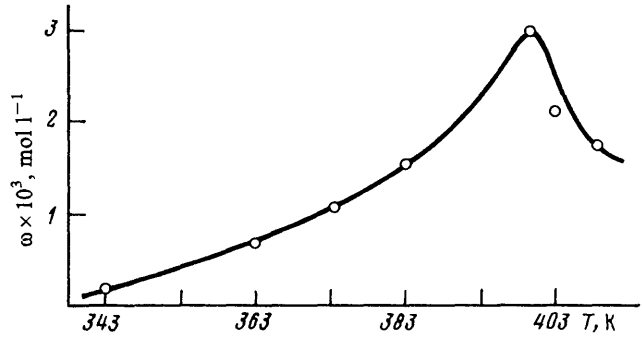


Figure 5. The effect of temperature on the rate of oxidation of ethylbenzene by Co(2+) macrocomplexes.[50]

There may be several reasons for such unusual temperature behaviour. One reason is the occurrence of destructive process initiated in the polymer matrix by the metallo-complexes especially at elevated temperatures. The appearance of descending branches of the curves may also be a consequence of the aggregation of metallo-complexes, occurring vigorously on increase in temperature.

However the most probable reason is the effect of temperature on the phase transformations in the metallo-complex matrices on heating. With increase in temperature the reaction rates at first increase in accordance with the Arrhenius law, and then after the

§ Binuclear complexes cannot be formed, while only one Cu(2+) ion occurs in each polymer globule at high dilution (< 0.05 mass% of the polymer). In this case infinite dilution conditions are modelled.[55]

second-order transition temperature (T_c) is reached or after softening of the polymeric support the rates of the reactions fall. Thus in the temperature range in which the chain segments possess adequate mobility and in which the relaxation processes associated with the reorientation of the entire macromolecular support become controlling, there is a change in the structure of the active centres (a change in the coordination unsaturated state of the transition metal, aggregation of the active centres, reduction of the metal, etc.).

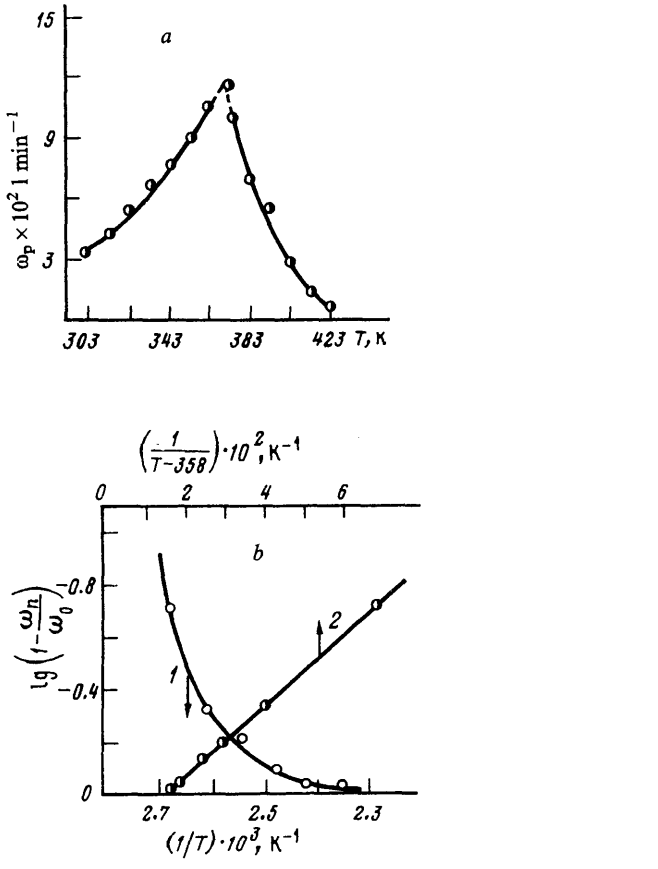


Figure 6. The variation in the rate of ethylene polymerisation in the gas phase as a function of temperature (*a*) (catalytic system, P4VP.VCl_3–$Al(C_2H_5)_2Cl$; the calculated rate is indicated by the dotted line) and the temperature dependence $\lg(1-\omega_p/\omega_0)$ (*b*) on $1/T$ (*1*) and $1/(T-358)$ (*2*).

In particular the rate of gas phase polymerisation of ethylene (P4VP.VCl_4 – $AlEt_2Cl$ system) is dependent on the mobility restoration temperature (the rate of the relaxation process).[62] In the Arrhenius region the process is reversible (Fig. 6) and E_a has a normal anionic-coordination polymerisation value (16 kJ mol^{-1}). In the T_{mp} range and higher the polymerisation temperature coefficient becomes negative (−130 kJ mol^{-1}). If one assumes that the decrease in polymerisation rate (ω_{II}) on the descending branch of the curve is caused by the exceptionally irreversible deactivation of active centres (n_p) caused by the movement of segments of the polymer chain, then

$$\omega_{II} = kn_p\left(1-\frac{\Delta n}{n_p}\right) = kn_p(1-\omega_D\Delta t),$$

where ω_D is the specific decay rate of the active centres according to any of the possible mechanisms. From here

$$\omega_D\Delta t = 1-\omega_{II}/\omega_0$$

(ω_0 is the polymerisation rate in the absence of deactivation). The form of the curve in Fig. 6*b* resembles the normal observed dependence for the relaxation time of segmental movement. The apparent activation energy increases sharply as the mobility defrosting temperature is approached. As usual in such cases the temperature dependence of the rate of the relaxation process is linearised in the coordinates $\lg\omega_D \sim (\Delta T)^{-1}$, i.e. it has the form

$$\omega_D = A\exp\left(-\frac{B}{T-T_0}\right).$$

The value B is associated with T_c and the free volume fractions (α_c) by the relationship:[62]

$$B = (T_c-T_0)/2.3\alpha_c.$$

In this specific case T_c = 360 K (α_c = 0.025) and this is the temperature at which the mobility of the P4VP segments is restored and at which a marked fall in the rate of polymerisation commences. Hence the increase in the progressive diffusion n_p is one of the important factors for the deactivation of immobilised metallo-complex catalysts for the polymerisation of olefins.

The temperature dependences of the rate of polymerisation by gel-immobilised systems also pass through a maximum (in the T_{mp} range of polyethylene). They are totally temperature-reversible, i.e. the decrease in rate in the elevated temperature range was not due to thermal deactivation n_p. An important feature of gel-immobilised systems is their structural and conformation adaptation,[63] i.e. at elevated temperatures microsyneresis of the polyhydrocarbon gel occurs in the aromatic solvent medium, leading to a decrease in the concentration of the monomer in the vicinity of the active centres present in this type of gel. Therefore in the case of local overheating in a particular region of a granule of the immobilised catalyst, temporary retardation of the exothermic reaction occurs. Other authors have suggested that such an inverse relationship ensures the "self-defence" of the catalyst from irreversible thermal deactivation.[63] This is yet another basic similarity between the immobilised catalysts and biomembranes into which enzymes have been incorporated.

At the same time restoration of the mobility may ensure that different sized aggregates of the particles are formed from the zero-valent metals, and the activity of such aggregates is possibly higher than the activity of isolated atoms. Such a local convergence of the metallo-complexes is found to have a favourable influence on hydrogenation and other processes. This phenomenon was studied in greatest detail in the case of gaseous phase hydrogenation of ethylene by Rh complexes attached to triple copolymers consisting of styrene and diphenyl-*p*-styrylphosphine (DRSP) (5–10%) cross-linked with divinylbenzene (2%).[64,65] The temperature dependence is readily reproducible over a broad range. At T_c a discontinuity in

the Arrhenius curve is found (Fig. 7). The activation barrier of the reactions at $T > T_c$ remains essentially the same, i.e. all changes in the rate constant are associated with the entropic factor. This phenomenon arises as a result of the restoration of the mobility of the polymeric segments and the creation of the most suitable configuration of the active centre for the catalytic act. One also cannot rule out the effect of other factors. When $T > T_c$, relaxation of the micro-Brownian movement promotes diffusion and an increase in the probability that the substrate collides with the active centres. Furthermore movement of the adjacent groups and ligands may increase steric hindrances for the coordination of ethylene and may reduce the stability of the bond of the coordinated substrate.[65] Finally a change in the nature of the movement in the polymer leads also to structural transformations of the active centre, since in this case there are changes in the coordinating capacity of the functional groups, their configuration, and the coordination non-saturation of the transition metal, etc. Furthermore the anomalous nature of the temperature dependence cannot be associated either with an increase in ethylene diffusion into the small pores of the catalyst (which would become limiting close to the T_c) or with the fact that at a certain temperature the overall rate of the process begins to be determined by another stage (since the slope of the Arrhenius plot remains virtually constant).

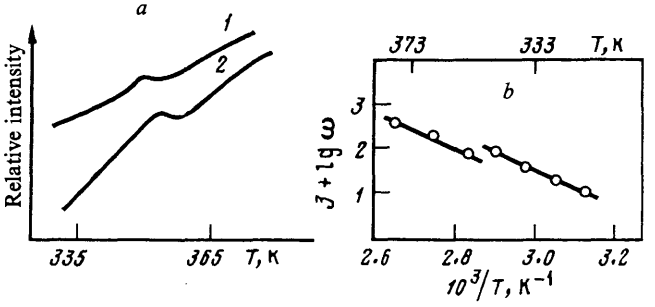


Figure 7. Differential scanning calorimetry curves (*a*) (*1*, T_c = 349; *2*, T_c = 354 K) and the Arrhenius dependence of the rate of ethylene hydrogenation in the gas phase on the rhodium macrocomplex (*b*).

The reversible discontinuity in the Arrhenius dependence may be explained, if one assumes the existence of two different coordination states differing in catalytic activity in the T_c region. The somewhat nonuniform slope of the curve at different sides from the T_c (33 kJ mol^{-1} at higher and 35 kJ mol^{-1} at lower temperatures) may probably be attributed to the fact that the enthalpy or entropy of ethylene coordinated at various Rh-centres differs somewhat on account of the movement of the polymer network.

It is interesting that similar effects are also found in soluble metallo-polymeric catalysts. Thus the effective rate constant (k_{eff}) for the oxidation of cholesterol by molecular O_2 in the presence of soluble porphyrin-containing metallo-polymers temperature-dependent,[66] and there were no analogies in normal homogeneous catalysis. The nonmonotonous nature of the dependence $k_{ef}(T)$ (Fig. 8) indicates that conformational transitions possibly occur in such systems. One such transition may be caused by the disruption of the ordering of polymeric fragments associated with hydrogen bonds, coordinate bonds, and other bonds during their concomitant rupture. In this temperature range the temperature dependence of the characteristic viscosity has the form $\eta = \eta_0 \exp(-E/RT)$, as in any activation process which is also associated with conformational transitions in metalloporphyrin-containing macromolecules. In the transition region a significant fluctuation of the conformations of the chains in the solutions is found, and each conformation corresponds to its reaction rate constant value, because of the difference in the pre-exponential multiple, which reflects steric factors, or because of the mutual effect of the active centres. Since there is a set of different rate constants corresponding to metastable conformational states in the transition region, the dependence $k_{eff}(T)$ also has a non-Arrhenius extremal nature.

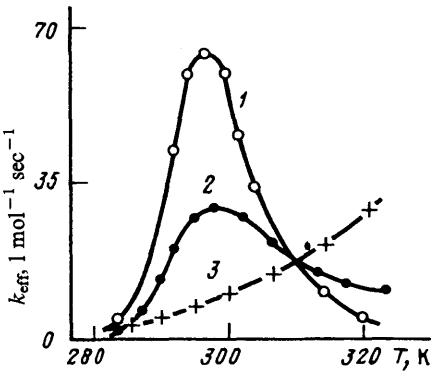


Figure 8. The dependence of the k_{eff} of cholesterol oxidation in the presence of $NaBH_4$ and copolymers of N-Mn-porphyrinate acrylamide with methacrylate (*1*) and butylacrylate (*2*) on the temperature (*3*, the analogous dependence for the low molecular weight analogue, magnesium tetraaminophenylporphyrinate).[66]

In principle such effects may influence not only the activity but also the selectivity of the immobilised catalysts. Only one example will be presented, viz. a reduction in temperature during the synthesis of cyclopropane ethers leads to an increase in the proportion of the *cis*-isomer, probably as a consequence of the limitation in the mobility of the macromolecular chain.[67]

Finally one should also mention such an important phenomenon as the total thermo-reversibility of the binding of MX_n by certain ligands, which form the basis of the construction of "thermo-regulatable" immobilised catalysts. The line diagram of this phenomenon may be represented in the following form:

$$\left|\text{—L—MX}_n\right| \xrightarrow{\text{catalysis}} \left|\text{—L} + \text{MX}_n\right| \xrightarrow{\text{Isolation of the catalyst}} \left|\text{—L—MX}_n\right|$$

Low temperature (Immobilised catalyst)	High temperature (homogenous catalyst)	Low temperature (Immobilised catalyst)

Complexes of $ClRh(PPh_3)_3$ with phosphinated ethylene oligomers are an example of thermo-regulatable catalysts.[68] At 373 K the macrocomplexes dissolved in xylol operate as hydrogenation catalysts, but when the reaction medium is cooled to 298 K, the catalyst is quantitatively (losses of Rh do not exceed 0.1% per cycle) bound to the support. This method is especially effective when the so-called "undeposited" homogeneous catalysts are used.

The question of the thermostability of the immobilised complexes warrants special examination. Binding of MX_n is usually accompanied by a change in the structural organisation of the system and leads to an increase in its thermostability. The best known example is the binding of first transition series metal ions with nucleic acids into a stable complex, which ensures the resistance of the complex to elevated temperatures and its conservation in the denaturation area.

IX. The contribution of energy of non-equilibrium configurations of the chain to catalysis

Not only the nature of the polymeric support and its functional groups but also the distribution profile of L with respect to the copolymer chain (statistical, modular, alternant), and the stereoregular, conformational and configurational structure of the macroligand affect the composition, structure and stability of the macrocomplexes during their formation. There is only a limited amount of information on these questions. Thus, during the oxidative coupling of 2,6-xylenol the activity of the Co(2+) chelates attached to atactic and isotactic polyacrylamidoximes (PAAO) significantly differ.[69] The kinetics of the reactions in both cases obey the Michaelis–Menten equation, although the k_2 value (constant for the second stage determining the rate of the process) is higher for the isotactic ligand (at 303 K, k_2 = 0.304 and 0.284 min^{-1} respectively), whereas the Michaelis constants have similar values (0.274 and 0.282 mmol l^{-1}). These phenomena are caused primarily by an increase in entropy. Since the chain of the isotactic macroligand has a spiral ordered form, it has a lower $\Delta S^{\neq}$ value (Table 6).

Table 6. Thermodynamic and activation parameters of the oxidative combination of 2,6-xylenone at 303 K.[69]

Catalyst PAAO–Co(2+)	ΔG, kJ mol^{-1}	ΔH, kJ mol^{-1}	ΔS, J mol^{-1} deg^{-1}	$\Delta G^{\neq}$, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} deg^{-1}
Isotactic	20.6	58.4	260.4	88.2	35.7	−172.2
Atactic	20.7	45.4	218.4	89.0	40.0	−163.6

The Rh and Ru complexes attached to isotactic or atactic phosphorylated polystyrene exhibit different activities in oxidation, hydrolysis and isomerisation, etc. reactions,[26] although it is difficult to make clear conclusions on the causes of this phenomenon.

The activity is dependent on the form of the macromolecules containing attached MX_n. For example Rh and Ru attached to alternating copolymers of maleic acid and vinyl esters and occurring in the reaction medium in the more compact configuration (in *n*-octane) express lower activity in the hydrogenation reaction.[70] In many cases the nature of the solvent is also important. At 343 K modified polystyrene in *n*-hexadecane is present in the glassy state, but occurs in the gum-like state in aromatic solvents. Furthermore, when the chain is compressed, the principal fragment of the metal is localised within the polymer and is not involved in the catalysis. However on oxidation of the hydroquinone by Cu(2+) with a partially quaternised P4VP, an increase in pH, temperature, and the degree of quaternisation of the macroligand on introduction of the electrolytes leads to a decrease in viscosity of the system, to the compression of the polymer chain, and to the creation of conditions required to form intramolecular chelates, which promotes a charge transfer between the neutral hydroquinone or semihydroquinone anion and the Cu(2+) ion of the polymer complex.[71] This causes an increase in catalytic activity, whereas the reverse factors promoting the extension of the polymer chain and hindering the formation of the chelate reduce the catalytic activity.

The rate of oxidation of di-substituted phenols in the presence of Cu(2+) on the copolymer formed from styrene and 4-VP or dimethylaminostyrene increases with increase in the proportion of aminogroups ([N]) to 0.4.[72] This is associated with a change in the activation parameters caused by an increase in the conformational mobility of the intermediates during the deformation of the intermediate catalyst-substrate complex, the formation of which precedes the electron transfer from the substrate to Cu(2+) (limiting stage of the process). In addition at small [N] values in the copolymer there are steric hindrances, which hamper the formation of the binuclear triple complex. At least six intermediate styrene units are required to form the bridging binuclear complexes.[73]

A feature of the soluble macrocomplexes is that not only the structure and conformation of the chain but also chain length has a significant effect on their activity and selectivity. Thus the rate of oxidation of tetralin increases ten-fold with increase in the length of PEG containing attached MCl_2 (M = Co, Mn, Cu) (Table 7).[74,75]

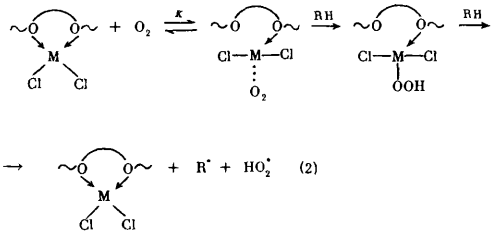
Table 7. Variation in the decomposition of rates (ω_i) of hydroperoxide and the oxidation (ω_0) of tetralin as a function of the relative molecular mass of PEG (355 K, $[ROOH]_0$ = 0.4 mol l^{-1}, O_2).[75]

Relative molecular mass of PEG	ω_0, mol O_2/(g-ion Co min^{-1})	ω_i, mol ROOH/ /(g-ion Co min^{-1})	ω_s/ω_i
4 000	180	35	5
20 000	900	40	22.5
40 000	1800	33	54.5

Macrocomplexes function as initiators and the PEG chain length affects the rate of the initiation stage. In contrast to the oxidation rate the rate of decomposition of ROOH is essentially not dependent on the molecular mass of the polymer. Since E_a is also not

dependent on the molecular mass of PEG, differences in activity are associated with a change in the pre-exponential factor in the reaction rate equation, i.e. with entropy factors. This is an example of a new effect in catalysis, an increase in rate of the process owing to the energies of non-equilibrium configurations of the polymer chains arising in the course of the reaction. The energy increases with increase in chain length, and under certain conditions (for example when the rate of the catalytic act is greater than the rate of relaxation of the polymer nonequilibrium) may be transmitted to the reacting components, thereby increasing the rate at which they undergo transformation.

We shall analyse the mechanism of this phenomenon with a specific example. Macrocomplexes PEG.MCl_2 in tetralin occur as globules, the dimensions of the latter being less than those of the corresponding globules of the original PEG. However activation of O_2 at the metal ion may be accompanied by the temporary rupture of one of the M–O–PEG bonds (according to the type of substitution of ligands in the macrocomplexes described in Section II). This leads to the appearance of the nonequilibrium configuration of the macromolecule striving to unfold. Such an irreversible process is characterised by a constant K, the magnitude of which is determined by a change in the free energy of macrocomplex formation, $RT \ln K = \Delta G$.



(2)

In turn ΔG may be provisionally divided into two components. One component (ΔG_x) is determined by the rupture of old and the formation of new chemical bonds with the metal ion, while the other component (ΔG_{ts}) is determined by the operating of chain stretching which was "stored away" during macrocomplex formation. The entropy component ($T\Delta S_{ts}$ is precisely the function of the molecular mass of PEG and increases with increase in molecular mass) makes the principal contribution to the equation $\Delta G_{ts} = \Delta H_{ts} - T\Delta S_{ts}$. Then $\Delta G = \Delta G_x + \Delta G_{ts}$. From the expression

$$K = \exp(\Delta S/RT) \exp(\Delta S_{ts}/R) \exp(-\Delta H/RT) = K_0 \exp(-\Delta H/RT)$$

it follows that the K values for the polymer complexes and their low molecular weight analogues differ in magnitude ($\Delta S_{ts}/R$) which is part of the pre-exponential factor in the overall reaction rate equation and is dependent on the molecular mass of the macroligand.

Thus one condition for the appearance of the effect examined in the catalysis is an increase in the rate of the catalytic reaction over the rate of relaxation of nonequilibrium conformations of the macroligand.

Apparently this is a common effect and occurs in processes catalysed by soluble immobilised complexes.¶ This effect is similar to the energy recuperation effect in enzymic catalysis in which the protein molecule assumes the role of an energy reservoir. The energy released in the course of the reaction is not dissipated as heat but is utilised to activate the reagents. During the enzymic reaction the protein macromolecule may be transformed from the equilibrium into the nonequilibrium state. The energy of this transition is utilised to overcome the substrate transformation activation barrier, whereas the energy released as a result of the reaction is utilised to return the protein molecule to the original equilibrium state.[77]

Other hypotheses suggest that the small height of the activation barrier of the enzymic reactions may be attributed to the fact that even before the enzyme-substrate complex is formed in the active centre of the enzyme a functional group with high potential energy is present {the hypothesis of the eptatic [entatic? (Ed. of Translation)] state of the active centre of the enzyme}.[78] For example the zinc ion within carboxypeptidase or carbonic anhydrase is much more reactive than zinc occurring in the normal ionic form or in a complex with a low molecular weight ligand. The reason is that in the active centre the zinc atom is only partially associated with protein ligands (as in M in Scheme 2), forming the stressed configuration of the deformed tetrahedron. Such formations are a specific feature of protein macromolcules with secondary and tertiary structures.

X. Cooperative stabilisation of active centres in the immobilised systems

A significant number of segments in the polymer chain is usually involved in the binding of MX_n (and active centres based on these structures). The rupture of one of the bonds between the metal ion and the macroligand unit requires the expenditure of approximtely the same amount of energy as for the rupture of the bond in the complex with the low molecular weight ligand analogue. However these losses in the first case are not compensated by the appearance of new progressive degrees of freedom (i.e. they are not accompanied by an increase in configurational entropy). Thus the probability that the active centre in the immobilised systems is disrupted under stable equal conditions sharply declines, whereas the stability of the intermediate forms may be increased owing to the rapid spontaneous conformational transformations in adjacent units in the chain, fluctuations in its structure, etc. Cooperative interactions of this type increase the stability and activity of immobilised catalysts. Thus in polymers based on Rh(1+)-bis-(4,4'-diisocyanodiphenyl)chloride (the catalyst for the hydrogenation of olefins)[79] in which the Rh is arranged regularly in a tetragonal or

¶ The value of the Michaelis constant (K_m) and the activation parameters for the oxidation of 2-mercaptoethanol by molecular O_2 in the presence of complexes of sodium Co(2+)-phthalocyaninetetrasulphonate with polyvinylamine (PVAm) are dependent on the degree of polymerisation of the latter,[76] which are associated with conformational transformations of the globule. The $\overline{M}_n$ of the 2,4-ionene type of quaternised polyammonium resin is found to have an effect on the charge density of the polymer chains. On increase in $\overline{M}_n$ from 1740 to 6600 the constant K changes from 11.3 to 6.8 mol l^{-1}, whereas the turnover number alters from 3700 to 3300 sec^{-1} (for polyvinylamine with $\overline{M}_n = 3 \times 10^4$ these values are 90 mol l^{-1} and 2800 sec^{-1} respectively).

hexagonal environment where each rhodium atom is associated with 2 or 4 isocyanate ligands, there are three types of active centres (Fig. 9). The first of these (a) incorporates Rh at the end of chain, the second (b) incorporates Rh is the macroligand chain, and the third (c) incorporates Rh on the outer side (001) of the material. The number of centres active in catalysis does not exceed 1% of the number of Rh atoms, but cooperative interactions are observed between the centres (a) arranged at close distances from each other, which increase the activity of the catalyst in the isomerisation of the substrate, whereas the cooperative effect created by the interaction between centres (b) and (c) or adjacent centres (b) is the reason for the increase in activity in the hydrogenation reactions (in this case the Rh–Rh interactions have the characteristics of a metal bond). The relationship between the different centres is dependent on the previous history and the method of preparation of the catalyst, its topography, ρ_s value, temperature, and other factors.

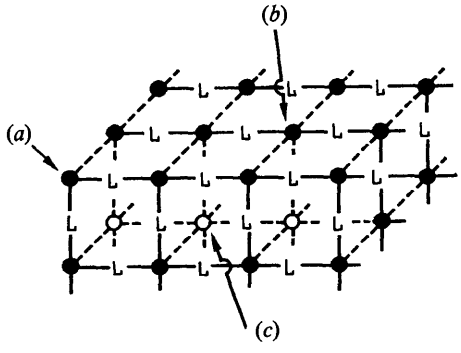
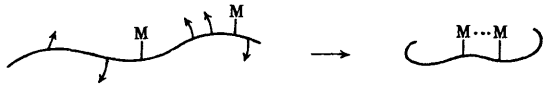


Figure 9. Types of active centres in Rh(1+)-bis-(4,4′-diisocyanodiphenyl)chloride polymers.[79]

In those cases in which matrix isolation of the active centres is an important condition for the completion of the reaction, cooperative interactions of the segments in the chains may lead to their deactivation.



In order to establish the reason for the stability of attached catalysts for ethylene polymerisation, the decomposition of individual organometallic Ti(4+) compounds (which form the basis of active centres of homogeneous catalysts and catalysts heterogenised by polymeric supports of the catalysts)[80] was studied. Decomposition of $RTiCl_3$ type compounds is known to occur mainly as a result of the completion of processes within the coordination sphere of the transition metal, including β-elimination or disproportionation reactions. The activation energies of these stages are lower than metal–carbon bond energy, and therefore to increase the stability of organometallic compounds it is essential to exclude completely the possibility of the occurrence of inner sphere reactions of the alkyl group. For example CH_3TiCl_3 complexes with 4-substituted derivatives of pyridine decompose in the homogeneous system even below room temperature with the splitting of the $Ti-CH_3$ bond and with the formation of methane according to a coordinated mechanism in the coordination sphere of titanium, and in the course of these reactions Ti(4+) is not reduced. The macrocomplex PE-pr-P4VP.CH_3TiCl_3 is more stable. The Ti–C bond is gradually decomposed only at 298 K with the formation of methane, ethane, and C_4 hydrocarbons. Above 353 K there is an increase in the proportion of homolytic decomposition of the Ti–C bond with the formation of CH_3 radicals, and this is accompanied by the reduction of Ti(4+) to Ti(3+) (Table 8).

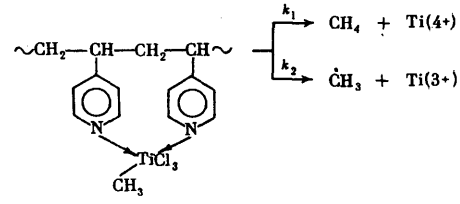


Table 8. Ratio between the rate constants k_1 and k_2 and the quantities of Ti(3+) and Ti(4+) during the decomposition of the complex CH_3TiCl_3.PE-pr-P4VP.[80]

T, K	$k_1 \cdot 10^4$, c^{-1}	$k_2 \cdot 10^4$, c^{-1}	k_2/k_1	Ti(3+)/Ti(4+)
303	0,59	–	–	0
313	0,77	–	–	0
323	1.0	0.7	0,7	0,6
333	1,3	2,1	1,7	1,5
348	1,6	8,0	5,0	2,3

The rate constant value for the coordinated decomposition reaction (k_1) of the macrocomplex examined is two orders of magnitude lower than that for the decomposition of the CH_3TiCl_3 complex with the monomeric ligand. This may be attributed to the extremely low value of the pre-exponential factor ($10^{-2}-10^{-3}$ sec^{-1} against 10^3-10^5 sec^{-1} for the homogeneous system) since the "fine tuning" (deformation) of the polymeric ligand essential for the coordinated reactions to take place, requires significant changes in entropy in the transition state in comparison with the monomeric analogue. It is important that the rate of homolysis of the $Ti-CH_3$ bond occurring with the formation of free radicals (the rate constant of this reaction k_2) in the heterogenised and homogeneous systems are identical.

Thus the thermodynamic stability of the Ti–C bond (and hence the active centres) in the systems compared remains essentially unchanged (similar bond energies). Therefore the stability and high activity of the immobilised systems for example during the polymerisation of ethylene (Fig. 10) are mainly caused by the sharp fall in rate of the coordinated processes in the coordination sphere of the transition metal.

One more important situation should be noted. Apparently reactions leading to the deactivation of active centres require significantly more rearrangement of the ligand environment of titanium than reactions in which the polymerisable ethylene is introduced at the Ti–C bond,[81] which is indicated by the closeness of the rate constants of the chain elongation reactions in the systems compared.[52] An extremely interesting phenomenon is the "fine tuning' of the polymer matrix to create the most favourable configuration of the catalytic centre. Thus on heterogenisation of the bulky $Ti(OC_4H_9)_4$ on the polymer the structure of the active centre is probably such that the energy barrier of the introduction reaction is small, and the effective activation energy for ethylene polymerisation is significantly (up to 11 kJ mol^{-1}) lower than that in the homogeneous system (58 kJ mol^{-1}). However in this case K_p essentially does not change. It therefore follows that there is a sharp decrease in the pre-exponential multiple of the reaction rate constant. The compensation effect indicates that in reactions in which these active centres are involved many closely lying fragments of the polymeric ligands are affected, and hence there is a fall in entropy.

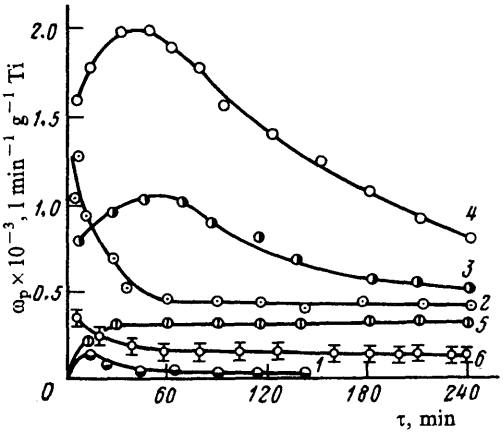


Figure 10. Variation in the rate of ethylene polymerisation by heterogenised systems based on $Ti(OC_4H_9)_4/Al(C_2H_5)_2Cl$ as a function of the reaction time. Polymeric supports: *1*, without support (homogeneous system); *2*, PE-pr-poly(diallylamine); *3*, PE-pr-poly-(allylamine); *4*, PE-pr-poly(allyl alcohol); *5*, PE-pr-PAA; *6*, hydrolysed copolymer of styrene with vinylacetate.

However other patterns are also observed. Thus the rate constants of the homolytic splitting of the Co–R bond in monomeric (R = benzyl) and polymer-associated (R = chloromethylated CSDVB) cobaloximes (L = Py or DMSO)

$$RCo(DH)_2L \overset{h\nu}{\rightleftarrows} R^{\cdot} + Co(2+)(DH)_2L$$

in DMSO have similar values (1×10^{-2} sec^{-1}).[8] In benzene $k_{mono}/k_{poly} = 4.2$. This is associated with the promoting action of the polymer chain on photodecomposition and may be attributed to energy migration along the polymer chain containing aromatic rings, which have the ability to absorb photoenergy. This may be attributed to the fact that the polymer-associated cobaloxime is partially decomposed also on irradiation with light at a wavelength below 350 nm, whereas with benzyl cobaloxime this process occurs only on irradiation with light at a $\lambda_{max} = 450-550$ nm.

Their interaction with the microligand surface caused by the presence of functional groups and surface imperfections and also by physical causes creates yet another possibility for the cooperative stabilisation of the active centres. This has been analysed in greatest detail in the case of the hydroperoxide (tert-butyl hydroperoxide, TBHP) epoxidation of cyclohexane (CH) by Mo(6+) complexes attached to cellulose phosphate (Mo):[82]

$$Mo + TBHP \overset{K_r}{\rightleftharpoons} Mo \cdot TBHP,$$

$$Mo + CH \overset{K_D}{\rightleftharpoons} Mo \cdot CH,$$

$$Mo \cdot TBHP \cdot CH \xrightarrow{k} Mo + CHO + TBA,$$

where CHO is cyclohexane oxide, TBA is tert-butyl alcohol, k is the rate constant of the inherent catalytic act which is achieved in the triple bi-substrate complex, catalyst–hydroperoxide–olefin.

Table 9. Activation parameters of the principal stages in the epoxidation of cyclohexene by heterogenised and homogeneous molybdenum systems.[82]

Rate constant of the reaction	ΔH ($\Delta H^{\neq}$), kJ mol^{-1}	ΔS ($\Delta S^{\neq}$), J mol^{-1} deg^{-1}	E_a, kJ mol^{-1}
K_r	−72	−220	
K_D	−36	−130	
k	133	290	136
K_r'	−24	−92	
k'		166	72

Enthalpy values for the formation of intermediate complexes of the catalyst with reagents (i.e. enthalpies of their chemosorption at the active centres containing Mo) and the activation energies of the decomposition stage of the triple complex into the reaction products are presented in Table 9. For comparison the corresponding parameters of the homogeneous reaction of the direct oxidation of cyclohexene by the molybdenum diperoxocomplex with hexamethylphosphortriamide are presented.[83] The enthalpy and entropy changes during complex formation of diperoxomolybdate with cyclohexene (the rate constant of this reaction, K_r') and also the activation energies and entropies of the transformation of the triple complex (rate constant k') are indicated. The comparative analysis shows that a similar stage of the decomposition of the triple bisubstrate complex Mo.TBHP.CH on the support surface is distinguished by a significantly higher activation energy and by a simultaneously higher positive activation energy. This difference is apparently caused by the heterogeneous nature of the catalyst. The triple complex immobilised on the support matrix is apparently stabilised on account of the addition interaction with the surface and it occurs in a highly ordered, and as a frozen, state. Therefore it

requires a higher activation energy, whereas the release of the products formed into solution is accompanied by a more abrupt disordering of the system. This effect is apparently quite often encountered in catalysis by immobilised complexes.†

A change in the bond energy of the substrate with the support area by 5–10 kJ mol^{-1} may significantly affect the mechanism and selectivity of the reaction. Thus the rate of styrene hydrogenation in the presence of Pd(0) on functionalised CSDVB sharply increases when supports are used containing functional groups which have the ability to form π-complexes with styrene and thereby to increase the lifetime of the adsorbed complexes of the substrate.[27]

XI. The selectivity of immobilised catalysts

Usually immobilised metallo-complexes not only increase the rate of the overall process but also improve its selectivity. Examples are known of the inversion of the selective action of MX_n when they are attached to the support.

In contrast to the homogeneous catalysts the immobilised catalysts are mainly more sensitive to the steric effects of the substituents in the substrate. This is confirmed by the distinct dependence of the reaction rate on geometric sizes of the molecules. Geometrical or matrix selectivity is one of the important features of the processes in immobilised catalysts. For example the rate of hydrogenation decreases on transition from an acrylic to a cyclic olefin. This applies to both individual compounds and components of different fractions or mixtures. The activity of polymer-bound $PdCl_2$ during hydrogenation of substrates forms the following series:[58] dienes > allyl alcohol > alkene-1 > alkene-2 > methyl-alkene-2. The stability of such contacts reaches 1000 or more cycles.

A particularly high order of selectivity is attained on reduction of aromatic and heteroaromatic substrates, including those containing functional groups. Catalysts obtained in this way are suitable for the preparation of cyclohexanol from phenol, and polyols from sugars, and for converting inner alkenes into α-alkenes.[85] The regio-selectivity is especially pronounced in olefin hydroformulation reactions (the ratio of alehydes with the normal structure and the isostructure), and hydrosilylation (α- and β-addition) and oxidation (the predominant formation of a particular product) reactions, and in the formation of an enantiomeric excess (enantioselectivity).

Essentially the same factors which affect the activity of the catalysts also affect selectivity, i.e. the nature and topography of the bonded complex, the nature of the matrix and ligand, the L:M ratio, and also the reaction conditions. For example since the selectivity is associated with the specific adsorption of one of the reagents or the product on the surface, the selectivity of the reaction is dependent on whether the catalyst is swollen or not swollen. The selectivity decreases, also as a consequence of the side reactions including those in which vacant functional groups are involved (hydrolysis, esterification, re-esterification, amination, etc.) and in which the solvent in addition to the substrate is involved. Furthermore, owing to the dissociation of a certain portion of the ligands, the pH of the medium may be altered, which also affects the selectivity. Such effects are extremely varied. For example the ratio between the quantities of ammonia and hydrazine formed in the presence of the titanocene polymers is markedly dependent on the rigidity of the polymeric chain, which regulates the formation of mono- and binuclear diazo complexes of Ti.[86]

During the dimerisation of ethylene by "nickel" immobilised systems the isomeric butenes are primary products, whereas the ratio between *cis*- and *trans*-isomers is regulated at the stage of the transition state in which the ethylene molecules occur at the time of dimerisation.[51] Double bond migration processes and also the geometric isomerisation mainly occur prior to the release of the butylene molecule from the "cell", and the secondary isomerisation reaction arising after its displacement by ethylene is reduced to a minimum. This confers "isomerisation passivity" upon the immobilised complexes in numerous reactions and increases their selectivity. Attention has already focussed on the ratio of isomerisation and hydration active centres (see Fig. 9).[79]

The conformation of the macroligand has a controlling effect on the catalytic properties and selectivity. There are many examples of this effect, which especially concerns polymers possessing the α-helical structure with accurately fixed distances between the ions of the bonded metals. This phenomenon is typical of enantioselective catalysis, where an increase in the stereospecificity is accomplished by limitation of conformational diversity, for example on oxidation of *L*(+)-ascorbic acid catalysed by *trans*-$[Fe(2,2',2'',2'''\text{-}Py_4).(OH)_2]^+$ bonded by Na-poly-(*L*- or *D*-glutamate).[87] When the complex is fixed on a peptide chain it becomes "renaturated" which is associated with the emergence of conformational asymmetry in the metallo-polymeric chains, and asymmetric induction proportional to the content of α-helices in the polymer (stereospecificity factor K_{FeD}/K_{FeL}) is observed. This is associated with a change in the standard free energy of the diastereomer transition states G_{LL} and G_{DL}. The diastereomer *DL* undergoes less steric hindrance than diastereomer *LL*. Consequently electron transport occurs more efficiently because of the more preferable changes in the activation parameters ($G^{\neq}_{LL} - G^{\neq}_{DL}$ = 1.25–3.4 kJ mol^{-1}, Fe_{FeD}/K_{FeL} = 1.5–4.0 on increase in chain load, f = 0.01–0.20) and an increase in relative conformational mobility of intermediate formations of segments in the chain.

Thus the effect of the conformation on asymmetric induction may be associated on the one hand with the formation of a suitable chain structure and on the other hand with a difference in affinity (stability of intermediate complexes) of enantiomers of the substrate and the catalyst. Such a substrate complex should probably contain at least two bonded Cu(2+) ions (on oxidation of 3,4-dihydroxyphenyl-alanine) so that stereoselection is achieved in the catalytic act (Fig. 11).[88] Like enzymic catalysis such a method ensures the generation of large quantities of the enantiomeric product from catalytic quantities of chiral materials.

In principle the selectivity of immobilised complexes may be increased by introduction of a second (supplementary) metal.

XII. The problem of polyfunctional catalysis

Systems consisting of several transition metal compounds (including those bound by a uniting ligand) may be used in different variants in catalysis. They may act either in parallel in one or several unbound rings or independently in sequential stages or in reactions or coordinatively in one reaction.[89] Polyfunctional catalysts, by means of which it is possible to react with successive stages of one multi-stage reaction, are extensively used in the chemical industry.[90] The attachment of two metals within one

† However converse examples are also known. Grafting of peroxides increases the rate of their decomposition, which is associated with their destabilisation as a result of the interaction of the peroxy group with functional groups on the surface.[84]

reaction centre, or statistically in one catalyst grain, often causes a synergistic effect of increasing activity and selectivity.

The role of the additionally introduced metal (M_1) in catalytic hydrogenisation, oxidation, (co)polymerisation and other reactions may be very diverse. On the one hand M_1 (usually nontransitional) may serve as a "trap" for active centres, binding them more firmly with the support and preventing migration and aggregation. On the other hand these effects may be achieved as a result of the insertion of the introduced metal ion between the attached complexes (the $-M-M_1-M-$ type), which promote their matrix isolation. In addition the chemical interactions (formation of weak $M-M_1$ bonds, co-crystallisation, formation of intermetallic compounds, and alloys, etc. on the support) may promote an increase in catalyst yield (as a result of an increase in activity or an increase in concentration of single centres) and its selectivity. For example immobilised bimetallic chloride complexes $AlCl_3-TiCl_4$ on CSDBV,[89] $AlCl_3-SnCl_4$ on polystyrene,[90] and $AlCl_3-FeCl_3$ and especially $AlCl_3-CuCl$ on polystyrene ($CuAlCl_4$/polystyrene)[91] etc. are the strongest solid superacids. Immobilisation of such "dibasic" acids not only increases the acidity but also prevents their irreversible deactivation in a moist atmosphere.

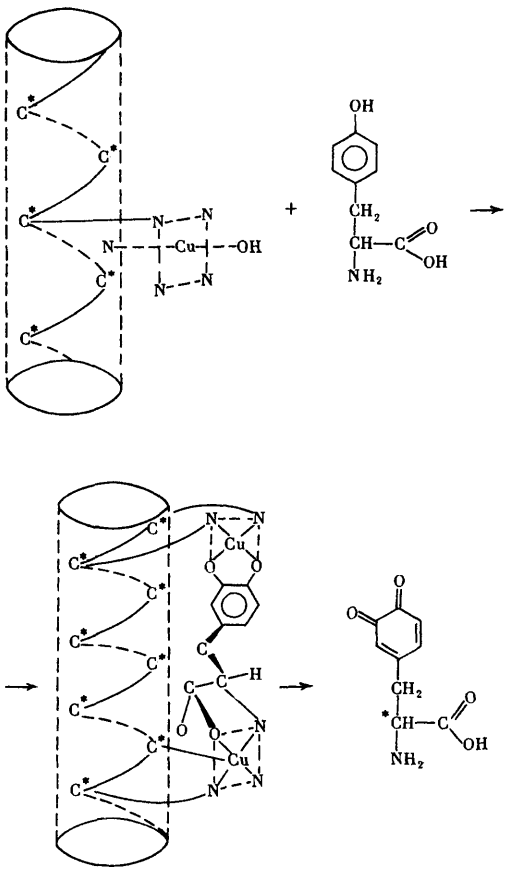
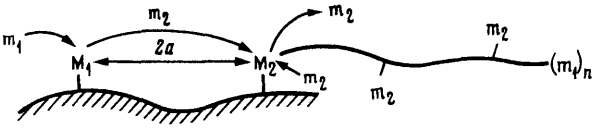


Figure 11. Model of the bifunctional coordination and oxidation of 3,4-dihydroxyphenylalanine on Cu(2+)–poly(L-lysine).[88]

However, those cases in which each of the bonded complexes achieve (according to the coordinated mechanism in the optimal variant) its own stage in the multi-stage process are of more interest. Only one of the most typical examples in the author's opinion will be presented. The case in point is the relay (coordinated) copolymerisation in the presence of immobilised complexes in which two types of active centre (dimerising and copolymerising) are bonded on to one support.[92,93] The line diagram of the process examined may be presented as follows:



The original monomer (in this case ethylene) at the active centre M_1 [for example Ni(2+)] is converted into monomer m_2 as a result of a simple reaction of di-, tri- and oligomerisation, etc. (in particular as a result of the dimerisation of ethylene into butene). In situ copolymerisation of m_1 with m_2 occurs at the active centre M_2 [for example Ti(4+), V(4+), etc.]. The size of the microcell containing different types of active centres is a, which comprises half of the average distance between the centres of pairs of the bifunctional catalyst. The distance between M_1 and M_2 is required during the construction of such catalysts.

The stationary mass-transfer in an individual microcell of this type is determined by the equation:[94]

$$D_i \frac{d^2C_i}{dx^2} = 0 \qquad (i = 1, 2),$$

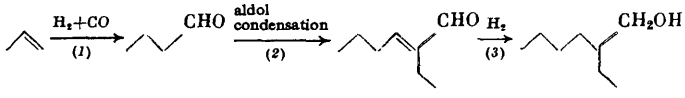
where C_i and D_i is the concentration and effective diffusion coefficient of monomer m_i in microcell respectively. The composition of the copolymer formed (in this case a copolymer of ethylene with butene, so-called branched polyethylene or linear low-density polyethylene) is characterised by the ratio of effective reaction rates of co- and homopolymerisation. In addition to other factors the regulation of the degree of branching is also attained by varying the average distance between different types of centres and has an extremal nature.

The effect of the cell in the immobilised bifunctional centre in principle may lead to an increase in the factor of the first encounters and also to an increase in the contact time of the reacting molecules (to an increase in the number of repeating encounters with the active centre). The metaphor used by the authors is that the operation of the bimetallic centre is "like the action of a conveyer on which each participant operates with great skill and speed".[95] This is promoted by the possibility of more precise control of the synthesis of active centres in the immobilised systems. However, as on a real conveyer, fragments are also found during the operation of such a centre. The complex composition of the gas mixture and the incompletely understood dependence of the behaviour of the centre on the reaction conditions hinder the control of "relay" copolymerisation and even its quantitative description.

The macroligand essentially possesses unlimited combination possibilities within the single matrix of active centres differing widely in nature, so that diffusional limitations should be less than when the corresponding number of monofunctional catalysts are used if a multi-stage reaction is performed on such a catalyst. The magnitude

of the areas of the monofunctional action of the active centres has been estimated to be 12 Å.[96] Both types of active centres should react on the substrate molecule, so that the coordinated mechanism is realised. It has already been mentioned that the most complicated task in the construction of polyfunctional systems is the coordination of the action of the diverse centres and the prevention of their autonomous operation. The main approach to resolve this problem is the control of the spatial arrangement of the active centres, which determines the extension of the transfer pathways of reagents between them, regulates diffusional limitations, and promotes the existence of the bifunctional catalysis itself.[94]

This may be shown in the case of the three-stage synthesis of 2-ethylhexanol from propylene and synthesis gas.[97] The process includes the formation of butyric aldehyde (stage 1), its aldol condensation (stage 2), and hydrogenation (stage 3).



It may be achieved by the use of both two monofunctional catalysts (hydroformylation and hydrogenation) and also one bifunctional catalyst [chloromethylated CSDVB, modified by secondary amino groups with grafted $RhCl(PPh_3)_2(CO)$] (Fig. 12). The rate of the first, second, and third stage on the bifunctional catalyst is 5-, 15- and 30-fold higher respectively than that on two monofunctional immobilised catalysts.

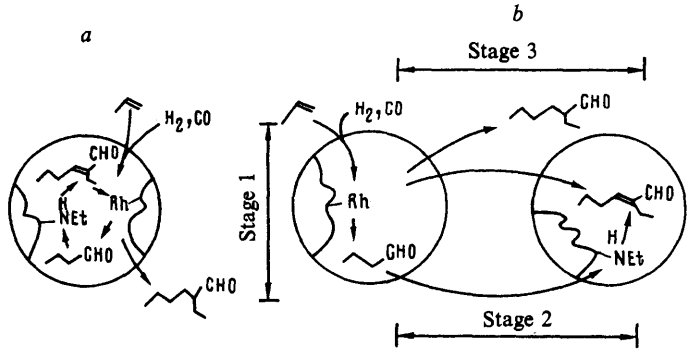


Figure 12. Comparison of diffusional inhibition in reactions catalysed by one bifunctional (*a*) and two monofunctional (*b*) catalysts in the case of the three-stage synthesis of 2-ethylhexanol.[97]

Yet another typical example relates to the reduction of O_2 to H_2O_2. Although the electroreduction of O_2 to H_2O_2 occurs readily on electrodes coated with immobilised metallo complexes, the catalysts used for the reduction of H_2O_2 to H_2O exhibit low efficiency in the O_2 reduction reaction. However it has been found basically possible to bond more than one type of metallo complex on to one graphite electrode.[98] The method involving the modification of the electrode surface by a single bifunctional catalyst for the total 4-electron reduction of O_2 was based on this principle. Ru(3+) and Cu(2+) on a chlorinated copolymer of methacrylic acid and methyl methacrylate are used as such a catalyst.[99]

The range of such examples has been extended significantly in recent years. We shall refer only to the oligomerisation of butadiene with the hydroformylation of vinyl cyclohexene on Ni–Rh-complexes bonded to phosphorylated CSDVB and the preparation of 4-methyl-2-pentanone on composites of polymers consisting of polyamines and polycarboxylic acids impregnated with PVC and incorporating two transitional metals.[100]

All examples mentioned above relate to immobilised heterometallic clusters, which have higher stability than that of the monometallic clusters under the conditions of the catalysed reactions. A search for methods to construct such systems is a promising direction for metallocomplex catalysis.[101]

The action of polyfunctional immobilised complexes is the most adequate model of catalysis by enzymes (an example is the attachment of Mo(6+)–Fe(3+) within a single elementary unit of phosphorus-containing ampholytes, the nitrogenase mode).[102] Such analogies are extremely deep-rooted and they can be extended also to polynuclear metalloenzymes. In the latter the role of multifunctionality consists of the creation of favourable energy and probability factors owing to the optimal use of the respective active centres at each stage of the reaction. In other words in the catalyst-substrate complex there is a restriction of the number of inefficient diffusional movements from the standpoint of the catalytic reaction which do not lead to the formation of products.[103]

An important condition for the realisation of catalytic synchronous processes is the possibility of the dynamic adaptation of the form of the catalytic matrix to the structure of the substrate and the active centres changing in the course of the reaction (fine-tuning). Rapid and reversible conformational transitions both in enzymes and in macroligands and also fluctuations in the matrix structure ensure the necessary structural adaptation. The specific characteristics of the enzyme systems reside in the presence of secondary and tertiary structures, which limit the spatial orientation of metal ions and the possibility of side reactions occurring. By using synthetic metalloproteins it has still not been possible to create a model which under similar conditions (pH, temperature, catalyst, and substrate concentrations) would approach enzyme systems in activity and selectivity. However, the extent to which such a condition can be approached is quite high, for example the efficiency of the binding of O_2 by metallopolymeric complexes is equivalent to the level of efficiency of haemoglobin and myoglobin.[104]

XIII. Conclusion

The author considers that by analysing the fundamental problems considered in this review it is possible to explain the growing scientific interest in catalysis by immobilised complexes and the characteristics of their operation. During the study of immobilised systems new patterns and phenomena have been revealed which are of fundamental importance (it is sufficient to mention those studies in which chelatogenic macroligands,[105] polymerisation and transformation products of metallomonomers,[106] and the use of the lanthanides and transuranium elements etc. have been investigated).

The macroligand stabilises the mononuclear complexes incorporated into unidimensional chains, two-dimensional networks, and three-dimensional frameworks. This increases the thermodynamic and kinetic stability of such systems. The polymeric structure of the ligand environment hampers ligand exchange and

introduces specific properties to the electron transfer reactions and redox processes. Nonvalent interactions affect reactivity, especially the geometry of the transition state. The differences in the kinetic and activation parameters of the reactions of polymeric and monomeric complexes are associated with conformational changes in the macroligands. The systems examined are multi-parameter systems, and it is necessary to take into account the effect of many factors, in order to optimise their activity and selectivity. Total optimisation with respect to all variables would be an incredibly complicated experimental objective. Theoretically founded economically-viable methods for its resolution in immobilised systems are only beginning to be developed.

Catalysis by immobilised complexes is accompanied by a whole series of macromolecular effects, i. e. an increased local concentration of active centres and substrate in the macromolecular globules or in domains close to the active centres, the effect of the spatial structure and polymer chain length, etc. Evolutionary transformations of multinuclear complexes into associates in the immobilised systems occur to a lesser extent than in homogeneous systems.

The realisation of the potentials of these interesting systems (for example in membrane catalysis, when by regulation of the rate at which a substrate passes through a metallopolymeric membrane it is possible to increase the selectivity of the process) will help to explain in detail both homogeneous and heterogeneous catalysis, whereas the information obtained will help to explain the basis of the catalytic action.

Finally the methodological approaches developed during the construction, study and use of immobilised complexes will be extremely useful in a new field of science, chemical biomimetics, in the physicochemical modelling of processes occurring in living nature. Thus the cooperative actions of the macroligand and Zn(2+) or Co(2+) ions as biomimetic catalysts have been found in the study of the hydrolysis of *p*-nitrophenylpicolinate.[107]

References

1. Yu I Ermakov, V A Zakharov, B N Kuznetsov *Zakreplennye Kompleksy na Okisnykh Nositelyakh v Katalize* (Complexes Attached to Oxide Supports in Catalysis), Nauka, Novosibirsk, 1980, 248 pp
2. G V Lisichkin, A Ya Yuffa *Geterogennye Metallokompleksnye Katalizatory* (Heterogeneous Metallo-Complex Catalysts), Khimiya, Moscow, 1981, 160 pp
3. Y Chauvin, D Commereuc, F Dawans *Prog. Polym. Sci.*, 1977, **5** 95
4. F Hartley *Bonded Metal Complexes. A New Generation of Catalysts* (Translated into Russian), Mir, Moscow, 1989, 360 pp
5. A D Pomogailo *Polimernye Immobilizovannye Metallokompleksyne Katalizatory* (Polymeric Immobilised Metallo-Complex Catalysts), Nauka, Moscow, 1988, 303 pp
6. A D Pomogailo, E B Baishiganov, G M Khvostik *Kinet. Katal.*, 1990, **21** 1535
7. T Suzuki, F Shirai, N Hojo *Polym. J.*, 1983, **15** 409
8. H Nishikawa, E-I Terada, E Tsuchida, Y Kurimura *J. Polym. Sci., Polym. Chem. Ed.*, 1978, **16** 2453
9. D B Rorabacher, M J Martin, M Malik, et al. *179th Am. Chem. Soc. Nat. Meet., Houston (Tex.)*, 1980, Abstr. Pap., Washington, 1980, p. 98
10. L G Domaruma, S Kiton, G Walsworth, et al. *Macromolecules*, 1979, **13** 435
11. M Sato, K Kondo, K Takemoto *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17** 2729; 1980, **18** 101
12. E Tsuchida, S Kiyotaka, K Yoshimi *J. Polym. Sci., Polym. Chem. Ed.*, 1974, **12** 2207
13. E Tsuchida, S Kiyotaka, K Yoshimi *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13** 1457
14. P Denisevich, K W Willman, R W Murray *J. Am. Chem. Soc.*, 1981, **103** 4727
15. J Topich *Inorg. Chim. Acta*, 1980, **46** L97
16. N Ueyama, E Kamada, A Nakamura *Polym. J.*, 1983, **15** 519
17. A V Vannikov, A D Grishina *Usp. Khim.*, 1989, **58**(12) 2056 [English translation in *Russ. Chem. Rev.*, 1989(12)]
18. M Ohyanagi, H Nishide, K Suenaga, E Tsuchida *Macromolecules*, 1988, **21** 1590
19. A B Solov'eva, E I Karakozova, L V Karmilova, S F Timashev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2445
20. G Challa, H C Meinders *Relations Between Homogeneous and Heterogeneous Catalysis*, Lion, 1977, p. 309
21. H Nishide, E Tsuchida *Makromol. Chem.*, 1982, **183** 1883
22. S Mao, Z Z Miao, W Gao, et al. *J. Nucl. Radiochem.*, 1987, **9** 34
23. H Nishide, H Kawakami, Y Kurimura *J. Macromol. Sci. A*, 1988, **25** 1339
24. M Sugimura, T Okubo, M Ise *Intern. Symp. Macromol. Pisa*, 1980, Vol. 4, p. 174; *Macromolecules*, 1981, **14** 124
25. G Challa *Intern. Symp. Macromol. Pisa*, 1980, Vol. 1, p. 101
26. C Carlini, G Sbrana *J. Macromol. Sci. A*, 1981, **16** 323
27. G Bar-Sela, A Warchawsky *React. Polym.*, 1983, **1** 149
28. R H Fisch, A D Thormodsen, H Heinemann *J. Mol. Catal.*, 1985, **31** 191
29. A W Nikitin, A D Pomogailo, W L Rubailo *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, p. 36
30. A A Efendiev, G L Shik, L F Vekilova, T N Shakhtakhtinskii *Katalizatory Soderzhashchie Nanesennye Kompleksy* (Catalysts Containing Applied Complexes), Papers Presented at the Symposium, Institute of Catalysis, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk, 1980, Part 2, p. 179
31. A A Efendiev, D D Orudzhiev, T N Shakhtakhtinskii, V A Kabanov *Kinet. Katal.*, 1986, **27** 520
32. V G Popov, N M Fomina *Kompleksnye Metalloorganicheskie Katalizatory Polimerizatsii Olefinov* (Complex Organometallic Catalysts for the Polymerisation of Olefins), Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka, 1991, Collection 11, p. 59
33. G Braca, C Carlini *Inf. Chim.*, 1987, (175) 149
34. O V Krylov *Mekhanizymy Kataliza* (Mechanism of Catalysis), Institute of Catalysis, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk, 1984, Part 1, p. 51
35. A D Pomogailo *Kataliz Immobilizovannymi Kompleksami* (Catalysis by Immobilised Complexes), Nauka, Moscow, 1991
36. J D Andrade, W-Y Chem *Surf. Interface Anal.*, 1986, **8** 253
37. H Widdecke *Prague Meet. Macromol. 30th Microsymp. Polym. Supported Org. Reagents and Catal.*, Prague, 1987, Programme P. L14
38. A W Schultz, P Strauss *J. Phys. Chem.*, 1972, **76** 1767
39. V N Parmon, Dissertation for Doctor of Chemical Sciences, Institute of Catalysis, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk, 1985, 707 pp

40. F K Shmidt *Kataliz Kompleksami Metallov Pervogo Perekhodnogo Ryada Reaktsii Gidrirovaniya i Dimerizatsii* (Catalysis of Hydration and Dimerisation Reactions by First Transition Series Metal Complexes), Irkutsk State University, Irkutsk, 1986, p. 158
41. S B Echmaev, I N Ivleva, A D Pomogailo, et al. *Kinet. Katal.*, 1986, **27** 394
42. S V Vonsovskii *Magnetizm* (Magnetism), Nauka, Moscow, 1971, p. 65
43. I N Ivleva, A D Pomogailo, S B Echmaev, et al. *Kinet. Katal.*, 1979, **20** 1282; 1983, **24** 663
44. S B Echmaev, I N Ivleva, A D Pomogailo, et al. *Kinet. Katal.*, 1983, **24** 1428
45. A D Pomogailo, A T Nikitaev, F S D'yachkovskii *Kinet. Katal.*, 1984, **25** 166
46. A Guyot, C Graillat, M Bartholin *J. Mol. Catal.*, 1977/1978, **3** 39
47. E W Thornton, H Knozinger, B Tesche, et al. *J. Catal.*, 1980, **62** 117
48. H Grubbs, C P Lau, R Currier, C H Brubaker, Jr. *J. Am. Chem. Soc.*, 1977, **99** 4517
49. E A Karakhanov, E B Neimerovets, V S Pshezhetskii, A G Dedov *Khim. Geterotsikl. Soedin.*, 1986, 303
50. L F Velikova, E A Blyumberg, A A Efendiev, et al. *Azerb. Khim. Zh.*, 1987, (3) 79
51. A D Pomogailo, F A Khrisostomov, F S D'yachkovskii *Kinet. Katal.*, 1985, **26** 1104
52. A D Pomogailo, F S Dyachkovskii *Acta Polym.*, 1984, **35** 41
53. M S Jarell, B C Gates, E D Nicholson *J. Am. Chem. Soc.*, 1978, **100** 5727
54. E A Bekturov, S E Kudaibergenov, V A Sigitov *Polymer*, 1986, **27** 1269
55. J H Schutten, P Piet, A L German *Makromol. Chem.*, 1979, **180** 2341; *Angew. Chem.*, 1980, **89** 201
56. T M Ushakova, I L Dubnikova, I N Meshkova, et al. *Vysokomol. Soedin., Ser. A*, 1979, **21** 2713
57. J C W Chien, J T T Hsieh *Coordination Polymerization* (Edited by J C W Chien), Acad. Press, New York, 1975, p. 305
58. A A Belii, L G Chigladze, M E Vol'pin, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2678; 1989, 1961
59. E N Rasadkina, T V Kuznetsova, A T Teleshov, et al. *Kinet. Katal.*, 1974, **15** 969
60. G P Potapov *React. Kinet. Catal. Lett.*, 1983, **23** 281
61. M V Klyuev *Zh. Org. Khim.*, 1984, **20** 1908; 1987, **23** 581
62. G V Vinogradov, A Ya Malkin *Reologiya Polimerov* (The Rheology of Polymers), Khimiya, Moscow, 1977, 438
63. V V Volodin, A N Shupik, A M Shapiro, et al. *Vysokomol. Soedinen., Ser. B, Krat. Soobshch.*, 1987, **29** 496
64. T Uematsu, F Saito, M Miura, H Hashimoto *Chem. Lett.*, 1977, (2) 113
65. T Uematsu, Y Nakazawa, F Akutsu, et al. *Makromol. Chem.*, 1987, **188** 1085
66. A B Solov'eva, Dissertation for Doctorate of Chemical Sciences), Lomonosov Institute of Fine Chemical Technology, Moscow, 1989, 253 pp
67. P Viout, I Artaud *J. Chem. Soc., Perkin Trans. 1*, 1984, (6) 1351
68. D E Bergbreiter, R Chandrar *J. Am. Chem. Soc.*, 1987, **109** 174
69. Wei Chen, Guangfu Ma, Zhaoying Lo, Mangjun Gao *J. Macromol. Sci. A*, 1987, **24** 243
70. G Valentini, G Braca, G Sbrana, et al. *Inter. Symp. Macromol. Pisa*, 1980, **4** 143
71. Y Lin, B Zou *J. Catal.*, 1985, **6** 273
72. C E Koning, F J Vierson, G Challa, J Reedijk *J. Mol. Catal.*, 1988, **44** 245
73. W Breemhaar, H C Meinders, G Challa *J. Mol. Catal.*, 1981, **10** 33
74. A V Artemov, V A Seleznev, E F Vainshtein *Izv. Vuzov. Khim. Khim. Tekhnol.*, 1983, **26** 1298; 1984, **27** 64
75. V A Seleznev, Yu P Tyulenin, E F Vainshtein, A V Artemov *Kinet. Katal.*, 1983, **4** 1085; *Neftekhimiya*, 1981, **21** 114
76. K H Streun, P Piet, A L German *Eur. Polym. J.*, 1987, **23** 941
77. A P Purmal, L A Nikolaev *Usp. Khim.*, 1985, **54**(5) 786 [English translation in *Russ. Chem. Rev.*, 1985(5)]
78. R J Williams, P A Serman, I Feinstein-Jaffe *J. Mol. Catal.*, 1989, **51** 117 [this reference appears to be incorrect (Ed. of Translation)]
79. S A Lawrence, P A Serman, I Feinstein-Jaffe *J. Mol. Catal.*, 1989, **51** 117
80. I V Serebryanaya, N E Khrushch, A D Pomogailo, et al. *Kinet. Katal.*, 1986, **27** 389; 1990, **31** 540
81. F S Dyachkovskii, A D Pomogailo *Homogeneous and Heterogeneous Catalysis* (Edited by Yu Yermakov, V Likholobov, VNU Science Press, Utrecht, 1986, p. 447
82. A P Filippov, O A Polishchuk *Kinet. Katal.*, 1984, **25** 1341, 1348
83. H Akarawa, Y Morooka, A Ozaki *Bull. Chem. Soc. Jpn.*, 1974, **47** 2958
84. N Yablokova, A V Ganyushkin, G B Sadikov, Yu A Aleksandrov *Vysokomol. Soedin., Ser. B, Krat. Soobshch.*, 1985, **27** 553
85. E Bayer, W Schumann *J. Chem. Soc., Chem. Commun.*, 1986, (12) 949
86. M Koide, E Tsuchida, Y Kurimura *Makromol. Chem.*, 1981, **182** 749; *Makromol. Chem., Rapid. Commun.*, 1981, **2** 627
87. M Barteri, B Pispisa *Intern. Symp. Macromol. Pisa*, 1980, **4** 155; B Pispisa, M Barteri, M Farinella *Inorg. Chem.*, 1983, **22** 3166
88. M Hatano, T Nozawa, S Ikeda, T Yamamoto *Makromol. Chem.*, 1971, **11** 11, 31
89. R Ran, W Pei, Kh Jia, et al. *Gaofen'tsy Tunsyun* (Polym. Commun.), 1986, (6) 453
90. R Ran, Kh Jia, X Wu, et al. *Chem. J. Chin. Univ.*, 1986, **7** 645; 1987, **8** 1141
91. N Toshima, K Kanaka, M Komijma, H Hirai *J. Macromol. Sci. A*, 1988, **25** 1349
92. N S Enikolopyan, L N Raspopov, A D Pomogailo, et al. *Dokl. Akad. Nauk SSSR*, 1984, **278** 1392; *Vysokomol. Soedin., Ser. A*, 1989, **31** 2624
93. V A Kabanov, V I Smetanyuk, V G Popov, et al. *Vysokomol. Soedinen., Ser. A*, 1980, **22** 335
94. N F Surkov, S P Davtyan, A D Pomogailo, F S D'yachkovskii *Kinet. Katal.*, 1986, **27** 714
95. V A Likholobov, A S Lisitsyn *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1989, **34** 340
96. K G Ione *Polifunktsional'nyi Kataliz Na Tseolitakh* (Polyfunctional Catalysis on Zeolites), Novosibirsk, 1982, 272 pp
97. R F Batchelder, B C Gates, F J P Kuijpers *6th Intern. Congress on Catalysis*, London, 1976, Preprint A40
98. N Oyama, F C Anson *J. Am. Chem. Soc.*, 1979, **101** 3450

99. K Shigehara, F C Anson *J. Electroanal. Chem.*, 1982, **132** 107
100. C U Pittmann, Jr., Y Kawabata, Y F Liang *179th Am. Chem. Soc., Nat. Meet. Houston (Tex.)*, 1980, Abstr. Pap., Washington, 1980
101. I I Moiseev *Itogi Nauki i Tekhniki. Kinetika i Kataliz* (Advances in Science and Technology. Kinetics and Catalysis), All-Union Institute of Scientific and Technical Information, Moscow, 1984, Vol. 13, p. 147
102. V D Kopylova *Teoriya i Praktika Sorbtsionnykh Protsessov* (Theory and Practice of Sorption Processes), Voronezh State University Press, Voronezh, 1986, No. 18, p. 3
103. G I Likhtenshtein *Mnogoyadernye Okislitel'no-Vosstanovitel'nye Metallofermenty* (Multinuclear Redox Metalloenzymes), Nauka, Moscow, 1979, 323 pp
104. E Antonini, M Brunori *Haemoglobin and Myoglobin in Their Reaction with Ligands*, North-Holland Publ. Co., Amsterdam, 1971, 349 pp
105. A D Pomogailo, I E Uflyand *Makromolekulyarnye Metallokhelaty* (Macromolecular Metallo-Chelates), Khimiya, Moscow, 1991, 304 pp
106. A D Pomogailo, V S Savost'yanov *Metallosoderzhashchie Monomery i Polimery Na Ikh Osnove* (Metal-Containing Monomers and Polymers Based on Them), Khimiya, Moscow, 1988, 384 pp
107. R S Brown, M Zamkaneli, J L Cocho *J. Am. Chem. Soc.*, 1982, **106** 5222

Translated from *Uspekhi Khimii* 61 293–319 (1992) U.D.C. 541.128+541.145

Photocatalysis by transition metal complexes

O V Gerasimov, V N Parmon
Institute of Catalysis, Siberian Division of the Russian Academy of Sciences, Novosibirsk

ABSTRACT. The principal tendencies in the development of homogeneous photocatalysis by transition metal complexes are examined. Attention is concentrated on the photocatalytic reactions of organic substrates.

The bibliography includes 164 references.

Contents

I. Introduction 154
II. What is understood by the term "photocatalysis"? 155
III. Photocatalytic reactions with participation of transition metal complexes as photocatalysts 156
IV. Conclusion 165

I. Introduction

Transition metal complexes are well known as excellent highly active catalysts of many homogeneous processes, capable of ensuring not only a high selectivity of the chemical reactions but also the possibility of studying their detailed mechanisms. This makes it possible to act specifically on such reactions by modifying the structure or composition of the catalytic complexes.[1–7] Photochemists have found in their turn that model complexes are objects whose structure and properties can be described quite satisfactorily by modern theories and have used photochemical reactions with participation of transition metal complexes as, on the one hand, an instrument for further improvement of these theories and, on the other, as a means of achieving new chemical reactions which are frequently not merely of academic interest.[8–13] At the junctions of these two fields—homogeneous coordination catalysis and transition metal photochemistry—a new field of physical chemistry, namely photocatalysis by transition metal complexes, has been established and has developed quite vigorously.

Unfortunately the available Russian language monograph and review literature provides an inadequate description of these studies, because it deals mainly with the extremely specific problem of the application of photocatalysis by metal complexes to the direct transformation of solar energy into the energy of chemical fuels (see, for example, Refs. 14–21). The monograph of Kryukov and Kuchmii[13] provides a description of a series of photocatalytic processes on the basis of the photochemical reactions of titanium and iron complexes in aqueous and aqueous organic media. Shul'pin's monograph,[7] devoted to metal complex catalysis as a whole, presents many examples of organometallic photocatalysis, but these are disjointed and are discussed in the context of the problem of the usual thermal catalysis. The only review in Russian devoted directly to the problem of photocatalysis by transition metal complexes is that of Lyashenko.[22]

In the present article, an attempt is made to survey and deal systematically with studies in homogeneous photocatalysis by transition metal complexes in order to acquaint Russian speaking readers with the development and prospects of such research.

In connection with this aspect of the review, the latter is hardly concerned with questions related to the nature of the primary photophysical and photochemical stages of the processes discussed below. Nevertheless, before describing the main material of the review, mention should be made of certain principal characteristics of the nature of the photochemical activity of transition metal complexes.[8]

The following electronic transitions capable of initiating primary photochemical processes take place under the influence of light in transition metal complexes.

Ligand field transitions (LF transitions) or $d-d$ transitions ($f-f$ transitions) occur between orbitals referring to the central ion and are usually observed in the visible region. They are symmetry forbidden for octahedral complexes and the corresponding extinction coefficients are therefore usually small (10^1-10^2 litre mol^{-1} cm^{-1}).

Charge-transfer transitions (CT transitions) are characterised by the transfer of an electron localised predominantly on the central atom to the unoccupied orbitals of the ligand [transition with charge transfer from the metal to the ligand (CTML)] or conversely [transition with charge transfer from the ligand to the metal CTLM)]. Charge-transfer transitions are recorded in the UV region and in the blue part of the visible spectrum. The corresponding extinction coefficients are fairly large—of the order of 10^4 litre mol^{-1} cm^{-1}. A related variety of the transition is phototransfer of an electron from the central metal ion to a solvent molecule or conversely.

Electronic transitions of the above types are responsible for the vast majority of photocatalytic reactions with participation of transition metal complexes. Nevertheless, in many cases other primary photophysical processes, listed below, also play a definite role.

Intraligand transitions (IL transitions), which are frequently called $\pi-\pi$ transitions (because intraligand transitions with participation of σ orbitals lie as a rule in the far UV region and are not manifested in the usual sphere of the complexes), are located in the UV region (with rare exceptions) and are characterised by extinction coefficients up to 10^5 litre mol^{-1} cm^{-1}.

Mention should also be made of charge-transfer transitions which can occur in ion pairs. In dinuclear and polynuclear complexes, there is a possibility of transitions with charge transfer from one metal ion to another (the so called intervalent transitions usually manifested in the presence of a bridging ligand) and also (in the presence of metal–metal bonds) transitions between molecular orbitals) localised on two or more metal ions.

As a result of the absorption of a light quantum, a molecule of the complex receives a large dose of energy: a quantum energy of 2–3 eV corresponds to the visible light and one up to 6 eV corresponds to UV light, while the quantity kT amounts to 0.025 eV at room temperature and the activation energies for the usual thermal ("dark") reactions rarely exceed 1 eV (about 100 kJ mol^{-1}). However, the absorption of a light quantum cannot be regarded as selective 'heating' of an individual molecule. Not the magnitude of the adsorbed energy but a completely definite rearrangement of the electronic structure of the complex is important for the initiation of the photochemical reaction.

For example, as a result of a LF transition, an electron is transferred from a bonding orbital to a non-bonding or antibonding orbital (or from a non-bonding to an antibonding orbital) which entails a weakening of the bond between the central ion and the ligand. Therefore the preferred model of reactions with participation of excited LF states is dissociation or isomerisation of the complexes.

As a result of charge-transfer transitions

$$ML + h\nu \xrightarrow{CTML} M^+L^-$$

$$ML + h\nu \xrightarrow{CTLM} M^-L^+$$

(here and henceforth M and L are understood as the initial states of the metal ion and of one of the ligands of the complex respectively), species differing sharply from non-excited states in their oxidation-reduction properties are formed. Depending on the oxidation-reduction properties of the ligand and the central ion, the nature of the solvent, and the presence in the solution of other compounds, etc., reactions of the excited state of the complex with participation of both $M^+(M^-)$ and $L^-(L^+)$ can take place under these conditions.

Overall, the probability of the occurrence of the primary photochemical reaction in a particular direction can depend on the wavelength of the exciting light, the nature of the excited state, its lifetime, the nature of the solvent, the presence of other substances in solution, etc. Thus the lifetime of the excited state is a parameter which is particularly critical for bimolecular reactions. Indeed, for excitation lifetimes less than 10^{-10} s and reasonable concentrations of the reactants in a homogeneous solution or in the gas phase, the attempts to carry out a bimolecular reaction with participation of such an excited state are virtually hopeless. However, unimolecular reactions (including those with coordinated molecules of substrates) are entirely feasible even for such short times. By altering the wavelength of the exciting light, it is possible to generate more or less selectively various excited states of the same complex or to excite particular compounds among those present in the reaction system and influence thereby the mode of reaction.

Photocatalytic processes are more complex than "simple" photochemical reactions, because they usually include at least two stages. Therefore, before considering specific examples, it is useful to deal with questions of the terminology and classification of the phenomena in the field of photocatalysis.

II. What is understood by the term "photocatalysis"

The term "photocatalysis" and the concepts of "photocatalytic reaction" and "photocatalyst" associated with it are extremely widely encountered in the literature. A whole series of recent books and reviews are fully or partly devoted to photocatalysis.[14–36] At the same time there is as yet no rigorous and generally accepted definition of this concept, which has been noted by almost everyone who has attempted to deal systematically with the terms used in this branch of knowledge.[7,26,28–30,37–39] One of the common approaches consists in the widest possible treatment of the concept of "photocatalysis", which has been firmly expressed by the definition recommended by the IUPAC Commission:[40] "photocatalysis is catalytic reaction involving the absorption of light by the catalyst or the substrate". The reactions included in this definition can be described by the generalising equations

$$S \xrightarrow[K]{h\nu} P \text{ or } S + R \xrightarrow[K]{h\nu} P + Q.$$

Here and henceforth the symbols S and R denote the substrate and reactant molecules, the symbol K represents the initial form of the catalyst or the photocatalyst, and P and Q are reaction products. It is significant that this formulation embraces processes of most varied types. A more rigorous systematic treatment of the process under consideration is therefore proposed below (see also Parmon[39]).

1. Photogenerated (photoinduced photoinitiated) catalysis. The reaction proceeds in accordance with the scheme

$$\begin{aligned} K &\xrightarrow{h\nu} K', \\ S &\xrightarrow{K'} P. \end{aligned} \qquad (I)$$

Here light is used to generate the active form of the catalyst K′, which ensures the occurrence of the usual "dark" catalytic reaction. In principle, if this active form is not deactivated, the rate of the photoinitiated reaction should remain unchanged also after light has been switched off.

2. Catalysis of a photochemical reaction. The scheme

$$\begin{aligned} S &\xrightarrow{h\nu} {}^*S, \\ {}^*S &\xrightarrow{K} P. \end{aligned} \qquad (II)$$

or

$$\begin{aligned} S &\xrightarrow{h\nu} P', \\ P' &\xrightarrow{K} P. \end{aligned} \qquad (IIa)$$

corresponds to this case. After the absorption of light by the substrate S, its excited state *S or the primary photoproduct P′ undergo a catalytic reaction with formation of the final product P.

3. Photosensitised reaction. Reactions involving the transfer of energy from the photosensitiser K to the substrate S are usually referred to this type:

$$\begin{aligned} K &\xrightarrow{h\nu} K^*, \\ S + {}^*K &\rightarrow {}^*S + K, \\ {}^*S &\rightarrow P. \end{aligned} \qquad (III)$$

It is not noteworthy that the term "photosensitisation" is treated, like the term "photocatalysis", very broadly.[38] Thus reactions

involving the phototransfer of an electron, for example in accordance with the scheme

$$\begin{aligned} &K \xrightarrow{h\nu} {}^*K, \\ &{}^*K + S \rightarrow K^+ + S^-, \\ &S^- \rightarrow P, \\ &R + K^+ \rightarrow R^+ + K, \\ &R^+ \rightarrow Q. \end{aligned} \qquad \text{(IIIa)}$$

are frequently classified as photosensitised.

Such extended treatment is apparently not entirely legitimate because electron transfer is a chemical reaction, albeit of the simplest kind, in contrast to the transfer of excitation energy. A reaction in accordance with mechanism (IIIa) should therefore be referred to photocatalysis (type 4).

4. Photocatalysis proper. In the English language literature, reactions of this type are frequently designated as "photoassisted catalysis", i.e. "catalysis with the assistance of light". The simplest cases of photocatalysis are described, together with scheme (IIIa), also by the schemes

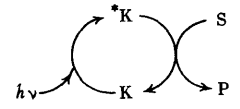
$$\begin{aligned} &K \xrightarrow{h\nu} {}^*K, \\ &S + {}^*K \rightarrow P + K. \end{aligned} \qquad \text{(IV)}$$

[the difference from scheme (III) consists in the absence of the transfer of electronic excitation to the substrate] or

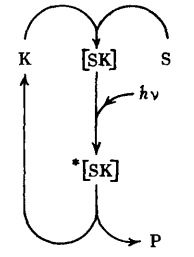
$$\begin{aligned} &S + K \rightarrow [SK], \\ &[SK] \xrightarrow{h\nu} {}^*[SK], \\ &{}^*[SK] \rightarrow P + K. \end{aligned} \qquad \text{(IVa)}$$

In this case, the catalyst participates directly both in the light absorption step, {either in the form of an individual compound of K via scheme (IV) or as a complex with the substrate [SK] via scheme (IVa)}, and in the step involving the catalytic conversion of S into P. Thus a photochemically active catalyst, i.e. the *photocatalyst* proper, is present in the system. In our view, this last factor justifies the naming of reactions of this particular type as truly photocatalytic.

Returning to the extended definition of photocatalysis proposed by IUPAC, we note that it does of course have the right to exist. This is because, for example, the real mechanisms of catalytic reactions occurring under the influence of light are frequently unknown, at any rate in the initial stages of the investigation. Therefore, if it has only been established that the reaction is catalytic and that light influences its rate or pathway, it is reasonable to refer to such reactions as photocatalytic *in a broad sense*. On the other hand, if it is found on closer examination that the reaction is in fact of the dark "thermal" type, as in scheme (I), or the catalyst is not involved in the absorption of light [i.e. is not a photocatalyst, as in scheme (II)], or the reaction is not catalytic at all [i.e. there is no chemical interaction between the light-absorbing compound and the substrate, as in scheme (III)], then in such cases one should avoid using the term "photocatalysis" and apply it only to designate processes illustrated by schemes (IIIa), (IV), and (IVa). This approach to the term "photocatalysis", which we have followed consistently during the last ten years,[15] is based on the definition of the concept of "catalysis" given by Boreskov.[41] The corresponding formulation is as follows: "photocatalysis is the change in the rate or excitation of chemical reactions under the influence of light in the presence of substances (photocatalysts) which, as a result of the absorption of light quanta by them, are capable of inducing chemical reactions of the reactants by entering into intermediate chemical interactions with the latter and regenerating their own chemical composition after each cycle of such interactions". Within the framework of this definition, two situations, illustrated by Schemes (IV) and (IVa), are possible, which can be represented, for greater clarity, by the following cyclic schemes respectively:



,



.

These cyclic schemes differ in the sequence in which light is absorbed and the photocatalyst reacts chemically with the substate. However, in both cases the photocatalyst participates in the two stages indicated.

III. Photocatalytic reactions with participation of transition metal complexes as photocatalysts

To facilitate the subsequent analysis, photocatalytic reactions with participation of transition metal complexes can be divided into two groups: (1) "inner sphere" reactions in which bonds are dissociated and/or formed in the inner sphere of the metal complex; (2) "outer sphere" reactions in which the main transformations of the substrate molecules occur outside the inner sphere of the complex. Reactions of the first type are in fact characteristic of transition metals with their unique ability to form a wide variety of coordinate bonds. Reactions of the second group are in our view not so specific to coordination compounds, because their first stage is always electron phototransfer—a process characteristic of a wide range of compounds, especially organic ones. Nevertheless, certain characteristic features of metals complexes enable them to occupy a special place also among photocatalytic reactions of the second type. The most characteristic features of reactions of both types are considered below in succession.

1. Inner sphere photocatalytic reactions

Among reactions of this type one can distinguish, in their turn, two subgroups: (1) reactions with participation of transition metal complexes with organic ligands; (2) reactions with participation of simple inorganic metal complexes. The difference as regards the type of ligands is extremely arbitrary because in reactions of the first subgroup compounds of the type CuCl frequently occur as initial photocatalytically active substances, while the substrates in reactions of the second group are usually organic compounds which are, in principle, capable of forming coordinate bonds with the ions of the photocatalytically active complex in some stage of the process. However, a significant difference between these subgroups nevertheless exists and is manifested by the nature of the initiated reactions.

Table 1. Inner-sphere photocatalytic reactions with participation of organometallic and other related complexes.

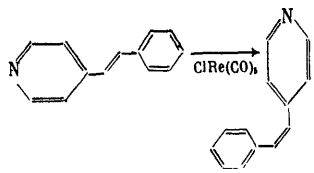
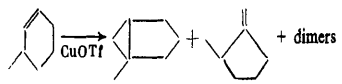
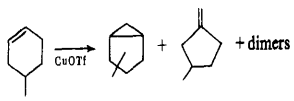
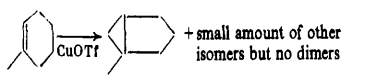
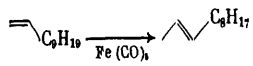
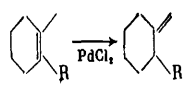
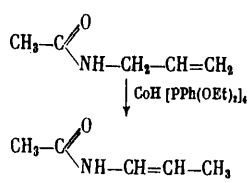
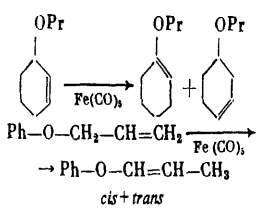
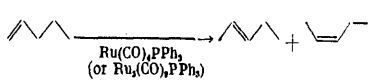
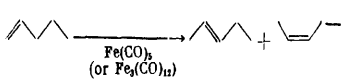
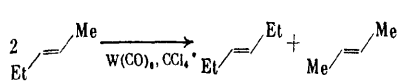
Type of reaction	Examples	Mechanism	Comments	References
Geometrical isomerisation of alkenes		PC	The non-catalytic reaction takes place only under the influence of UV light, while in the presence of $ClRe(CO)_5$ it occurs under the influence of light with $\lambda = 436$ nm	[43]
	Ditto in the presence of $W(CO)_6$	PG+PC		[23, 44]
Skeletal isomerisation of alkenes		PC		[45]
				
				
Allyl shift		PG		[46]
		PC	An anomalous allyl shift involving an increase in free energy takes place under the influence of light	[26]
		PG	Flash photolysis showed that the substrate is coordinated to the catalyst via the double bond and not the nitrogen atom	[47]
		PG	Reactions of this type usually occur on heterogeneous catalysts of the type KNH_2/Al_2O_3, but the first reaction does not occur on them at all while the second affords only the *cis*-product	[48]
		PG	φ reaches 400; the Ru_3 trimer is active in the visible region	[49]
		PG	The photogenerated catalyst exhibits a very high activity compared with the traditional "dark catalyst"	[50]
Metathesis		PG		[51]
	Ditto in the presence of $W(CO)_5L+ZrCl_4$ in *n*-heptane	PG	The reaction proceeds at room temperature with a high selectivity	[52]

Table 1 (cont'd).

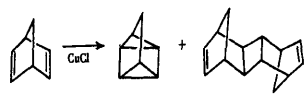
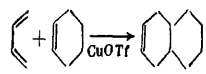
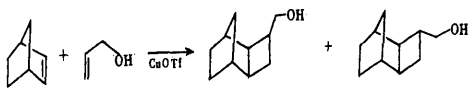
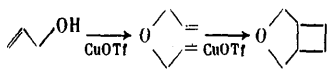
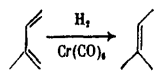
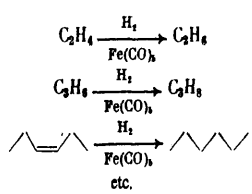
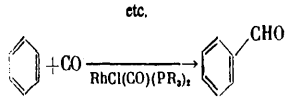
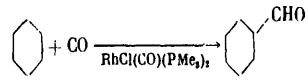
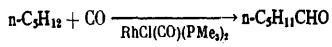
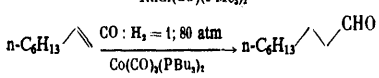
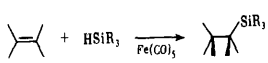
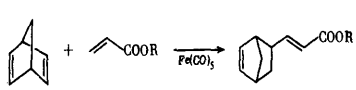
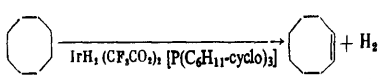
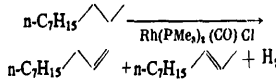
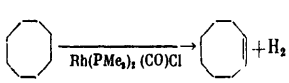
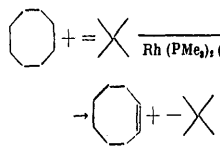
Type of reaction	Examples	Mechanism	Comments	References
Cycloaddition of alkenes		PC	The turnover number of the photocatalyst reaches almost 400; $\varphi = 0.34$ and is independent of the substrate concentration; the formation of a complex between the photocatalyst and the substrate in the ground state is confirmed by UV spectra	[53]
		PC		[54]
		PC	In contrast to the examples presented previously, not only hydrocarbons but also an oxygen-containing compound participates in the reaction	[55]
		PC		[56]
Hydrogenation		PG	The reaction continues for several hours after switching off the light	[57]
		PG	$Fe(CO)_5$ catalyses the reaction also in the absence of illumination but at $T > 150$ °C, while in the presence of light with $\lambda > 366$ nm the reaction takes place at room temperature or even at $T < 0$ °C	[58]
Carbonylation		PG	Flash photolysis showed that CO and not phosphine is split off under the influence of light	[59]
		PG		[60]
		PG		[61]
Hydroformylation		PG	$\lambda = 366$ nm; the photocatalytic reaction takes place at 85 °C but there is no thermal catalysis under these conditions	[62]
Addition to $\rangle C{=}C\langle$ bond		PG		[63, 64]
		PC		[65]
Dehydrogenation		PC		[66, 67]
		PC		[68]
		PC		[69]

Table 1 (cont'd).

Type of reaction	Examples	Mechanism	Comments	References
Dehydrogenation with transfer of hydrogen		PC		[69]
Reduction of CO_2	$CO_2 + N(CH_2CH_2OH)_3 \xrightarrow[Re(bipy)(CO)_3Cl]{} CO + TEA$ oxidation products	PC	See also Table 3	[70]
Water gas shift reaction	$CO + H_2O \xrightarrow[Co(CO)_4]{} CO_2 + H_2$	PG		[71]
	Ditto in the presence of Ir $[(\eta^5-Me_5C_5)Ir(bipy)X]^+$, where X=$Cl^-$ or H^-	PC		[72]
	Ditto in the presence of $HFe(CO)_4^-$	PC		[73]
Polymerisation	Polymerisation of methyl methacrylate, styrene, and other olefins in the presence of $Ti(CH_2Ph)_4$ or $Zr(CH_2Ph)_4$	PG		[74–76]

Note. PC = "true" photocatalysis; PG = photogenerated catalysis; φ = quantum yield.

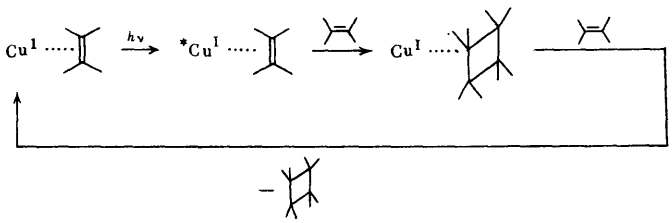
(a) Photocatalysis with participation of complexes containing organic ligands

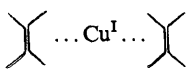
Photocatalysis with participation of complexes containing organic ligands, in particular "organometallic photocatalysis", is a dynamically developing research field (see, for example, the relevant reviews[23,25,26,29,30,38,42]). The wide variety of chemical reactions which have been achieved in systems of this type is noteworthy. Examples are presented in Table 1, which includes only the most typical and interesting reactions. Those wishing to do so, may find an extensive compilation of reactions of this type in another review[26] and also in recent publications.[38,42]

As can be seen from Table 1, this group includes alkene isomerisation reactions (geometrical and skeletal isomerisation, the allyl shift), metathesis, alkene cycloaddition reactions, hydrogenation, carbonylation, and other processes, i.e. reactions which are, in principle, usual for traditional homogeneous catalysis. Furthermore, the majority of the photocatalytically active compounds are at the same time also traditional (thermal) homogeneous catalysts [$M(CO)_n$, $M(CO)_nL_m$, $M(CO)_n(PPh_3)_mL_k$, CuOTf, $Co(OAc)_2$, etc., where M = Rh, Ir, Fe, Ru, etc. and OTf = trifluoromethanesulphonate]. This gives rise to an especially convenient possibility of comparing reactions occurring in photocatalytic and dark (thermal) catalytic regimes and to discover the characteristic features occurring in photocatalytic and dark (thermal) catalytic regimes and to discover the characteristic features of the photocatalytic method of effecting a number of organic reactions. Comparison shows that, firstly, photocatalytic reactions can occur under much milder conditions than the analogous dark reactions. The hydrogenation of olefins in the presence of $Fe(CO)_5$ can serve as an example: when the system is acted upon by light ($\lambda > 366$ nm), the reaction takes place at a temperature lower by ~150 °C than under dark conditions.[58] This feature may be fundamentally important in syntheses with participation of thermolabile reactants or products and the photocatalytic procedure is in such cases the only one possible. Secondly, the catalyst, formed as a result of its photochemical generation, is not usually inferior as regards its activity, and sometimes is actually superior, to the catalysts obtained under similar conditions by the thermal method.[50] This means that the generation of the catalyst under the influence of light can, in principle, compete with the usual thermal activation of the catalyst, ensuring under identical conditions a higher rate of reactions. Thirdly, direct thermal catalysis of reactions accompanied by a significant increase in free energy is as a rule altogether impossible. In such cases, the photocatalytic (or at least photochemical) method of effecting the reaction via the given pathway, capable of "pumping" energy into the system, is the only one possible. Examples of photocatalytic reactions accompanied by an increase in free energy are certain cycloaddition reactions[53] and the anomalous allyl shift[26] (see also Table 1). Fourthly, photocatalysis can promote the occurrence of photochemical non-catalytic reactions, which is manifested, for example, by spectral sensitisation. Thus direct photochemical *trans–cis* isomerisation of 4-styrylpyridine takes place only under the influence of UV light, whereas in the presence of the $ReCl(CO)_5$ photocatalyst it becomes possible under the influence of visible light with $\lambda = 436$ nm.[43] Similarly, the cycloaddition reactions of olefins in the presence of photocatalysts, for example, copper(I) salts, require milder UV light.[53]

The photocatalytic processes under discussion can proceed via one of two dominant mechanisms. The first is true photocatalysis, which can always be described in terms of a sequence of reactions [scheme (IVa)]. This mechanism has been demonstrated quite satisfactorily, for example, for the olefin cycloaddition reaction in the presence of copper(I) salts.[26] Trifluoromethanesulphonate (triflate, OTf^-) is frequently used as the negatively charged ligand, although the reactions take place also when copper(I) is present in the system as

halide salts (chlorides and bromides). In an olefin solution, the central copper(I) ion coordinates the olefin via its double bond. The presence of such coordination is confirmed by UV spectra—a charge-transfer band, more intense than the bands of the initial compounds, arises. This results, firstly, in an increase in the ability of the system to absorb light, which is actually of intrinsic importance because there exists also a purely photochemical reaction pathway. Secondly, the excitation of the copper(I)–olefin complex by light corresponding to the CTML absorption band leads to a redistribution of electron density among the π orbitals of the olefin, so that the cycloaddition reaction in conformity with the Woodward–Hoffmann rule is promoted. Thirdly, and finally, copper(I) can function as a common coordinating site for the two reacting molecules similarly to what happens in the usual coordination catalysis:[26]

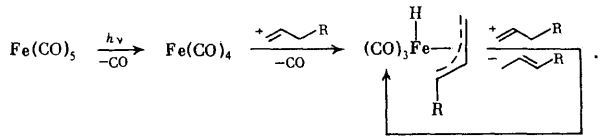


The interaction of the excited complex *Cu... with another olefin molecule (or the intramolecular transformation of the complex ) results in the formation of a saturated cyclobutane ring, which interacts with copper(I) much more weakly than the C=C bond and is therefore rapidly substituted by a new olefin molecule. The catalytic cycle is thus closed.

The second mechanism operating in the group of reactions considered is photogenerated catalysis [see scheme (I)]. The catalyst is photogenerated as a rule as a consequence of an increase in the lability of complexes in the *d–d* excited state. As already mentioned, the rate of reaction proceeding via the photogenerated catalytic mechanism should ideally remain unaltered after light has been switched off. In certain cases, the observed reactions do indeed continue for a long time after light has been switched off, as happens, for example, in the hydrogenation of 2-methylbuta-1,3-diene in the presence of $Cr(CO)_6$.[57] However, the deactivation of the active form of the photogenerated catalyst is frequently extremely rapid, i.e. the reaction actually takes place only in the light and is outwardly manifested as a true photocatalytic process. Thus the isomerisation of pent-1-ene to a mixture of *cis-trans*-pent-2-enes in the presence of iron carbonyls ceases after light has been switched off less than 5 s.[50] The activation of the photogenerated catalyst usually takes place as a result of the occurrence of processes which are the reverse of those which take place during its generation. For example, the active form of iron pentacarbonyl is the coordinatively unsaturated compound $Fe(CO)_4$:

$$Fe(CO)_5 \underset{\text{generation}}{\xrightarrow{h\nu}} Fe(CO)_4 + CO \underset{\text{deactivation}}{\longrightarrow} Fe(CO)_5.$$

If the rate of coordination of $Fe(CO)_4$ to the substrate does not exceed appreciably the rate of the reverse addition of CO, then the turnover number of such a species in the catalytic process from the instant of generation to the instant of deactivation will be relatively small, which actually happens in the pent-1-ene isomerisation reaction. The catalytic reaction proper proceeds via the mechanism usual for processes of this type:



The quantum yield of this reaction can reach several tens, which permits its entirely definite assignment to photogenerated catalytic processes.

(b) Photocatalysis with participation of metal complexes containing simple inorganic ligands

Typical photocatalysts of this group are $TiCl_4$, $FeCl_4^-$, CuCl, $CuCl_2$, VCl_3, $SnCl_4$, oxo-compounds of molybdenum and tungsten, and certain others. However, as in the case examined above, a common factor here is not only and not so much the nature and structure of the photocatalysts themselves as the reactions achieved with their aid. Examples of reactions of this group are compiled in Table 2. These are in the main reactions involving addition to the double bond (C=C and C=X) as well as a wide variety of oxidation reactions. Among the latter, those in which the oxidant employed is not oxygen (or any kind of other traditional oxidant, for example, hydrogen peroxide) but protons (hydronium cations), present in water or in mixed aqueous organic media, have attracted special attention. Simultaneously with the oxidation of organic compounds, such processes involve the reduction of water or other proton-containing compounds to molecular hydrogen. A reaction of this kind frequently represents stoichiometrically the dehydrogenation of organic compounds. For example, in the very first study of this topic,[90] the process

$$C_2H_5OH \xrightarrow[VCl_3]{h\nu} CH_3CHO + H_2, \qquad (1)$$

which is equivalent to the dehydrogenation of alcohol to acetaldehyde, was described. Unfortunately the occurrence of processes with photocatalysts of the type indicated requires as a rule UV light, the proportion of which in the solar spectrum is very small. The photocatalytic generation of hydrogen with the aid of such complexes from water and other readily available hydrogen-containing and/or electron-donating compounds, which is attractive from the standpoint of the utilisation of solar energy, is hardly promising for practical application.

The difference between the mechanisms of the reactions under discussion is significant. Thus in the reactions of the first group, described in the previous Section, the primary photochemical processes are as a rule either intramolecular transformations of substrates coordinated to the photocatalyst or photodissociation with formation of a coordinatively unsaturated species responsible for the catalytic activity. On the other hand, the primary chemical step in reactions of the second group is electron phototransfer from the metal ion or to the metal ion. Here the second reactant may be the ligand of the initial complex or directly the substrate present in the first or second coordination sphere. The detailed mechanism of primary photoprocesses of this kind has been investigated in detail[102–112] in relation to iron(III) and copper(II) chloride complexes. In the presence of an organic substrate, whose concentration is sufficient to ensure the presence of substrate

Table 2. Inner-sphere photocatalytic reactions with participation of metal complexes with simple inorganic ligands.

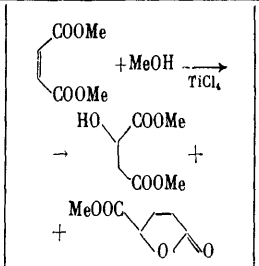
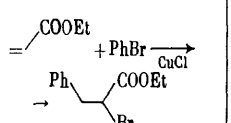
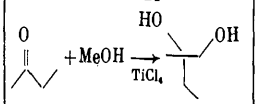
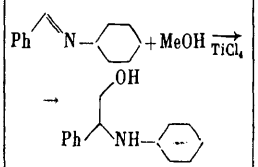
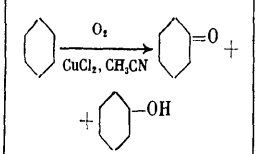
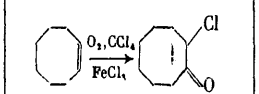
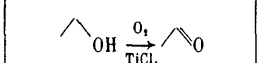
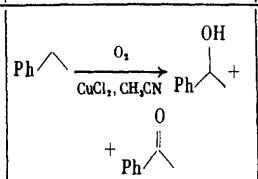
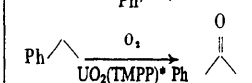
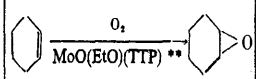
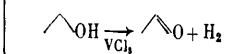
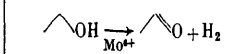
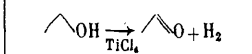
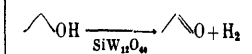
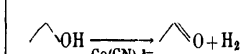
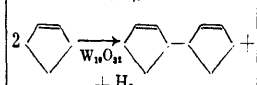
Type of reaction	Examples	Mechanism	Comments	References
Addition to C=C bond		PC	Similar reactions occur in the presence of $UOCl_2$	[77]
		PC		[78]
Addition to C=X bonds		PC		[13, 77, 79–81]
		PC		[77]
Oxidation of alkanes		PC		[82]
	$C_2H_6 \xrightarrow[Hg^{2+}]{O_2} CO_2$ (main product)	PC in the first stage, noncatalytic photochemical reaction (λ_{irr} = 254 nm) in subsequent stages		[83]
	$CH_4 \xrightarrow[\text{polyoxotungstates}]{O_2} HCHO + HCOOH$	PC	CO_2 is hardly formed	[84]
Oxidation of alkenes		PC		[85]
Oxidation of alcohols		PC	$\varphi \simeq 5-7$ as a consequence of chain initiation of the oxidation process	[86]
Oxidation of arenes and alkylarenes	$PhCH_3 \xrightarrow[FeCl_3]{O_2} PhCH_2OOH$	PC		[81]
	Alizarin S $\xrightarrow[Co(NH_3)_5Br]{H_2O_2}$ colourless oxidation products	PG		[87]

Table 2 (cont'd).

Type of reaction	Examples	Mechanism	Comments	References
		PC		[82]
		PC		[88]
Epoxidation		PG(?)		[89]
Evolution of hydrogen		PC	Aqueous ethanol solution	[90, 13]
		PC		[91]
		PC		[92]
		PC		[93, 94]
	$H_2O + CN^- \xrightarrow[Co(CN)_5^{3-}]{} {}^1/_2 H_2 +$ $+ OH^- + CN^-$ oxidation products	PC		[95]
		PC		[96]
		PC		[97]
	$H_2O + SO_3^{2-} \xrightarrow[CuCl_2]{} H_2 + SO_4^{2-}$	PC	The presence of I^- as cocatalyst is necessary	[98, 99]
Decomposition of hydrogen peroxide	$H_2O_2 \xrightarrow[Cu^{2+}_{aq}]{} H_2O + {}^1/_2O_2$	CPCR***		[100, 101]
	Ditto in the presence of Fe(EDTA)	CPCR***		[101, 102]

* TMPP = 5,10,15,20-tetrakis(4-methoxyphenyl)porphinate.
** TTP = 5,10,15,20-tetrakis(4-tolyl)porphinate.
*** CPCR = catalysis of photochemical reaction; see also the footnotes to Table 1.

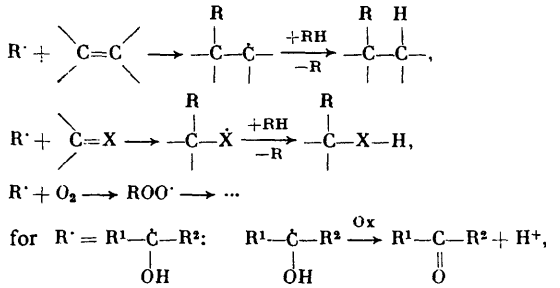
molecules in the second coordination sphere, the following processes take place in the system:

$$MCl_n \xrightarrow[CTLM]{h\nu} {}^*MCl_n$$

$${}^*MCl_n + RH \rightarrow M^-Cl_n \ldots R^{\cdot} + H^+,$$

$$M^-Cl_n \ldots R^{\cdot} \rightarrow M^-Cl_n + R^{\cdot}.$$

The organic radical $R^{\cdot}$ can enter into a wide variety of reactions which depend on the structure of the radical itself and on the presence in solution of other organic compounds, for example:[26]



for $R^{\cdot} = R^1-\dot{C}(OH)-R^2$: $R^1-\dot{C}(OH)-R^2 \xrightarrow{Ox} R^1-C(=O)-R^2 + H^+$,

for $R^{\cdot} = R^1COO^{\cdot}$: $R^1COO^{\cdot} \rightarrow (R^1)^{\cdot} + CO_2$.

The completion of the photocatalytic cycle requires the return of the metal ion to the initial oxidation state. In the example presented, this can be achieved either by the "dark" (thermal) oxidation of the reduced metal ion by a sufficiently strong oxidant, for example:

$$M^-Cl_n + O_2 \rightarrow MCl_n + O_2^-,$$

or photochemically. In the latter case, it is possible to use extremely weak or kinetically inert oxidants:

$$M^-Cl_n + RH \xrightarrow{h\nu} MCl_n + R^- + H^{\cdot}.$$

Thus the most important common feature of photocatalytic reactions of the second group is their free-radical mechanism.

In conclusion, we shall attempt to make a prediction of the development of studies in the given field of photocatalysis. Firstly, this will undoubtedly be the search for new types of reactions capable of being effected under photocatalytic conditions. It is extremely likely that such search will lead to the creation of commercially interesting photocatalytic syntheses. Secondly, one may expect a general increase in the quality of the photochemical aspect of the research into photocatalytic processes, for which an urgent need exists. The point is that, among the large total number of publications on the field under discussion, the proportion of studies carried out at a satisfactory photochemical level is relatively small. This is apparently due to the fact that the majority of studies have been performed by specialists in the field of traditional catalysis and not by photochemists. In many of the published investigations, the experiment consisted merely in the irradiation of the catalytic system by light for a fixed time with subsequent analysis of the final products. By no means all the investigations involve the measurement of the quantum yields of the products. So far the only examples remain those where the reaction mechanisms were investigated by the technique of flash photolysis, which makes it possible to identify the intermediates in photochemical reactions (among these studies, mention should be made of Refs. 47, 50, 59, 113, 114). Thus further progress in this field of photocatalysis requires the joint efforts of specialists in catalysis and photochemists.

2. Outer-sphere photocatalytic reactions

The reactions proceeding via Scheme (3a) or via analogous schemes in which the primary step in the outer-sphere biomolecular stage of the electron transfer are described in this Section. At first sight, these reactions have no specific features which would distinguish them from processes initiated by non-metal complex compounds (for example, organic dyes). However, the transition metal complexes widely used in such reactions [the most popular among them is $Ru(bipy)_3^{2+}$, where bipy = 2,2′-bipyridyl] exhibit an important difference from the organic dyes mentioned above despite the similarity of their photophysical, photochemical, and electrochemical characteristics. The point is that the catalytic cycle in Scheme (IIIa) includes the products of the one-electron oxidation (reduction) of the photocatalyst. In the case of organic dyes, such products are organic radical-cations or radical-anions, which are known to enter extremely readily into fact disproportionation, nucleophilic or electrophilic addition or substitution, etc. reactions.[115] This greatly restricts the range of reactions (and their conditions) in which the K^+ and K^- species can participate. On the other hand, in transition metal complexes, usually the metal ion itself undergoes oxidation-reduction. As a result of this, many transition metal complexes can exist in two, three, or even more forms differing in the oxidation state. The transitions between these forms are usually characterised by a high degree of reversibility.

As mentioned above, the initiation of oxidation-reduction reactions by photocatalysts becomes possible by virtue of the significant difference between the oxidation-reduction properties of the complex in the excited state and its properties in the initial state. In principle, these differences arise not only in a charge transfer transition but also in any other types of excitation (intraligand transitions, $d-d$ transitions, etc.). The predominant involvement of precisely the CT-excited states in oxidation-reduction reactions is mainly due to kinetic factors which are favoured by the corresponding redistribution of electron density on excitation of the complex. The formal oxidation-reduction potentials (ORP) of the excited state of the photocatalytic complex can be estimated knowing the formal oxidation-reduction potential of its ground state and the electronic excitation energy. For example, the electrochemical oxidation and reduction potentials of the complex $Ru(bipy)_3^{2+}$ are -1.28 and $+1.26$ V relative to the normal hydrogen electrode (NHE) respectively.[116] The energy of the longest-lived and chemically most reactive excited state of this complex, determined from the position of the luminescence band, is 2.12 eV.[116] Consequently the formal electrochemical oxidation and reduction potentials of ${}^*Ru(bipy)_3^{2+}$ are $-1.28 + 2.12 = 0.84$ V and $+1.26 - 2.12 = -0.86$ V respectively. Thus the complex, which is extremely inert in the ground state, becomes a powerful oxidant and reductant simultaneously as a result of excitation.

It is also important to emphasise that the photocatalytic oxidation-reduction reactions via the outer-sphere mechanism are frequently induced, in contrast to the processes described above, under the influence of visible and not UV light. This permits the employment of sunlight, which increases the interest in processes of this kind.

(a) Photochemical decomposition of water

Among the outer-sphere oxidation-reduction photocatalytic reactions, the reaction involving the decomposition of water into hydrogen and oxygen has undoubtedly attracted most attention:

$$2H_2O \xrightarrow{h\nu\ K} 2H_2 + O_2.$$

Numerous review articles (see, for example, Refs. 14–21 and the literature quoted therein) have been devoted to the discussion of this process. The photocatalytic decomposition of water can be described by Scheme (IIIa), where the role of the substrates S and R is assumed by the same substance (H_2O). The decomposition of water under the influence of light is a functional analogue of the natural photosynthesis in green plants with the sole difference that the place of the extremely complex process involving the reduction of CO_2 to carbohydrates is taken in this instance by the simpler reaction in which water is reduced to hydrogen. The effective occurrence of this reaction under the influence of visible light (sunlight) would be of enormous practical importance, because it would make it possible to obtain an inexhaustible source of hydrogen—an ecologically clean fuel with a high heat generating capacity. This is why the vast majority of studies on outer-sphere photocatalysis have been devoted to the decomposition of water.

The idea of creating an artificial analogue of plant photosynthesis apparently arose at the very beginning of the study of its mechanism. However, practical applications appeared only in the first half of the 1970s.[117,118] In particular, during this period the trisbipyridylruthenium(II) complex $Ru(bipy)_3^{2+}$ became the first candidate for the role of the photocatalyst of the decomposition of water.[119–121] The most important advantage of this complex is its photochemical activity when the system is acted upon by visible (green and blue) light, the reduction potential of the complex $*Ru(bipy)_3^{2+}$ in the excited state (−0.86 V) being sufficient to reduce water to hydrogen over the entire pH range, while the potential of the oxidised form $Ru(bipy)_3^{3+}$ (+1.26 V) is sufficient for the oxidation of water to oxygen, also over the entire pH range. The achievement of the following photocatalytic cycle is therefore extremely attractive:

$$Ru(bipy)_3^{2+} \xrightarrow{h\nu} *Ru(bipy)_3^{2+}, \quad (2)$$

$$*Ru(bipy)_3^{2+} + H_2O \rightarrow Ru(bipy)_3^{3+} + {}^1/_2H_2 + OH^-, \quad (3)$$

$$Ru(bipy)_3^{3+} + {}^1/_2H_2O \rightarrow Ru(bipy)_3^{2+} + {}^1/_4O_2 + H^+. \quad (4)$$

However, the operation of this scheme requires the preliminary solution of a number of serious problems. In the first place, the oxidation-reduction reactions with direct participation of $Ru(bipy)_3^{2+}$ are one-electron processes, whereas the water reduction and oxidation reactions are respectively two- and four-electron processes. Therefore the formation of the molecular water decomposition products requires the use of additional catalysts. Furthermore, the chemically reactive excited state $*Ru(bipy)_3^{2+}$ is short-lived (620 ns in water at 298 K) and is evidently incapable of participating directly in the catalytic reaction (3). As a consequence of this, the use of an intermediate electron acceptor and the inclusion in the photocatalytic cycle of "auxiliary" reactions with an intermediate electron acceptor A, instead of reaction (3), is inevitable:

$$*Ru(bipy)_3^{2+} + A \rightarrow Ru(bipy)_3^{3+} + A^-, \quad (5)$$

$$A^- + H_2O \rightarrow A + {}^1/_2H_2 + OH^-. \quad (6)$$

An alternative version involves the use of an intermediate electron donor D:

$$*Ru(bipy)_3^{2+} + D \rightarrow Ru(bipy)_3^{+} + D^+, \quad (7)$$

and the introduction of the stages

$$D^+ + H_2O \rightarrow D + {}^1/_4O_2 + H^+, \quad (8)$$

instead of reaction (4). The inclusion of the additional stages (5)–(8) leads to energy losses, which in practice means a narrowing of the pH range in which the reduction (or oxidation) of water is possible. Finally, the main problem consists in the high probability of the recombination of powerful reductants [$*Ru(bipy)_3^{2+}$, A^-, etc.] and powerful oxidants [$Ru(bipy)_3^{3+}$, D^+, etc.], formed as a result of the absorption of light and the occurrence of primary photochemical reactions. In order to solve these problems, studies on the individual stages of the above hypothetical scheme (2)–(8) and their optimisation have been prosecuted since the second half of the 1970s (Table 3).

Photocatalytic reduction of water to hydrogen at the expense of the oxidation of an irreversibly consumed electron donor (usually an organic compound) which is "sacrificed". The communication describing reaction (1) under the influence of UV light[90] was followed by the appearance of a publication[122] by the same authors in which organic dyes sensitive to visible light were used as photocatalysts. After this, systems based on $Ru(bipy)_3^{2+}$ were proposed in a whole series of communications.[123–129] The use of other metal complexes as photocatalysts is also known, among which the most interesting are structural analogues of chlorophyll—metalloporphyrins.[145]

Photocatalytic oxidation of water to oxygen at the expense of the reduction of an irreversibly consumed electron acceptor, which is "sacrificed". This reaction was achieved for the first time in systems, which were in fact based on $Ru(bipy)_3^{2+}$,[130–133] although examples of its occurrence with participation of metalloporphyrins are also known.[146,147]

Processes involving the separation in space and stabilisation of strong one-electron reductants and oxidants, generated under the influence of light, in microheterogeneous stucturally organised systems. The occurrence of such processes makes it possible to prevent the recombination of the primary photogenerated species by direct collisions. Among systems used to carry out processes of this group, the most promising are believed to be lipid vesicles.[148–151] The first advances were achieved using natural and synthetic porphyrins.[152–155] Subsequently much more effective systems based on $Ru(bipy)_3^{2+}$ and its derivatives were proposed.[156–160]

The coupling of all three fragments of the water photochemical decomposition mechanism, which follows logically from studies carried out the first stage of the research, proved extremely difficult. Although examples of the simultaneous photocatalytic generation of both hydrogen and oxygen in suspensions of lipid vesicles are known,[161] there are as yet no experimental data indicating the complete coupling of all three stages. The results of studies of the possibility of the coupling of the processes involving the reduction of water to hydrogen with photochemical charge separation processes in microheterogeneous systems via the phototransfer of an electron through the bilayer membranes of lipid vesicles are hopeful.[162,163] On the other hand, the attempts to couple the water oxidation reaction to the transmembrane charge separation in such systems have encountered appreciable difficulties.[164] Thus the complete water photodecomposition cycle has so far unfortunately not been achieved owing to the existence of a whole series of serious unsolved problems. The present state and prospects of studies in this field are discussed in a monograph.[21]

(b) Photochemical reduction of CO_2

Another problem solved mainly within the framework of outer-sphere catalysis and also associated with the modelling of photosynthesis is that of the photochemical reduction of carbon dioxide. Hitherto, it has been possible to create chemical analogues of bacterial photosynthesis having achieved the reduction of CO_2 at the expense of the oxidation of irreversibly consumed organic compounds (electron donors). The reaction usually proceeds via the mechanisms

$$*Ru(bipy)_3^{2+} + D \rightarrow Ru(bipy)_3^{+} + D^{+}.$$

$$2Ru(bipy)_3^{+} + CO_2 + H_2O \xrightarrow[cat.]{} 2Ru(bipy)_3^{2+} + HCOO^{-} + OH^{-}$$

(or other CO_2 reduction products, for example CO, CH_4, etc.)

$$D + \rightarrow \text{oxidation products};$$

or

$$*Ru(bipy)_3^{2+} + A \rightarrow Ru(bipy)_3^{3+} + A^{-},$$

$$2A^{-} + CO_2 + H_2O \xrightarrow[cat.]{} 2A + HCOO^{-} + OH^{-},$$

$$*Ru(bipy)_3^{3+} + D \rightarrow Ru(bipy)_3^{2+} + D^{+}.$$

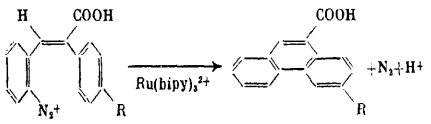
$$D^{+} \rightarrow \text{oxidation products}.$$

Evidently, the photocatalytic CO_2 reduction cycle is virtually identical with the corresponding mechanisms of the evolution of hydrogen from water in "sacrificial" systems. Therefore, in proton-containing media, the usual obstacle to the successful occurrence of the dark stage of the reduction of CO_2 is the occurrence of the competing water reduction reaction. Nevertheless, by selecting the reaction conditions, the CO_2 reduction catalysts, and intermediate electron transferring agents, it has been possible to solve the problem successfully in many instances (Table 3).

(c) Other reactions

In principle, many other chemical reactions requiring the involvement of one-electron oxidants or reductants can proceed via Scheme (IIIa). Thus a system has been proposed in which the hydrogenation and hydroformylation of ethylene and acetylene take place in the presence of $Ru(bipy)_3^{2+}$ and a water-soluble analogue of Wilkinson's complex.[140] A number of photocatalytic reactions described have some kind of bearing on biology. For example, certain enzymic processes (the synthesis of aminoacids and other organic acids by amination or insertion of CO_2), occurring under the influence of NADPH (reduced nicotinamide-adenine dinucleotide phosphate) as the reductant, have been achieved, the reductant being regenerated in the photocatalytic cycle with participation of $Ru(bipy)_3^{2+}$.[141–143] Studies on these lines are apparently promising as regards the development of photocatalytic small-scale syntheses of valuable organic products, biologically active substances, medicinal drugs, etc. Such syntheses may become an alternative to biotechnological industrial processes, particularly if it should become possible to find stable, relatively non-toxic, and relatively cheap compounds to replace enzymes and other substances of biological origin.

Table 3. Outer-sphere photocatalytic reactions with participation of $Ru(bipy)_3^{2+}$ and related compounds.

Reaction	Scheme*	References
Reduction of water	$H_2O + Red \xrightarrow[MV^{2+},\ cat._{H_2}]{Ru(bipy)_3^{2+}} {}^1/_2H_2 + OH^- + Red$ oxidation products	[123–129]
Oxidation of water	${}^1/_2H_2O + Ox \xrightarrow[cat._{O_2}]{Ru(bipy)_3^{2+}} {}^1/_4O_2 + H^+ + Ox$ reduction products	[130–133]
Reduction of CO_2	All the reactions presented below take place in the presence of $Ru(bipy)_3^{2+}$	
	$CO_2 + Red \xrightarrow[MV^{2+}]{} HCOO^- + Red$ oxidation products	[134]
	$CO_2 + Red \rightarrow HCOO^- + Red$ oxidation products	[135, 136]
	$CO_2 + Red \xrightarrow[Ru(bipy)_n(CO)X]{} HCOO^- + Red$ oxidation products	[135–137]
	$CO_2 + Red \xrightarrow[Co(bipy)_3^{2+}]{} CO + Red$ oxidation products	[138]
	$CO_2 + Red \xrightarrow[MPVS,\ Ru_{cat}]{} CH_4 + Red$ oxidation products	[139]
Hydrogenation and hydroformylation	All the reactions presented below take place in aqueous solution in the presence of $Ru(bipy)_3^{2+}$ and of a water-soluble Rh(I) complex Ascorbate $\rightarrow H_2$ + dehydroascorbate C_2H_2 + ascorbate $\rightarrow H_2 + C_2H_4$ + dehydroascorbate C_2H_4 + ascorbate $\rightarrow H_2 + C_2H_6$ + dehydroascorbate $C_2H_2 + CO$ + ascorbate $\rightarrow H_2 + C_2H_5CHO$ + dehydroascorbate	[140]
Amination, carboxylation, reduction of CO_2	The reactions presented below take place in the presence of $Ru(bipy)_3^{2+}$, Red, MV^{2+} on which analogues, $NADP^+$ and the corresponding enzymes: $CH_3-CO-COOH \xrightarrow{CO_2} HOOC-CHOH-CH_2-COOH$ $HOOC-CHOH-CH_2-COOH \xrightarrow[-H_2O]{} HOOC{=}CH-COOH$ $HOOC-CH{=}CH-COOH \xrightarrow{\text{Glutamic acid}} HOOC-CHNH_2-CH_2-COOH$ $HOOC-CO-CH_2-CH_2-COOH \xrightarrow{CO_2} HOOC-CHOH-CH(COOH)-CH_2-COOH$ $CO_2 \rightarrow HCOOH$	[141–143]
Pschorr reaction		[144]

*Notation: Red = irreversibly oxidisable organic compounds (amines, sulphur-containing compounds, etc.); MV^{2+} = dication of Methyl Viologen (*N,N'*-dimethyl-4,4'-bipyridyl); $cat._{H_2}$ = finely dispersed Pt, Pd, Rh, etc.; Ox = irreversibly reducible oxidants [$Co(NH_3)_5Cl^{2+}$, $S_2O_8^{2-}$)]; $cat._{O_2}$ = RuO_2 or Co^{2+}; MPVS = zwitter-ionic Viologen [*N,N'*-di-(3-sulphonato)propyl-3,3'-dimethyl-4,4'-bipyridyl]; Rh(I) $[ClRh^{I}L_3]^{3-}$, where L = 4-sulphonatophenyl-diphenylphosphine; $NADPH^+$ = reduced nicotinamide-adenine dinucleotide phosphate.

IV. Conclusion

The brief survey of the principal types of photocatalytic reactions with participation of transition metal complexes indicates the considerable undiscovered possibilities of this field of science which has arisen at the junction between photochemistry and catalysis. The reactions considered may be of interest for the creation on their basis not only of the fairly widely discussed processes involving the transformation of solar energy but also organic synthetic processes. Speaking of the possibility and usefulness of the practical application of photocatalysis for the purpose of synthesis, one should, however, bear in mind the inevitability of using in this case artificial light sources. Since artificial light is much more expensive as a variety of energy than heat, it is necessary to have, first, an idea about the economic desirability of a particular process being carried out under photocatalytic conditions. Nevertheless, a number of advantages of photocatalytic organic synthesis may serve as a stimulus to the development of studies in the field of photocatalysis with participation of metal complexes. Thus photocatalytic reactions can occur under milder conditions than the analogous dark processes. The activity of photogenerated catalysts is not inferior and is sometimes actually superior to that of catalysts obtained by the thermal method under analogous conditions. If the reaction proceeds with an increase in free energy, then the photocatalytic procedure proves to be the only possible way of achieving it (or of increasing significantly the yield of the product). Photocatalysis can facilitate the occurrence of photochemical non-catalytic reactions. Mention should also be made of the great variety of reactions which may be achieved by the photocatalytic method and also of the advantages of light as one of the reactants (the possibility of varying its properties—intensity and wavelength—widely and smoothly). Finally, the action of light on catalytic systems, which is a convenient means of obtaining intermediate reactive species, may become an important instrument in the study of the usual thermal catalysis.

References

1. G N Schrauzer (Editor) *Transition Metals in Homogeneous Catalysis*, Dekker, New York, 1971, 415 pp
2. R Ugo (Editor) *Aspects of Homogeneous Catalysis* (Translated into Russian), Mir, Moscow, 1973, 283 pp
3. H Alper (Editor) *Transition Metal Organometallics in Organic Synthesis*, Acad. Press, New York, 1976, Vol. 1, 258 pp; 1978, Vol. 2, 188 pp
4. J K Kochi *Organometallic Mechanism and Catalysis: The Role of Reactive Intermediates in Organic Processes*, Acad. Press, New York, 1978, 623 pp
5. G Henrici-Olivé, S Olivé *Coordination Catalysis* (Translated into Russian), Mir, Moscow, 1980, 421 pp
6. C Masters *Homogeneous Transition-Metal Catalysis* (Translated into Russian), Mir, Moscow, 1983, 300 pp
7. G B Shul'pin *Organicheskie Reaktsii Kataliziruemye Kompleksami Metallov* (Organic Reactions Catalysed by Metal Complexes), Nauka, Moscow, 1988, 286 pp
8. V Balzani, V Carassiti *Photochemistry of Coordination Compounds*, Acad. Press, London, 1970, 432 pp
9. A W Adamson, P D Fleischauer (Editors) *Concepts of Inorganic Photochemistry*, Wiley Intersci., New York, 1975, 299 pp
10. G L Geoffroy, M S Wrighton *Organometallic Photochemistry*, Acad Press, New York, 1979, 335 pp
11. G L Ferraudi *Elements of Inorganic Photochemistry* Wiley Intersci., New York, 1988, 248 pp
12. *State-of-the-art Symposium on Inorganic Photochemistry*, J. Chem. Educ., 1983, Vol. 60, p. 783
13. A I Kryukov, S Ya Kuchmii *Fotokhimiya Kompleksov Perekhodnykh Metallov* (Photochemistry of Transition Metal Complexes), Naukova Dumka, Kiev, 1989, 240 pp
14. K I Zamaraev, V N Parmon *Usp. Khim.*, 1980, **49**(8) 1457 [English translation in *Russ. Chem. Rev.*, 1980(8)]
15. K I Zamaraev, V N Parmon *Usp. Khim.*, 1983, **52**(9) 1433 [English translation in *Russ. Chem. Rev.*, 1983(9)]
16. T S Dzhabiev, A E Shilov *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1980, **25** 503
17. K I Zamaraev (Editor) *Fotokataliticheskoe Preobrazovanie Solnechnoi Energii* (Photocatalytic Transformation of Solar Energy), Nauka, Novosibirsk, 1985, Vols. 1 and 2
18. M Gretzel (Editor) *Energy Resources Considered in Terms of Photochemistry and Catalysis* (Translated into Russian), Mir, Moscow, 1986, 630 pp
19. V N Parmon, K I Zamaraev *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1986, **31** 537
20. V Ya Shafirovich, A E Shilov *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1986, **31** 542
21. K I Zamaraev, V N Parmon (Editors) *Fotokataliticheskoe Preobrazovanie Solnechnoi Energii* (Photocatalytic Transformation of Solar Energy), Nauka, Novosibirsk, 1991, 360 pp
22. L V Lyashenko *Kataliz i Katalizatory*, 1985, **23** 3
23. M S Wrighton, D S Ginley, M A Schroeder, D L Morse *Pure Appl. Chem.*, 1975, **41** 671
24. H Hennig, P Thomas, R Wagener, et al. *Z. Chem.*, 1977, **17** 241
25. M S Wrighton, J L Graff, R J Kazlauskas, et al. *Pure Appl. Chem.*, 1982, **54** 161
26. R G Salomon *Tetrahedron*, 1983, **39** 485
27. M Julliard, M Chanon *Chem. Rev.*, 1983, **83** 425
28. G G Wubbels *Acc. Chem. Res.*, 1983, **16** 285
29. C Kutal *Coord. Chem. Rev.*, 1985, **64** 191
30. H Hennig, D Rehorek, R D Archer *Coord. Chem. Rev.*, 1985, **61** 11
31. H Hennig, D Rehorek *Photchemische und photokatalytische Reaktionen von Koordinationsverbindungen*, Akad. Verlag, Berlin, 1987, 164 pp
32. M Schiavello (Editor) *Photoelectrochemistry, Photocatalysis and Photoreactors: Fundamentals and Developments*, NATO ASI Ser. Ser. C., Kluwer, Netherlands, 1985, Vol. 146, 631 pp
33. M Schiavello (Editor) *Photocatalysis and Environment. Trends and Applications*, NATO ASI Ser. Ser. C., Kluwer, Netherlands, 1988, Vol. 237, 706 pp
34. M Chanon, L Eberson *Photoinduced Electron Transfer* (Edited by M A Fox, M Chanon), Elsevier, Amsterdam, 1988, Part A, p. 409
35. N Serpone, E Pelizzetti (Editor) *Photocatalysis. Fundamentals and Applications*, Wiley Intersci., New York, 1989, 650 pp
36. H Hennig, D Rehorek, R Stich, L Weber *Pure Appl. Chem.*, 1990, **62** 1489
37. P Kisch *Photocatalysis. Fundamentals and Applications* (Edited by N Serpone, E Pelizzetti), Wiley Intersci., New York, 1989, p. 1

38. F Chanon, M Chanon *Photocatalysis. Fundamentals and Applications* (Edited by N Serpone, E Pelizzetti), Wiley Intersci., New York, 1989, p. 489
39. V N Parmon *Fotokataliticheskoe Preobrazovanie Solnechnoi Energii* (Photocatalytic Transformation of Solar Energy) (Edited by K I Zamaraev, V N Parmon), Nauka, Novosibirsk, 1991, p. 7
40. *Glossary of Terms Used in Photochemistry*, Pure Appl. Chem., 1988, Vol. 60, p. 1055
41. G K Boreskov *Geterogennyi Kataliz* (Heterogeneous Catalysis), Nauka, Moscow, 1986, p. 5
42. P C Ford, A F Friedman *Photocatalysis. Fundamentals and Applications* (Edited by N Serpone, E Pelizzetti), Wiley Intersci., New York, 1989, p. 541
43. M S Wrighton, D L Morse, L Pdungsap *J. Am. Chem. Soc.*, 1975, **97** 2073
44. M S Wrighton, G S Hammond, H B Gray *Mol. Photochem.*, 1973, **5** 179
45. J Th M Evers, A Mackor *Tetrahedron Lett.*, 1978, 2321
46. F Asinger, B Fell, K Schrage *Chem. Ber.*, 1965, **98** 372
47. M Onishi, S Oishi, M Sakaguchi, et al. *Bull. Chem. Soc. Jpn.*, 1986, **59** 3925
48. A J Hubert, A Georis, R Warin, P Teyssie *J. Chem. Soc., Perkin Trans. 2*, 1972, 366
49. J L Graff, R D Sanner, M S Wrighton *J. Am. Chem. Soc.*, 1979, **101** 273
50. J C Mitchener, M S Wrighton *J. Am. Chem. Soc.*, 1981, **103** 975
51. P Crausz, F Garnier, J E Dubois *J. Am. Chem. Soc.*, 1975, **97** 437
52. T Szymanska-Buzr, J J Ziolkowski *Photochemistry and Photophysics of Coordination Compounds. Proceedings of 7th International Symposium* (Edited by H Yersin, B Vogler), Stringer, 1987, p. 259
53. D P Schwendiman, C Kutal *J. Am. Chem. Soc.*, 1977, **99** 5677
54. J Th M Evers, A Mackor *Tetrahedron Lett.*, 1978, 2317
55. R G Salomon, A Sinha *Tetrahedron Lett.*, 1978, 1367
56. J Th M Evers, A Mackor *Tetrahedron Lett.*, 1978, 821
57. M A Schroeder, M S Wrighton *J. Am. Chem. Soc.*, 1976, **98** 551
58. M S Wrighton, M A Schroeder *J. Am. Chem. Soc.*, 1987, **95** 5764
59. D A Wink, P C Ford *J. Am. Chem. Soc.*, 1987, **109** 436
60. T Sakakura, M Tanaka *Chem. Lett.*, 1987, 1113
61. T Sakakura, M Tanaka *J. Chem. Soc., Chem. Commun.*, 1987, 758
62. M J Mirbach, N Topalsavoglou, T N Phu, et al. *Chem. Ber.*, 1983, **116** 1422
63. M A Schroeder, M S Wrighton *J. Organomet. Chem.*, 1977, **128** 345
64. F Seitz, M S Wrighton *Angew. Chem., Int. Ed. Engl.*, 1988, **27** 289
65. H Schmid, P Naab, K Hayakawa *Helv. Chim. Acta*, 1978, **61** 1427
66. M J Burk, R H Crabtree, D V McGrath *J. Chem. Soc., Chem. Commun.*, 1985, 1829
67. M J Burk, R H Crabtree *J. Am. Chem. Soc.*, 1987, **109** 1829
68. T Sakakura, T Hayashi, M Tanaka *Chem. Lett.*, 1987, 859
69. J A Maguire, W T Boese, M E Goldman, A S Goldman *Coord. Chem. Rev.*, 1990, **97** 179
70. J Hawecker, J-M Lehn, R Ziessel *Helv. Chim. Acta*, 1986, **69** 1990
71. H Nagorski, M J Mirbach, M E Mirbach *J. Organomet. Chem.*, 1985, **297** 171
72. R Ziessel *J. Chem. Soc., Chem. Commun.*, 1988, 16
73. C Pac, K Miyake, T Matsuo, et al. *J. Chem. Soc., Chem. Commun.*, 1986, 1115
74. H G Alt *Angew. Chem., Int. Ed. Engl.*, 1984, **23** 766
75. U Zucchini, E Albizzatti, U Giannini *J. Organomet. Chem.*, 1971, **26** 357
76. D G H Ballard, P W van Lienden *Makromol. Chem.*, 1972, **154** 177
77. T Sato, S Yoshie, T Imamura, et al. *Bull. Chem. Soc. Jpn.*, 1977, **50** 2714
78. M Mitani, M Nakayama, K Koyama *Tetrahedron Lett.*, 1980, 4457
79. T Sato, H Kaneko, S Yamaguchi *J. Org. Chem.*, 1980, **45** 3778
80. T Sato, S Yamaguchi, H Kaneko *Tetrahedron Lett.*, 1979, 1863
81. A I Kryukov, S A Ivanitskaya *Ukr. Khim. Zh.*, 1968, **34** 3
82. G V Nizova, M M Kats, G B Shul'pin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 698
83. E S Rudakov, S A Mitchenko, N A Miroshnichenko *Kinet. Katal.*, 1987, **28** 187
84. N Z Muradov, M I Rustamov *Kinet. Katal.*, 1989, **30** 248
85. E Murayama, A Kohda, T Sato *Chem. Lett.*, 1978, 161
86. A I Kryukov, Z A Tkachenko *Dokl. Akad. Nauk SSSR*, 1972, **203** 372
87. S D Varfolomeev, S V Zaitsev, T E Vasil'eva, I V Berzin *Dokl. Akad. Nauk SSSR*, 1974, **219** 895
88. G B Shul'pin, G V Nizova *Zh. Obshch. Khim.*, 1990, **60** 2124
89. Y Matsuda, H Koshima, K Nakamura, Y Murakami *Chem. Lett.*, 1988, 625
90. B V Koryakin, T S Dzhabiev, A E Shilov *Dokl. Akad. Nauk SSSR*, 1976, **229** 128
91. T I Serdyukova, S Ya Kuchmii, A I Kryukov *Ukr. Khim. Zh.*, 1987, **53** 679
92. A I Kryukov, A V Korzhak, S Ya Kuchmii *Teor. Eksp. Khim.*, 1984, **20** 169
93. E V Savinov, S S Saidkhanov, V N Parmon, K I Zamaraev *React. Kinet. Catal. Lett.*, 1981, **17** 407
94. E N Savinov, S S Saidkhanov, V N Parmon *Kinet. Katal.*, 1983, **24** 68
95. A V Gogolev, I A Potapov, M B Rozenkevich, Yu A Sakharovskii *Kinet. Katal.*, 1980, **21** 384
96. A G Myakon'kii, E V Makhonina, M B Rozenkevich, et al. *Khim. Vys. Energii*, 1989, **23** 257
97. T Yamase, T Usami *J. Chem. Soc., Dalton Trans.*, 1983, 183
98. V N Parmon, E N Savinov, S S Saidkhanov *Zh. Fiz. Khim.*, 1984, **58**(10) 2555 [English translation in *Russ. J. Phys. Chem.*, 1984(10)]
99. USSR P. 1 092 895; *Byul. Izobret.*, 1985, (24) 270
100. J N Baxendale, J A Wilson *Trans. Faraday Soc.*, 1957, **53** 344
101. V M Berdnikov, Yu N Kozlov, A P Purmal' *Khim. Vys. Energii*, 1969, **3** 321
102. V M Berdnikov, Yu N Kozlov *Zh. Fiz. Khim.*, 1973, **47**(3) 598 [English translation in *Russ. J. Phys. Chem.*, 1973(3)]
103. Zh P Kachanova, Yu N Kozlov *Zh. Fiz. Khim.*, 1973, **47**(8) 2107 [English translation in *Russ. J. Phys. Chem.*, 1973(8)]
104. O B Kiseleva, V F Plyusnin, N M Bazhin *Khim. Vyz. Energii*, 1978, **12** 87

105. V F Plyusnin, N M Bazhin, O M Usov *Zh. Fiz. Khim.*, 1979, **53**(10) 2673 [English translation in *Russ. J. Phys. Chem.*, 1979(10)]
106. V F Plyusnin, N M Bazhin *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1980, 8
107. V F Plyusnin, N M Bazhin, O M Usov *Koord Khim.*, 1980, **6** 856
108. V F Plyusnin, N M Bazhin *Khim. Vys. Energii*, 1981, **15** 142
109. I V Khmelinskii, V F Plyusnin, M P Gritsan, N M Bazhin *Khim. Fiz.*, 1985, **4** 1666
110. N P Gritsan, V F Plyusnin, N M Bazhin *Teor. Eksp. Khim.*, 1986, **22** 39
111. V P Grivin, I V Khmelinsky, V P Plyusnin, et al. *J. Photochem. Photobiol. A: Chem.*, 1990, **51** 167
112. V P Grivin, I V Khmelinsky, V P Plyusnin *J. Photochem. Photobiol. A: Chem.*, 1990, **51** 379
113. D A Wink, P C Ford *J. Am. Chem. Soc.*, 1985, **107** 5566
114. D A Wink, P C Ford *J. Am. Chem. Soc.*, 1986, **108** 4838
115. Z V Todres *Ion-Radikaly v Organicheskom Sinteze* (Radical-Ions in Organic Synthesis), Khimiya, Moscow, 1986, 238 pp
116. K Kalyanasundaram *Coord. Chem. Rev.*, 1982, **46** 159
117. N N Semenov *Nauka i Obshchestvo* (Science and Society), Nauka, Moscow, 1983, p. 109
118. V Balzani, L Moggi, M F Manfrin, et al. *Science*, 1975, **189** 852
119. C Creutz, N Sutin *Proc. Natl. Acad. Sci. USA*, 1975, **72** 2858
120. R C Young, T J Meyer, D G Whitten *J. Am. Chem. Soc.*, 1975, **97** 4781
121. C R Rock, T J Meyer, D G Whitten *J. Am. Chem. Soc.*, 1975, **97** 2909
122. B V Koraykin, T S Dzhabiev, A E Shilov *Dokl. Akad. Nauk SSSR*, 1977, **233** 620
123. J-M Lehn, H-P Sauvage *Nouv. J. Chim.*, 1977, **1** 449
124. K Kalyanasundaram, J Kiwi, M Graetzel *Helv. Chim. Acta* 1978, **61** 2720
125. A Moradpour, E Amouyal, P Keller, H Kagan *Nouv. J. Chim.*, 1978, **2** 547
126. B Dukham, W J Dressick, T J Meyer *J. Chem. Soc., Chem. Commun.*, 1979, 381
127. P J Dalaive, B P Sullivan, T J Meyer, D G Whitten *J. Am. Chem. Soc.*, 1979, **101** 4007
128. G M Broun, B S Brunschwig, C Creutz, et al. *J. Am. Chem. Soc.*, 1979, **101** 1298
129. M Kirsch, J-M Lehn, J-P Sauvage *Helv. Chim. Acta*, 1979, **62** 1345
130. K Kalyanasundaram, M Grätzel *Angew. Chem.*, 1979, **91** 759
131. J-M Lehn, J-P Sauvage, R Ziessel *Nouv. J. Chim.*, 1979, **3** 423
132. V Ya Shafirovich, N K Khannanov, V V Strelets *Dokl. Akad. Nauk SSSR*, 1980, **250** 1197
133. N K Khannanov, V Ya Shafirovich *Dokl. Akad. Nauk SSSR*, 1981, **260** 1418
134. N Kitamura, S Tazuke *Chem. Lett.*, 1983, 1109
135. J Hawecker, J-M Lehn, R Ziessel *J. Chem. Soc., Chem. Commun.*, 1985, 56
136. J-M Lehn, R Ziessel *J. Organomet. Chem.*, 1990, **382** 157
137. H Ishida, K Tanaka, T Tanaka *Chem. Lett.*, 1987, 1035
138. R Ziessel, J Hawecker, J-M Lehn *Helv. Chim. Acta*, 1986, **69** 1065
139. H Dürr, H-P Trierweiler, I Willner, R Maidan *Nouv. J. Chim.*, 1990, **14** 317
140. I Willner, R Maidan *J. Chem. Soc., Chem. Commun.*, 1988, 876
141. I Willner, R Mandler, A Riklin *J. Chem. Soc., Chem. Commun.*, 1986, 1022
142. R Mandler, I Willner *J. Chem. Soc., Chem. Commun.*, 1986, 851
143. R Mandler, I Willner *J. Chem. Soc., Perkin Trans. 2*, 1988, 997
144. H Cano-Yelo, A Deronzier *J. Chem. Soc., Perkin Trans. 2*, 1984, 1093
145. J R Darwent, A Douglas, A Harriman, et al. *Coord. Chem. Rev.*, 1982, **44** 83
146. P Christensen, A Harriman, G Porter, P Neta *J. Chem. Soc., Faraday Trans 2*, 1984, **80** 1451
147. O V Gerasimov, S V Lymar, V N Parmon *J. Photochem. Photobiol. A: Chem.*, 1991, **56** 275
148. S V Lymar', V N Parmon *Fotokataliticheskoe Preobrazovanie Solnechnoi Energii* (Photocatalytic Transformation of Solar Energy) (Edited by K I Zamaraev), Nauka, Novosibirsk, 1985, Vol. 2, p. 186
149. K I Zamaraev, S V Lymar, M I Khramov, V N Parmon *Pure Appl. Chem.*, 1988, **60** 1039
150. V Ya Shafirovich, S V Lymar', V N Parmon, et al. *Fotokataliticheskoe Preobrazovanie Solnechnoi Energii* (Photocatalytic Transformation of Solar Energy) (Edited by K I Zamaraev, V N Parmon), Nauka, Novosibirsk, 1991, p. 18
151. S V Lymar, V N Parmon, K I Zamaraev *Topics in Current Chemistry* (Edited by J Mattay), Springer, Berlin, 1991, Vol. 159, p. 1
152. M Mangel *Biochim. Biophys. Acta*, 1976, **430** 459
153. W E Ford, G Tollin *Photochem. Photobiol.*, 1982, **35** 809
154. W E Ford, G Tollin *Photochem. Photobiol.*, 1983, **38** 441
155. S V Lymar', I M Tvetkov, V N Parmon, K I Zamaraev *Khim. Fiz.*, 1982, **1** 405
156. W E Ford, J W Otvos, M Calvin *Nature (London)*, 1978, **274** 507
157. W E Ford, J W Otvos, M Calvin *Proc. Natl. Acad. Sci. USA*, 1979, **76** 3590
158. C Laane, W E Ford, J W Otvos, M Calvin *Proc. Natl. Acad. Sci. USA*, 1981, **78** 2017
159. V N Parmon, M I Khramov, I M Tsvetkov, et al. *Kinet. Katal.*, 1983, **23** 1023
160. E E Yablonskaya, V Ya Shafirovich *Kinet. Katal.*, 1983, **23** 1022
161. N P Luneva, V E Maier, V Ya Shafirovich, A E Shilov, *Kinet. Katal.*, 1987, **28** 505
162. I M Tsvetkov, E R Buyanova, S V Lymar, V N Parmon *React. Kinet. Catal. Lett.*, 1983, **22** 159
163. K I Zamaraev, V N Parmon *Photochemical Conversion and Storage of Solar Energy* (Edited by E Pelizzetti, M Schiavello), Kluver, Netherlands, 1991, p. 393
164. I M Tsvetkov, S V Lymar', V N Parmon, K I Zamarev *Kinet. Katal.*, 1986, **27** 109

Translated from *Uspekhi Khimii* **61** 320–331 (1992) U.D.C. 66.097.3:661.898

Modern approaches to the preparation of "palladium on charcoal" catalysts

V A Semikolenov
Institute of Catalysis, Russian Academy of Sciences, Novosibirsk

ABSTRACT. **The methods of preparation of deposited palladium catalysts on carbon carriers are discussed. The characteristics of the structures of porous carbon materials, the methods for the regulation of their structural and physicochemical characteristics, the methods for the deposition of palladium on a carbon carrier, and individual stages of a catalyst preparation process are examined.**

The bibliography includes 74 references.

Contents

I.	Introduction	168
II.	The structure of carbon carriers	168
III.	Methods for the deposition of palladium on a carbon carrier	170

I. Introduction

The vigorous development of the industrial manufacture of products of organic synthesis, including monomers, dyes, medicinal preparations, biologically active substances, and various valuable semi-finished products has aroused during the last decade considerable interest among investigators in the creation of highly selective catalysts for fine organic synthesis. Pd/C catalysts have found extensive applications in the processes involved in fine organic synthesis. Such applications are based on the catalytic chemistry of palladium with its rich content, including virtually the entire range of hydrogenation, isomerisation, dehydrogenation, and hydrogenolysis processes,[1–3] as well as the wide assortment of activated charcoals with extensive porous structures and their ready availability.

The composition of these catalysts is very simple. They include only two components—metallic palladium and the carbon carrier. However, by varying the structural characteristics of the palladium (dispersity, particle shape, distribution within the carrier grain) and of the carbon carrier (grain size, porosity, specific surface), it is possible to create a large set of catalysts for a wide range of processes.[4]

Numerous patents describing the methods of preparation of Pd/C catalysts do not answer the question which physicochemical processes occur at each stage of their preparation and how these processes can be controlled.

Although the available reviews[5,6] and fundamental studies published recently[7–15] throw some light on the structure of the Pd/C catalysts, nevertheless there are as yet no reliable methods for their purposeful construction.

The development of the scientific principles governing the preparation of catalysts should help to elucidate the factors determining their properties and to devise procedures for controlling these factors. The most important characteristics of the Pd/C catalyst are as follows:

the texture of the carbon carrier;

the size and structure of the deposited palladium particles;

distribution of the palladium particles on the carrier surface.

The present review is devoted to the consideration of modern methods for the preparation of Pd/C catalysts and the analysis of processes occurring in individual stages of their preparation.

II. The structure of carbon carriers

The structure of carbon carriers and the principal procedures for their preparation have been described in monographs and reviews.[16–21] Porous carbon materials usually employed as catalyst carriers belong to the class of carbon-graphite materials consisting predominantly of sp^2-hybridised carbon atoms with a definite ordered arrangement in space (extended networks or microcrystallites).

The structure of carbon carriers is illustrated in Fig. 1. The dimensions of the graphite microcrystallites can vary in the range L_a = 0.7–10.0 nm and L_c = 0.9–6.0 nm depending on the nature of the raw material employed and the conditions in their carbonisation.[17,18] High-temperature heat treatment of carbon materials makes it possible to increase the degree of crystallinity of the carbon, i.e. to increase the parameters L_a and L_c and to diminish the interplanar spacing d_{002} to a value close to that for graphite (0.3354 nm).[18]

In the majority of carbon carriers, the carbon microcrystallites are oriented at random on the surface (Fig. 2*a*). At the same time, there exist procedures for the deliberate orientation of basal faces or end faces of microcrystallites. In particular, the deposition of pyrolytic carbon on a solid support promotes the preferential emergence onto the surface of the basal faces of the graphite microcrystallites[22–24] (Fiog. 2*b*). Pyrolysis of hydrocarbons on catalyst particles (Ni, Fe) leads to the formation of carbon fibres and in this case the end faces emerge preferentially onto the surface[25] (Fig. 2*c*).

The chemical nature of the surface groups exerts a considerable influence on the adsorption interaction of the active component with the carbon carrier. Surface oxygen groups are of greatest interest for the preparation of deposited catalysts.

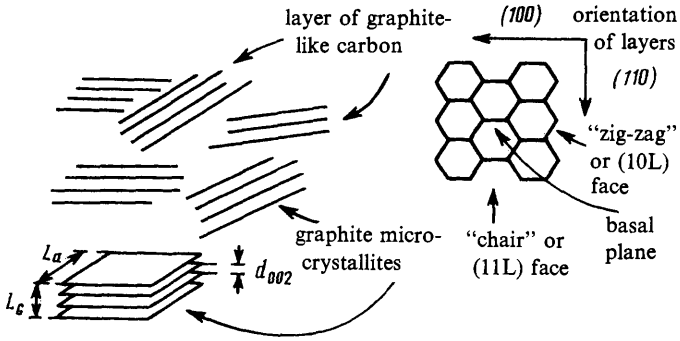


Figure 1. Schematic representation of the microstructures of carbon carriers (according to the data in Walker's book[17]).

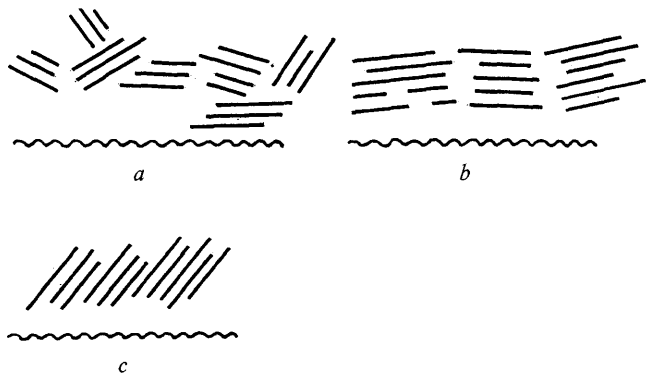


Figure 2. Orientation of graphite microcrystallites on the surfaces of carbon carriers obtained by carbonising cellulose (*a*), by the high-temperature gas-phase pyrolysis of hydrocarbons (*b*), and by the catalytic pyrolysis of hydrocarbons on transition metals (*c*),

Numerous data concerning the identification and study of the properties of such groups are available.[16,26–31] According to a classification,[28] mainly oxygen groups of four types, differing in acidity, are present on the surfaces of carbon carriers (Fig. 3).

The overall concentration of surface oxygen groups can be increased (or reduced) by heating the carbon carrier in an oxidising (or inert) atmosphere.[32] The proportions of groups of different types can be altered by selecting appropriate conditions for the treatment of the carrier and the nature of the oxidising agent.[19,33]

Basic surface oxygen groups can be formed as a result of the low-temperature chemisorption of oxygen on a carbon carrier subjected to a preliminary vacuum heat treatment.[28]

The porous structure of carbon carriers plays an important role in the transport processes involving the molecules of the reactants and reaction products.[31] According to the classification adopted by IUPAC, pores are divided into four types in terms of their dimensions:[34,35] micropores (r_{eq} < 0.6–0.7 nm); supermicropores (0.6–0.7 nm < r_{eq} < 1.5–1.6 nm); mesopores (1.5–1.6 nm < r_{eq} > 50–200 nm), and macropores (r_{eq} > 50–200 nm).

The traditional technological procedures for the preparation of porous carbon materials[18] involve the carbonisation of the initial raw materials and the activation of the carbon material. Pore-forming agents in the form of mineral additives or carbonised polymeric foam materials are used to increase the volume of the macropores.

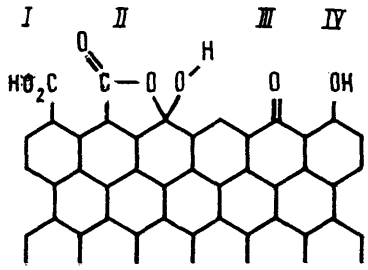


Figure 3. Types of surface oxygen groups: (I) carboxy-groups; (II) lactone groups; (III) carbonyl groups; (IV) phenolic groups.[28]

By using different kinds of carbonised raw material and by varying the parameters of its activation, it is possible to obtain a wide range of carbon carriers with an extensive system of micropores.[21,36]

Mesoporous carbon carriers, in which pores whose size is 2–10 nm predominate, can be obtained by carbonising mixtures of carbon black with a polymeric binder, for example, phenol–formaldehyde resin or furfuryl alcohol.[37]

A new class of porous materials called Sibunit has been developed for the preparation of deposited catalysts with a specified porous structure.[38,39] Sibunit is obtained by depositing a layer of pyrolytic carbon on the surface of technical carbon (Fig. 4). This results in the formation of a carbon–carbon composite material, in which the volume and size of the mesopores and macropores can be regulated by varying the dimensions of the primary globules of the technical carbon, their relative disposition, and the technical carbon/pyrolytic carbon ratio.[40,41] Activation of the composite carbon material with steam and oxygen makes it possible to increase the volume of the micropores and fine mesopores without altering significantly the size of the large pores.[42,43]

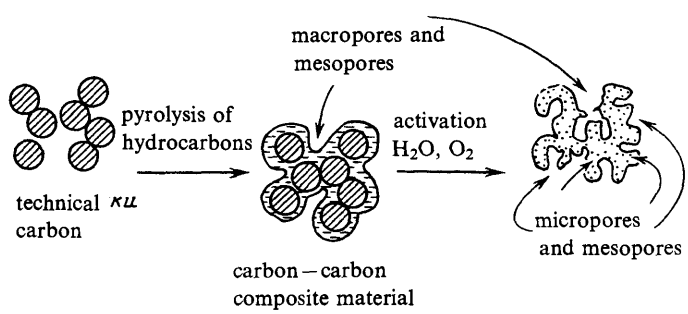


Figure 4. Schematic illustration of the formation of the porous structure of carbon carriers of the Sibunit type.

Thus there is a possibility of creating carbon carriers with specified structural and physicochemical characteristics.

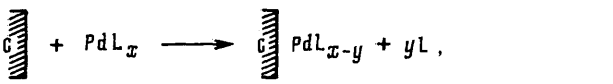
III. Methods for the deposition of palladium on a carbon carrier

In the general case, the preparation of Pd/C catalysts includes two stages—the deposition of the active component and reduction, leading to the formation of metallic palladium on the surface.

It is possible to differentiate three main procedures for the deposition of the active component.

1. Deposition of palladium compounds in the molecularly disperse state

In the general form, this method can be described schematically as follows:



where the surface of the carbon carrier is shown shaded.

Palladium compounds are fixed on the surface of the carbon carrier under these conditions by means of adsorption or chemical interaction.

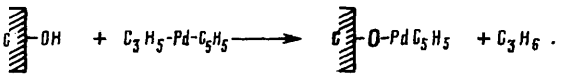
The complex PdL_x can be adsorbed as a result of the interaction of a palladium ion with the structural elements of the carrier surface. It has been shown in a number of studies[43–46] that palladium is adsorbed from solutions of its chloride complexes on the surface of the carbon carrier predominantly in the form of $PdCl_2$. On the surface of the carbon carrier, there are three types of adsorption centres: A_1, A_2, and A_3 which represent a set of surface structures containing unsaturated carbon–carbon bonds and differing in the strength of their interaction with $PdCl_2$. The centres for weak (A_1) and moderate (A_2) adsorption are located on the surfaces of mesopores and macropores, while the centres for strong adsorption (A_3) are in the micropores. The oxidation of the carrier surface by oxygen at 300 °C does not alter its adsorption properties, whilst the liquid-phase oxidation by powerful oxidants (H_2O_2, $KMnO_4$) diminishes appreciably the concentration of the above adsorption centres.[44]

The reduction with gaseous hydrogen of adsorbed palladium chloride complexes leads to the formation on the surface of the carbon carrier of metallic palladium particles, whose size ranges from 1–2 to 3.4–3.7 nm.[12] The reduced palladium particle size does not depend significantly on the volume of the micropores in the carbon carrier, but diminishes sharply after the treatment of the carrier with nitric acid,[15] which results in the formation of oxygen groups on the surface;[19,47,48] this should in turn tend to increase the palladium particle size by reducing the number of adsorption centres for palladium chloride.[44]

The increase in the dispersity of the metallic palladium as a result of the oxidation of the surface is apparently caused not by the adsorption of the chloride complexes but by the stabilisation of the metallic particles on the oxidised sections on reduction of the adsorbed compounds.

The adsorption of the palladium complexes PdL_x can proceed via the interaction of the ligands L with the surface of the carbon carrier. For example, the zerovalent palladium complex Pd_2DBA_3.DBA (where DBA = dibenzoylacetone) is adsorbed on the carbon carrier from a benzene solution. The thermal decomposition of the adsorbed complexes followed by reduction with hydrogen affords a catalyst in which the dominant metallic palladium particle size is approximately 2 nm.[49]

The chemical interaction of the active component with the carrier surface is widely used to obtain complexes fixed on the surface of oxide carriers in a molecularly disperse state.[50] This method has also been used in relation to carbon carriers.[51,52] Its essential feature is the interaction of the organopalladium compound with surface functional groups on the carrier, for example:

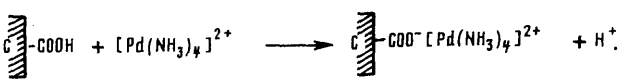


The subsequent reduction of the specimen in a stream of hydrogen leads to the formation of metallic particles on the surface having a particle size of 1–3 nm predominantly.

The chemical interaction of palladium compounds with a carbon carrier can also proceed as an oxidation-reduction process with participation of palladium(II) ions and surface groups having reducing properties (unsaturated carbon–carbon bonds, alcoholic groups, etc.).[53] This process has negative consequences, because palladium is deposited on the carrier surface in an uncontrolled fashion, giving rise to a bright film of metallic palladium. To prevent this process, palladium is deposited in the presence of oxidants: H_2O_2 [53] or Cl_2.[54]

Ion exchange on carbon carriers can also be used to prepare catalysts. The mechanism of the ion-exchange interaction between transition metal compounds and carbon adsorbents has been examined.[19,55] In the simplest case, such interaction takes place via the exchange of the acetate ligands in $Pd(OAc)_2$ for surface carboxylate groups:[56]

The reduction of surface compounds by hydrogen leads to the formation of highly disperse deposited palladium particles with an average size of ~2 nm. When this method is used, the surface concentration of carboxy-groups is important. A five-fold increase in the concentration of surface carboxy-groups after the oxidation of the initial carbon carriers with potassium permanganate diminishes the metallic palladium particle size to 1 nm. On the other hand, decarboxylation of the surface by vacuum heat treatment at 500 °C promotes the formation of large particles up to 10 nm.[56] The ion exchange method has been used most widely for the deposition of amminepalladium complexes:[12,15]

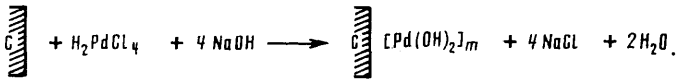


The subsequent reduction of the surface complexes in a stream of hydrogen leads to the formation of deposited palladium particles with an average size of 2.1–2.4 nm.[12] When this method is used, one should recall the significant role played by the texture and chemical composition of the carbon carrier. Thus, when palladium

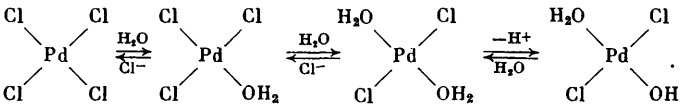
is deposited on the NORIT SXI GA 3/33 carbon carrier, the average particle size, determined from the adsorption of CO, is 48.3 nm. The activation of the initial carrier in a CO_2 atmosphere at 1200 K, involving the burning away of up to 23% of carbon which results in a decrease in the concentration of surface carboxy-groups, increases the palladium particle size to 120 nm.[14] The oxidation of the carrier surface with nitric acid (i.e. the formation of surface carboxy-groups) promotes a sharp decrease in the palladium particle size to 3 nm.[15]

2. Deposition of sparingly soluble palladium compounds

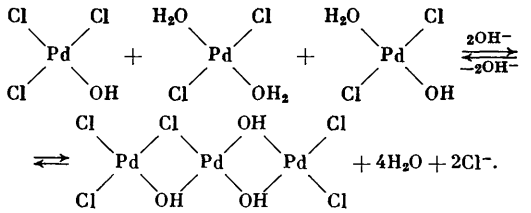
A traditional procedure for the preparation of a wide range of industrial catalysts involves the deposition of palladium hydroxide on the surface of a carbon carrier:



This method is based on the conversion of palladium chloride complexes in several stages. The first of these is the hydrolysis of H_2PdCl_4:

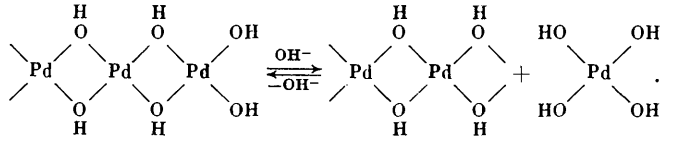


This stage is promoted by diluting the solution, by increasing the pH from 1 to 3, and by reducing the Cl^- concentration.[57-59] This is followed by the formation of a polymer:



The growth of the polymer is favoured by an increase in the concentration of palladium complexes, by an increase in pH from 3 to 8, and by a decrease in the Cl^- concentration.[59]

The polymer is degraded in a highly alkaline medium at pH > 12:



The size of the polymer molecules formed (a polynuclear hydroxo-palladium complex) can be regulated by selecting the pH, the Cl^- concentration, the temperature, and the duration of the "ageing" process.

Alkali metal hydroxides, carbonates, and bicarbonates are used for the deposition of polynuclear hydroxopalladium complexes on a carbon carrier. The Pd/C systems obtained using alkali metal carbonates and bicarbonates as the alkaline agent are the most active. Evidently this is due to the fact that pH 3–8, which is optimal for the formation of polynuclear hydroxo-complexes, is thereby established in the given instance.

When palladium is deposited on a carbon carrier, the order of the addition of the reactants can be various. When sodium carbonate is added to a suspension of activated charcoal in a chloropalladic acid solution,[60] a proportion of the palladium chloride complexes, corresponding to the adsorption capacity of the carbon carrier, is fixed on its surface via an adsorption mechanism, while the remaining palladium is deposited on the surface in the form of hydroxide particles (polynuclear hydroxo-complexes). This results in a multimodal size distribution of the palladium particles with a maximum at 2.0 nm and a plateau in the range from 6 to 16 nm.[47] When a solution of chloropalladic acid is added to a suspension of activated charcoal in a sodium bicarbonate solution,[61] the deposition takes place in a weakly alkaline buffer medium generated by sodium carbonate and the sodium form of the surface carboxylate groups of the carbon carrier.

When solutions of chloropalladic acid and the alkaline agent are added simultaneously to a suspension of the carbon carrier,[62] the deposition takes place at a constant pH 7.5–11.0, which ensures a more uniform size distribution of the palladium particles. Finally, preliminary mixing of solutions of chloropalladic acid and of the alkaline agent with subsequent deposition of the polynuclear hydroxopalladium complexes formed on the carbon carrier[15,63] makes it possible to attain a high dispersity of the palladium (2.0–3.0 nm) with a narrow size distribution of the particle.[63]

According to the mechanism of the hydrolysis of palladium chloride complexes,[59] an increase in the Cl^- concentration prevents an increase in the size of the particles of the polynuclear hydroxopalladium complexes. This may result in an increase in the dispersity of the palladium, which entails an increase in its activity. Indeed, an increase in the concentration of Cl^- during the deposition of palladium hydroxide on a carbon carrier makes it possible to increase by a factor of 1.5 the activity of the Pd/C catalyst in the hydrogenation of dinitrotoluene.[64]

3. Deposition of palladium in the form of colloidal particle sols

This method consists of two stages:

(1) the preparation of the colloidal solution (sol) of the palladium-containing compound $[Pd_c]L_x$, where L_x are ligands stabilising the colloidal palladium Pd_c particle in solution;

(2) deposition of the sol on the carbon carrier, which makes it possible to obtain catalysts with a uniform size distribution of the palladium particles and to regulate the particle size by selecting the conditions in the preparation of the colloidal solution and the palladium-containing compound:

Questions concerning the preparation of colloidal palladium solutions and the study of their properties have been surveyed in reviews.[65-68] It is possible to differentiate two main approaches to the preparation of these solutions. In one case, palladium vapour is

condensed in an inert solvent matrix. For this purpose, palladium is heated in a vacuum chamber and introduced to a stream of the inert solvent. The metal vapour formed is condensed together with the solvent on the walls of a trap cooled with liquid nitrogen. After heating the trap to the melting point of the solvent, a colloidal solution of palladium is obtained.

When methylcyclohexane is used as the solvent, the colloidal palladium solution thus obtained has an average particle size of 2.05 ± 0.5 nm and can be used to prepare deposited palladium catalysts.[65]

Another approach presupposes the reduction of palladium complexes in solution:

$$H_2PdCl_4 + xL \xrightarrow[-HCl]{Red} [Pd_c]L_x,$$

where Red is hydrogen, formaldehyde, sodium citrate, carbon monoxide, hydrazine, sodium formate, acrolein, titanium chloride, etc.[67]

The average size of the colloidal palladium particles formed in the chloropalladic acid–sodium formate–sodium hydroxide system can be regulated in the range from 47.0 to 12.5 nm by varying the pH in the range 2.1–11.2 and the duration of the reduction reaction from 1 to 180 h.

The use of sodium citrate as the reductant permits a decrease in the average palladium size to 7.5 nm.[67] Monodisperse palladium sols with an average metallic particle size from 0.9 to 7.5 nm have been obtained by reducing palladium chloride complexes with sodium citrate under an inert atmosphere at a controlled pH.[69] Pd/C catalysts in which the average metallic particle size is between 3.0 and 7.5 nm according to electron microscope data were prepared by this procedure.[70]

Table 1. The dispersity of palladium in the Pd/C catalysts prepared by different methods.

Method of deposition	Palladium compound	Average particle size, nm		References
		deposited	reduced	
Adsorption	H_2PdCl_4	Molecularly disperse state	3.4	[12]
			0.81–1.91	[15]
			1.0–2.0	[48]
	$Pd_2(DBA)_3.DBA$	Ditto	~2.0	[48]
Chemical interaction	C_5H_5–Pd–C_5H_5	»	1.0–3.0	[51]
Ion exchange	$Pd(OAc)_2$	»	~2.0	[56]
	$Pd(NH_3)_4^{2+}$	»	2.1–2.4	[12]
	$Pd(NH_3)_4^{2+}$	»	2.1–120	[15]
Deposition of sparingly soluble compounds	$Pd(OH)_2$	2.2	2.5	[71]
Deposition of palladium sol	Pd	2.5	3.0	[70]

When palladium is deposited both in the molecularly disperse state and in the form of the hydroxide or a sol, after the reduction of the catalyst the average particle size of the metallic palladium is in the range 1–3 nm (Table 1), which means that the process involving the migration of palladium during the reduction of the catalyst plays an important role in the formation of the deposited particles.

Indeed, the study of the characteristics of the reduction of deposited palladium compounds by hydrogen showed that the size and shape of the metallic particles formed depend on the concentration of palladium ions in the liquid phase.[71] The equilibrium concentration of Pd^{2+} ions in the solution over the palladium hydroxide deposited on the carbon carrier at pH ~ 7 is negligible and after reduction the size of the metallic particles corresponds to the size of the initial palladium hydroxide particles. In an acid or alkaline medium, the equilibrium Pd^{2+} concentration in the solution increases sharply by virtue of the formation of the $PdCl_4^{2-}$ or $Pd(OH)_4^{2-}$ complex. The reduction of the catalyst under these conditions leads to the formation of large palladium crystallites.[71]

The palladium reduction process can be represented in a general form by the scheme illustrated in Fig. 5, which makes it possible to explain the causes of the formation on the surface of the carbon carrier of particles of different size and with a wide variety of geometrical shapes. Thus the use of the procedures listed above leads to the possibility of the purposeful regulation of the dispersity of the deposited palladium particles.

The distribution of palladium with respect to the grain radii is one of the most important parameters determining the efficiency of granulated catalysts.[4] The traditional procedure for regulating the concentration profile of the active component are based on the diffusion of the deposited compound into the bulk of the carrier grain and its adsorption on the surface.[72,73]

The procedures for the regulation of the pore structure and chemical composition of the carbon carrier surface examined above can be used also for the selection of the optimum contributions of the processes involving the diffusion and adsorption of the deposited palladium compounds.

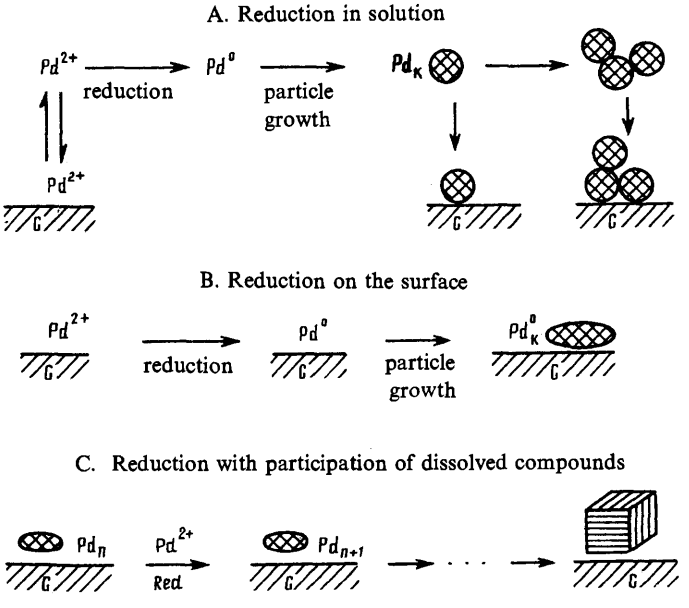


Figure 5. The formation of deposited metallic palladium particles during the reduction of the catalyst.

The preferential distribution of palladium in the outer layer of the catalyst grain can be achieved by the chemical reaction of the deposited component with the carbon carrier surface, for example, as a result of the reduction of palladium nitrate by the surface groups on the carbon carrier in an organic solvent.[74] A highly selective catalyst for the hydropurification of terephthalic acid was obtained in this way. It contained palladium particles, whose size was less than 3.5 nm and which were distributed in an outer layer of the grain up to 500 μm thick.

The deposition of palladium from colloidal solutions makes it possible to obtain crust type catalysts with a thickness of the active layer of ~50 μm.[63] Crust type catalysts can be prepared on carbon carriers with different microcrystalline structures, with pore volumes from 0.2 to 1.6 $cm^3\ g^{-1}$, mesopore and macropore sizes from 15 to 1000 nm, and specific surfaces from 10 to 1000 $m^2\ g^{-1}$.

References

1. P N Rylander *Catalytic Hydrogenation over Platinum Metals*, Acad. Press, New York–London, 1967, 550 pp
2. P M Maitlis *The Organic Chemistry of Palladium*, Acad. Press, New York, 1974, Vol. 2, 216 pp
3. H J Williams (Editor) *Catalysis in Organic Synthesis*, Acad. Press, New York–London, 1980, 314 pp
4. *Engelhard Catalysts and Precious Metal Chemical Catalog*, Engelhard Corporation, 1985, Newark, New Jersey
5. H Takidzava *Kagaku to Kogyo*, 1978, **52** 128
6. A A Krichko, M D Navalikhina *Tekhnologiya Organicheskikh Veshchestv* (Technology of Organic Substances), Izd. VINITI, Moscow, Vol. 4, p. 95 *Itogi Nauki i Tekhniki* (Advances in Science and Engineering)
7. D Pope, W L Smith, M J Eastlake, R L Moss *J. Catal.*, 1971, **22** 72
8. M Boudart, H S Hwang *J. Catal.*, 1975, **39** 44
9. T Mallat, E Polyanszky, J Petro *J. Catal.*, 1976, **44** 345
10. G Fagherazzi, G Cocco, L Schiffini, et al. *Chim. Ind. (Milan)*, 1978, **60** 892
11. M Gillet, A Renou *Surface Sci.*, 1979, **90** 91
12. A Benedetti, G Cocco, S Enzo, et al. *J. Chim. Phys.*, 1981, **78** 961
13. A Benedetti, G Cocco, S Enzo, et al. *J. Chim. Phys.*, 1981, **78** 875
14. G R Heal, L L Mkayula *Carbon*, 1988, **26** 803
15. G R Heal, L L Mkayula *Carbon*, 1988, **26** 815
16. M M Dubinin *Usp. Khim.*, 1955, **24** 518
17. P L Walker (Editor) *Chemistry and Physics of Carbon* (Translated into Russian), Mir, Moscow, 1969, 366 pp
18. G M Butyrin *Vysokoporistye Uglerodnye Materialy* (Highly Porous Carbon Materials), Khimiya, Moscow, 1976, 190 pp
19. I A Tarkovskaya *Okislennyi Ugol'* (Oxidised Coal), Naukova Dumka, Kiev, 1981, 197 pp
20. A Capelle, S de Vooys (Editors) *Activated Carbon... A Fascinating Material*, Norit, Amersfoort, 1983, 221 pp
21. K Kinoschita *Carbon, Electrochemical and Physicochemical Properties*, Wiley Intersci., Lawrence Berkeley Laboratory, Berkeley, California, 1987, 225 pp
22. A S Fialkov *Uglegrafitovye Materialy* (Carbon-Graphite Materials), Energiya, Moscow, 1979, 320 pp
23. P A Tesner *Obrazovanie Ugleroda iz Uglevodorodov Gazovoi Fazy* (The Formation of Carbon from Gas-Phase Hydrocarbons), Khimiya, Moscow, 1972, 136 pp
24. V Yu Gavrilov, V B Fenelonov, A L Chuvilin, et al. *Khimiya Tverdogo Topliva*, 1990, (2) 125
25. V I Zaikovskii, V V Chesnokov, R A Buyanov *Appl. Catal.*, 1988, **38** 41
26. H P Boehm *Adv. Catal.*, 1966, **16** 119
27. H P Boehm *Farbe und Lack*, 1973, (5) 419
28. H P Boehme, E Diehe, W Heck *Proceedings of the 2nd Conference on Industrial Carbon and Graphite*, Society of Chemical Industry, London, 1966, p. 369
29. H P Studebaker, K W D Huffman, A C Wolfe, L G Nabors *Ind. Eng. Chem.*, 1956, **48** 162
30. J B Donnet *Bull. Soc. Chim. Fr.*, 1970, 3353
31. T Van der Plas *The Structure and Properties of Adsorbents and Catalysts* (Translated into Russian), Mir, Moscow, 1973, p. 436
32. H P Boehm, G Bewer *Proceedings of the 4th Conference on Industrial Carbon and Graphite*, Society of Chemical Industry, London, 1976, p. 344
33. H P Boehm, E Diehl, W Heck, R Sappok *Angew. Chem., Int. Ed. Engl.*, 1964, **3** 669
34. M M Dubinin *Metody Issledovaniya Katalizatorov i Kataliticheskikh Reaktsii* (Methods for the Investigation of Catalysts and Catalytic Reactions), Nauka, Novosibirsk, 1971, Vol. 4, p. 37
35. *IUPAC Manual of Symbols and Terminology. Appendix 2. Part 1: Colloid and Surface Chemistry*, Pure Appl. Chem.,1972, Vol. 31, p. 578
36. T Wigmans *Carbon* 1989, **27** 13
37. US P. 4 029 600; *Chem. Abs.*, 1976, **85** 131 283
38. US P. 4 978 649
39. Yu I Yermakov, V F Surovikin, G V Plaksin, et al. *React. Kinet. Catal. Lett.*, 1987, **33** 435
40. V Yu Gavrilov, V B Fenelonov, A L Chuvilin, et al. *Khimiya Tverdogo Topliva*, 1990, (2) 125
41. G V Plaksin, V F Surovikin, V A Semikolenov, V A Likholobov *Trudy II Vsesoyuznogo Seminara po Adsorbtsii i Khromatografii Elastomerov* (Proceedings of the IInd All-Union Seminar on the Adsorption and Chromatography of Elastomers), Izd. TsNIITEneftekhim, Moscow, 1989, Vol. 1, p. 174
42. V Yu Gavrilov, V B Fenelonov, G V Plaksin, et al. *Khimiya Tverdogo Topliva*, 1990, (4) 124
43. Yu I Ermakov, V F Surovikin, V A Semikolenov *Adsorptsionnye Svoistva i Struktura Novykh Poristykh Uglerodnykh Nositelei dlya Katalizatorov* (The Adsorption Properties and Structures of New Porous Carbon Carriers for Catalysts), Moscow, 1988, 11 pp. Manuscript deposited at the TsNIITEneftekhim., 5-nkh 88
44. P A Simonov, V A Semikolenov, V A Likholobov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2719
45. P A Simonov, A L Chuvilin, V A Likholobov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1952
46. P A Simonov, E M Moroz, V A Likholobov, G V Plaksin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1478
47. N N Nemerovets, V F Surovikin, S V Orekhov, et al. *Khimiya Tverdogo Topliva*, 1980, (4) 120
48. A S Lisitsin, S V Gurevich, A L Chuvilin, et al. *React. Kinet. Catal. Lett.*, 1989, **38** 109

49. L P Gilyazetdinov, N A Silaev, S O Melamed, Yu M Stashenko *Khimiya Tverdogo Topliva*, 1978, (2) 129
50. Yu I Yermakov *J. Mol. Catal.*, 1983, **21** 35
51. Yu A Ryndin, M V Stenin, A I Boronin, et al. *Appl. Catal.*, 1989, **54** 277
52. Yu A Ryndin, O S Alekseev, P A Simonov, V A Licholobov *J. Mol. Catal.*, 1989, **55** 109
53. US P. 3 138 560
54. Polish P. 118 745; *Chem. Abs.*, 1984, **100** 13 271
55. I A Tarkovskaya, A N Tomashevskaya *Adsorbtsiya i Adsorbenty*, 1984, (12) 12
56. S V Gurewich, P A Simonov, A S Lisitsyn, et al. *React. Kinet. Catal. Lett.*, 1990, **41** 211
57. N K Pshenitsyn, S I Ginzburg *Izv. Sektora Platiny Akad. Nauk SSSR*, 1949, (2) 100
58. L F Kozin, N V Grushina, T I Saprykina *Tr. Inst. Organicheskogo Kataliza i Elektrokhimii Akad. Nauk Kazakh. SSR*, 1977, **15** 3
59. Ir R Wyatt *Chem. Week.*, 1966, **62** 310
60. US P. 3 271 327
61. USSR P. 692 618; *Byull. Izobret.*, 1979, (39) 11
62. BRD P. 2 530 759
63. V A Semikolenov, M E Boldyreva, Yu V Shmidt, A G Stepanov *J. Mol. Catal.*, 1989, **55** 415
64. US P. 2 857 337
65. J S Bradley, E Hill, M E Leonowicz, H Witzke *J. Mol. Catal.*, 1987, **41** 59
66. S C Davis, K J Klabunde *Chem. Rev.*, 1982, **82** 153
67. J Turkewich, G Kim *Science*, 1970, **169** 873
68. V A Sergeev, A Yu Vasil'kov, G V Lisichkin *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1987, **32**(1) 96
69. N A Zakarina, G D Zakumbaeva, N F Toktabaeva, et al. *React. Kinet. Catal. Lett.*, 1984, **26** 441
70. N A Zakarina, G D Zakumbaeva, N F Toktabaeva *Elektrokhimiya*, 1983, **19** 938
71. S P Lavrenko, V I Zaikovskii, V A Semikolenov *Kataliz v Neftekhimii i Neftepererabotke* (Catalysis in Petrochemistry and Petroleum Processing), Izd. Omsk. Ped. Inst., Omsk, 1990, p. 48
72. R G Vincent, R P Merrill *J. Catal.*, 1974, **35** 206
73. P Harriott *J. Catal.*, 1969, **14** 43
74. US P. 4 476 242; *Chem. Abs.*, 1989, **101** 230 150

Translated from *Uspekhi Khimii* **61** 332–355 (1992) U.D.C. 541.128.13

Mechanism of the hydrogenolysis of thiophene on bimetallic sulphide catalysts

A N Startsev
Institute of Catalysis, Siberian Division of the Russian Academy of Sciences, Novosibirsk

ABSTRACT. The structure of the sulphide bimetallic species (SBMS), which is the active component of hydrodesulphurisation catalysts, is examined. The main principles of the hydrogenolysis of thiophene on well-characterised sulphide catalysts have been analysed. A synchronous mechanism for the reaction of thiophene with hydrogen in the coordination sphere is considered and substantiated.

The bibliography contains 143 references.

Contents

I. Introduction 175
II. General principles for the hydrogenolysis of thiophene on sulphide catalysts 175
III. Structure of the active component of hydrodesulphurisation catalysts 177
IV. Reaction mechanism of the hydrogenolysis of thiophene 181
V. Conclusion 185

I. Introduction

The hydrogenolysis of the C–S bond of organosulphur compounds is one of the key reactions occurring in the hydropurification of petroleum fractions. From the volume of sulphur being refined, hydropurification processes occupy a leading place and their output is growing more rapidly than those of other petroleum refining processes at the present time. The great practical value of the hydrorefining processes for petroleum fractions explains the enhanced interest of investigators in the study of the active component of hydropurification catalysts and their mechanism of action.[1–25]

To clarify the mechanism of a catalytic reaction in a heterogeneous system is more complex than in a homogeneous system. In spite of the many possibilities which the recently developed physical methods for investigating the surfaces of solid catalysts have created, the obtaining of detailed information on the structure of active centres is hindered by the non-uniform chemical composition of the surface compounds in real heterogeneous catalysts. Some of these compounds may be generally inactive in catalysis and surface formations which differ in structure may catalyse a given chemical conversion by various routes and mechanisms. The effect of the reaction medium on the catalyst is important. One type of surface compound may be transformed into another under the conditions of a catalytic reaction at high temperatures and pressures; this may cause a change in the mechanism of the reaction being studied. The problem also arises of synthesising highly active catalysts containing surface formations of one predominant type which are responsible for carrying out just the catalytic reaction in question. A further problem is the checking of the state of the catalyst surface under reaction conditions.

As is known, all hydrorefining processes for petroleum fractions are effected on one type of catalytic system, based on a composition of Mo (or W) with Ni (or Co) as sulphides. The results of numerous original studies on the synthesis and properties of sulphide hydrodesulphurisation (HDS) catalysts, the structure of their active component and the mechanism of the catalytic action have been correlated in several reviews and monographs.[1–25] In each of the reviews, reflecting some aspects of the action of HDS catalysts, the authors form and assert their own point of view on the mechanism of action bringing in further arguments from neighbouring areas of chemistry. Nevertheless these studies are based on two main hypotheses. 1) The active component is Mo(W) and Ni(Co) plays the role of promoter. 2) The HDS reaction takes place with the participation of anionic vacant sites on the $MoS_2(WS_2)$ by an oxidation–reduction mechanism.

An attempt is made in the present review to analyse critically these hypotheses and a new mechanism is proposed for the action of HDS catalysts. This is based on studies carried out in the Institute of Catalysis, Siberian Division of the Russian Academy of Sciences, where highly active sulphide HDS catalysts have been synthesised and characterised. The catalysts were made by attaching metal complexes of Mo, W, Ni and Co to the surface of various carriers (Al_2O_3, SiO_2, and the new carbon material 'Sibunit') with subsequent decomposition of the surface compounds by H_2S.

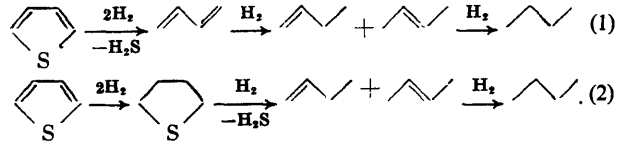
II. General principles for the hydrogenolysis of thiophene on sulphide catalysts

The hydrogenolysis reactions of thiophene and its derivatives are the slowest among the numerous reactions occurring during the hydrodesulphurisation of petroleum fractions, since the aromatic character of the thiophene ring hinders the elimination of sulphur from the molecule. Consequently the hydrogenolysis of thiophene and its derivatives is a generally accepted test for the properties of an HDS catalyst. From a scientific point of view the unsubstituted thiophene molecule is the most suitable for studying the mechanism of hydrogenolysis of the C–S bond, since substituents in the thiophene ring may have an appreciable effect on the coordination of the molecule to an active centre.

The hydropurification of crude petroleum is carried out at temperatures of 300–400 °C and H_2 pressures of 2–10 MPa.[1] The catalyst is in the sulphide state under the conditions of the

process. The inter-regeneration time of a catalyst is from several months to several years depending on the type of crude being refined and the specific consumption of a catalyst varies within the limits 15–60 g m^{-3} of crude.[26] These data indicate the high resistance of the catalysts to poisoning and becoming clogged with coke and the high thermal stability of the active component under process conditions.

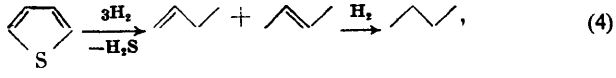
At the present time predominantly two possible routes for converting thiophene on sulphide catalysts are considered in the literature.[16]



In these cases the intermediate products are butadiene and tetrahydrothiophene (THT) respectively which are desorbed from the catalyst surface and may be detected in the gas phase. The possibility of the reaction proceeding by the following scheme may be considered as a variant of scheme (2).

$$T \rightarrow THT \rightarrow C_4H_6 + H_2S \rightarrow \text{products}, \quad (3)$$

where T is thiophene.[6] However a third route exists for the hydrogenolysis of thiophene,[27]



in which saturation of the thiophene ring and hydrogenolysis of the C–S bonds are effected at one active centre without loss of intermediates to the gas phase. This situation is effected on mono- and bimetallic sulphide catalysts both in bulk[28] and attached by various methods to SiO_2,[29] Al_2O_3 [30] and the carbon Sibunit carrier.[31] Catalysts are treated in H_2S at 400 °C before use to provide a steady level for their activity.[27–31] It was shown by special experiments[32] that the reaction route is not the consequence of the specific conditions of carrying out the process. The absence of butadiene and THT as intermediates in the hydrogenolysis of thiophene has also been recorded in other studies (see for example[33,34]), where the stationary activity of the catalysts was studied. We will return to the problem of possible routes for the conversion of thiophene after considering the reaction mechanism.

As already mentioned it is impossible to establish the mechanism of action of solid catalysts without knowing the structure of the active component. Traditional methods of preparing HDS catalysts are based on impregnating a preformed carrier with solutions of salts of the appropriate metals with subsequent drying, calcining and sulphurisation. This method does not allow a purpose-directed fixing of the composition of the active component or its immediate precursor.[35] The main reason for this is seemingly the complexity of the physicochemical conversions of the transition metals applied, including the processes of mass transfer and high temperature chemical interactions of the solid–solid type which are difficult to control.

The approach developed by Ermakov and collaborators[36,37] proved to be extremely productive when preparing catalysts with a fairly uniform content of active compounds on the surface. This comprises attachment of metal complexes of definite composition to a carrier surface and subsequently decomposing them under controlled conditions. This approach was also used for preparing highly dispersed sulphide catalysts.[29,30,38,39]

Catalysts are prepared in several stages. Initially organometallic or complex compounds of Mo or W are attached to the carrier (SiO_2 [29,38,39] or γ-Al_2O_3 [30]) and then, after appropriate treatment, Ni or Co are also applied to the Mo- or W-containing carrier in the form of organometallic or complex compounds. In several cases[30] the application of Ni(Co) was effected under conditions causing their adsorption to the Mo surface compounds. After drying, the catalysts were sulphurised in H_2S at 400 °C to provide a stationary level for their activity in the thiophene hydrogenolysis reaction.

Standard catalysts, prepared by the traditional impregnation method (ST), were studied in addition to the catalysts of metal complex (MC) origin. Among the former the greatest activity was possessed by catalysts obtained by a single impregnation (depending on the water content) of the carrier with an aqueous solution of the salts of the two metals with subsequent drying under an IR lamp, calcining in air at 500 °C and sulphurisation in H_2S at 400 °C. However the activity of standard catalysts prepared under optimum conditions was always less than the activity of samples of complex metal origin.[35]

Table 1. Specific (SCA) and atomic (ACA) activity of bimetallic sulphide catalysts in the hydrogenolysis of thiophene at 300 °C and the binding energy (E_b) of electrons at the Ni $2p_{3/2}$ level.[27–31,38–41]

Composition of and method of preparing catalysts *	SCA, mole $C_4H_4S \times 10^4$ / g.at (Ni+M).s	ACA, mole $C_4H_4S \times 10^3$ / g.at Ni.s	E_b** Ni $2p_{3/2}$, eV
0.18Ni/WS_2 (S_s = 10 m^2 g^{-1})	8.3 ***	28	853.8
0.60Ni/WS_2 (S_s = 39 m^2 g^{-1})	6.7 ***	25	854.0
(0.5Ni; 3.2W)/SiO_2 (MC)	156	48	854.0
(1.0Ni; 6.4W)/SiO_2 (ST)	50	15	–
(1.2Ni; 8.0W)/Al_2O_3 (ST)	48	16	–
(0.8Ni; 4.2W)/Sibunit (TC)	110	30	853.9
0.3Ni/MoS_2 (S_s = 9.0 m^2 g^{-1})	2.3 ***	4	853.9
(1.2Ni; 8.0Mo)/SiO_2 (MC)	89	16	853.9
(0.8Ni; 2.3Mo)/SiO_2 (ST)	30	8	–
(1.5Ni; 7.5Mo)/Al_2O_3 (MC)	103	42	854.2
(1.5Ni; 7.5Mo)/Al_2O_3 (ST)	21	9	854.0
(0.6Ni; 4.0Mo)/Sibunit (TC)	116	59	854.0

*The numbers before an element denote the content of the element in the catalyst, wt.%.

**E_b Ni $2p_{3/2}$ in α-NiS was 853.0 eV, and in $(NH_4)_2[Ni(WS_4)_2]$ was 853.8 eV.[38–41]

***Here SCA is in mole C_4H_4S m^{-2} s^{-1} × 10^8.

The specific activity of bimetallic sulphide MC catalysts applied to SiO_2 and Al_2O_3 was significantly greater than that of ST catalysts of closely similar composition (Table 1). In all cases the greatest

synergistic effect was observed at an atomic ratio Ni(Co):Mo(W) = 1:2 which corresponds with the majority of the known data.[8–14,21] The activity was reduced in the series (Ni, W) > (Ni, Mo) > (Co, Mo) > (Co, W).

Samples of similar chemical composition applied onto SiO_2 and Al_2O_3 by similar methods have approximately the same specific catalytic activity (SCA), however the SCA of catalysts applied to Sibunit is significantly greater. Possible reasons for this phenomenon will be examined in the following section.

The most characteristic feature of the reaction on all the bimetallic catalysts studied is the reduction in activation energy from 117 ± 8 kJ mol^{-1} in the temperature range 225–300 °C to 59 ± 8 kJ mol^{-1} in the range 300–400 °C (Fig. 1). Such a reduction in E_a is not a consequence of transition of the reaction into the diffusion region since it is characteristic of all catalysts independent of their pore structure and grain size, including the solid porous catalysts Ni/WS_2, Ni/MoS_2 and Co/MoS_2 which possess low specific activity.[29] Seemingly the reason must be sought in the change in the limiting stage of the reaction.

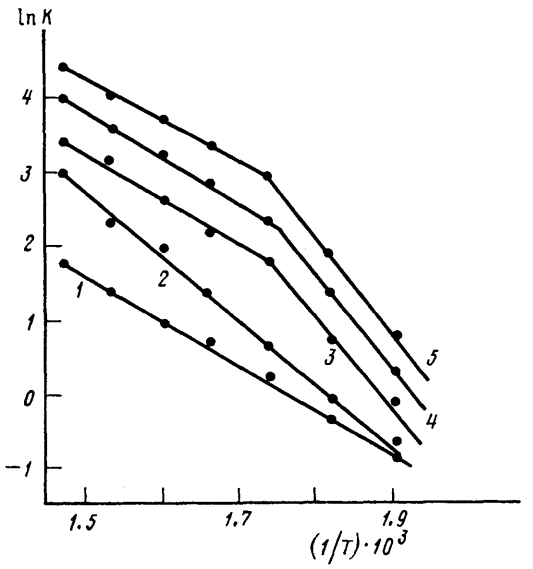


Figure 1. Temperature dependence of the reaction rate for the hydrogenolysis of thiophene on sulphide catalysts: *1*, Ni/Al_2O_3; *2*, Mo/Al_2O_3; *3*, Ni/MoS_2; *4*, $(Co-Mo)/Al_2O_3$; *5*, $(Ni-Mo)/Al_2O_3$.[29,30]

The products of the hydrogenolysis of thiophene on both mono- and bimetallic sulphide catalysts, prepared by various methods and on different carriers, contain only butene and butane in addition to H_2S.[27–31] Tetrahydrothiophene and butadiene are not present in the reaction products at the stationary level of activity of the catalysts. Trace quantities of butadiene were detected only on the most active (Ni–W) catalysts at a temperature of 400 °C and a degree of conversion of thiophene of 100%. The absence of possible intermediates from the reaction products is not a consequence of carrying it out with a large excess of hydrogen, since it was shown by special experiments[32] that a fairly high yield of THT may be obtained under the very same conditions on the very same Ni/SiO_2 and Mo/SiO_2 catalysts if, after sulphurisation, the catalysts are first reduced in H_2 at 400 °C. Significant quantities of butadiene (together with THT) were obtained under the same conditions on reduced zeolite NiY and MoY catalysts.[32]

The same principles for changing their activity in the hydrogenolysis of thiophene are characteristic of the sulphide catalysts (Ni, W), (Ni, Mo), (Co, Mo), and to a lesser extent (Co, W), applied by various methods onto Al_2O_3, SiO_2 and Sibunit. This indicates that the nature of the active component does not depend on the carrier type and method of preparation which affects only the level of activity of the catalysts. This inference does not pretend to be original, analysis of the vast scientific data on this problem leads readily to an analogous conclusion.

III. Structure of the active component of hydrodesulphurisation catalysts

The emergence at the beginning of the seventies of new methods of investigating the surface of a solid catalyst permitted an intensive study of the structure of the active component of HDS catalysts. According to the current classification,[20] 12 different models of the structure of the active component have appeared in the literature as ideas on the mechanism of action of the HDS catalysts have developed. The "Co–Mo–S phase" model is seemingly the most widespread[17,19,42–46] and was initially based on the results of an investigation of catalysts by Mössbauer emission spectroscopy and was then confirmed by the EXAFS method.

According to the "Co–Mo–S phase" model the active component is crystallised in the structural type of MoS_2, on a side face of a single patch of which Co atoms are localised. Other authors have subsequently arrived at a similar conclusion.[47–51] Though the similarity of the "Co–Mo–S phase" and MoS_2 structures is not in doubt there is no single opinion regarding the place of localisation of Co.

Substantially similar results on the structure of the active component of HDS catalysts were obtained in the Institute of Catalysis when studying the properties of highly active catalysts with a fairly uniform composition of surface compounds. A model for the structure of the active component was developed on the basis of the data obtained and was given the name sulphide bimetallic species (SBMS). The characteristic traits of this model will be examined.

1. Morphology of the surface of applied sulphide catalysts

The extended development of high resolution transmission electron microscopy (HRTEM) has enabled the limit of resolving ability of the electron microscope to be reached.[52] This method is used widely for studying the surface of applied catalysts containing ultradisperse particles of size less then 10 Å. On investigating HDS sulphide catalysts by the HRTEM method different authors obtained good agreement between their results.[31,53–58] When using various carriers (Al_2O_3, SiO_2, Sibunit, carbon) to obtain the catalysts, structures morphologically of a single type were detected on their surface irrespective of the method of preparation, the particle surface structure being characteristic of bulk MoS_2 and WS_2. The linear dimensions of the particles may vary within wide limits depending on the type of carrier and the method of preparing the catalyst. In the most disperse catalysts particles of size no greater then 20–25 Å

predominate,[56] but both finer (less than 10 Å) and more coarse (40–50 Å) particles may also be found on the surface.

In the majority of cases the active component is represented as single patches of $MoS_2(WS_2)$ the stabilisation of which is effected by abutting either the basal surface or the side face of the carrier. Well regulated structures which might be ascribed to Ni or Co sulphides were not detected in highly active catalysts. The reasons for the stabilisation of the highly disperse particles on the carrier surface will be examined.

Table 2. Structural characteristics of the carriers used for preparing sulphide HDS catalysts.[31,59,60]

Carrier	SiO_2	Sibunit	γ-Al_2O_3 *
Structure	Amorphous, chains of SiO_4 tetrahedra	Amorphous, flaky hexagonal	Cubic densely packed
Crystalline analogue	Tridymite, crystabolite	Graphite	Spinel $MgAl_2O_4$
Interatomic distances, Å	Si(1)–O(1)=1.6; Si(1)–Si(2)= =O(1)–O(2)=3.2; O(1)–O(1)=2.7; Si(1)–O(2)=4.0	d_{002}=3.356 C–C=1.42	Al_O–Al_O=O–O=2.79 Al_O–O=1.98; Al_T–O=1.71; Al_T–Al_T=3.42; Al_T–Al_O=3.29; O–O=3.95, 4.83

*Al_O and Al_T are aluminium atoms in spinel which occupy octahedral and tetrahedral positions respectively.

Table 3. Structural characteristics of Mo, W and Ni sulphides.[61]

Sulphide	MoS_2	WS_2	NiS
Structure	Flaky hexagonal	Flaky hexagonal	Very dense hexagonal
Structural type	Molybdenite MoS_2	Molybdenite MoS_2	Arsenide NiAs
Unit cell parameters, Å	a=3.16; c=12.395	a=3.187; c=12.52	a=3.427; c=5.31
Interatomic distances, Å	Mo–Mo=S–S=3.16; Mo–S=2.35; S–S=2.96 (patch thickness)	W–W=S–S=3.187; W–S=2.48; S–S=3.33 (patch thickness)	Ni–Ni=S–S=2.65; Ni–S=2.38

The structural characteristics shown in Tables 2 and 3 for sulphides and carriers indicate the closeness of the structures of $MoS_2(WS_2)$ and Sibunit. They belong to the same space group and crystallise in laminated hexagonal structures, the interplanar distances in Sibunit are close to the thickness of a single patch of $MoS_2(WS_2)$. Such a close similarity of structural types and interatomic distances assumes a possible epitaxial interaction of both the basal plane and the side faces. This picture was also observed in the electron microscopic prints. Single patches of the active component are disposed along the edges of the carbon carrier repeating its profile.[31] Evidently the oriented accretion of the active component on the Sibunit surface provides a limiting dispersity for the catalysts even when preparing them by the impregnation method and, as a result, a high activity in the thiophene hydrogenolysis reaction (see Table 1).

A closely similar picture is observed in the case of sulphide catalysts applied to SiO_2 using metal-complex precursors. In amorphous SiO_2 the SiO_4 tetrahedra are joined to one another by the apices in continuous chains which, interlinking with one another, form predominantly 6-membered units.[60] The interatomic O–O distances in the space lattice formed in this way are close to the S–S distance in the $MoS_2(WS_2)$ structure. Consequently on decomposing the surface metal complex in an atmosphere of H_2S the structure of an $MoS_2(WS_2)$ packet may be formed without fission of the Si–O–M chemical bond formed at the stage of applying the metal complexes. In this case also an epitaxial reaction of carrier and active component is therefore possible.

A different picture is seen for catalysts applied to γ-Al_2O_3. In spite of the absence of a geometric correspondence between the carrier structure and the structure of $MoS_2(WS_2)$, it is nevertheless possible to obtain highly dispersed sulphide particles which are thermally very stable and do not cake under the conditions of the catalytic process. Evidently for stabilisation of the highly disperse state it is sufficient either to interact the basal planes of the active component with the surface by Van der Waals forces or to form a relatively small number of bonds of the Al–S–M type between the side face of the active component and the surface of the Al_2O_3.[56]

Comparison of the particle sizes of the active component on the surface of SiO_2 and Al_2O_3 in catalysts prepared by various methods enabled the following conclusions to be drawn. The mean particle size in catalysts obtained on SiO_2 by impregnation was significantly greater than in MC catalysts which, together with the non-uniform composition of the surface compounds, may be one of the reasons for their comparatively low activity. On the other hand, sulphide particles in ST and MC catalysts applied to Al_2O_3 have approximately the same size,[56] consequently the lower activity of the impregnated samples may be explained either by the non-uniform composition of the sulphide particles or by the possibility of forming surface compounds during preparation which are not catalytically active. Evidently the most favourable situation arises on applying the active phase to Sibunit when highly active catalysts are successfully obtained by simple methods. In this case the geometric similarity of the structures of the carrier and the active component provide extreme dispersity for the latter and the carbon nature of the carrier enables phases inactive in catalysis to be avoided.

2. The electronic state of metals forming the active component

One of the main methods of studying the electronic state of metals in applied catalysts is X-ray photoelectron (XP) spectroscopy. The investigation of inorganic and coordination compounds of transition metals showed that the binding energy E_b of electrons in the inner levels of the central atom is a complex function of the oxidation level of the metal and the structure of its first coordination sphere.[62]

A large number of papers (see for example[55,58,63–66]) has been devoted to the study of sulphide catalysts by XP spectrometry. Most frequently the electronic state of Mo(W) in bimetal catalysts corresponds to their state in bulk $MoS_2(WS_2)$. The state of Co(Ni)

has not been assessed so unequivocally. The fact is that after sulphurisation of the impregnated catalysts the lines for Ni 2*p* and Co 2*p* in the XP spectra were markedly broadened, which is most probably linked with the presence of a certain quantity of Ni(Co) ions in the oxygen environment.[55,58,63,64,66] Consequently no changes of E_b were detected, compared to binary sulphide catalysts, for Ni $2p_{3/2}$ and Co $2p_{3/2}$ in bimetallic sulphide catalysts. At the same time a significant increase in E_b was noted for electrons of these levels in some studies,[31,40,64,65] while lines for Ni 2*p* and Co 2*p* in the spectra of MC catalysts were fairly sharp with a symmetrical maximum (Fig. 2), which indicates a similar environment for Co and Ni. The presence of an additional peak in the spectra of impregnated catalysts at a larger E_b shows that a certain quantity of Ni(Co) ions are in an oxygen environment.

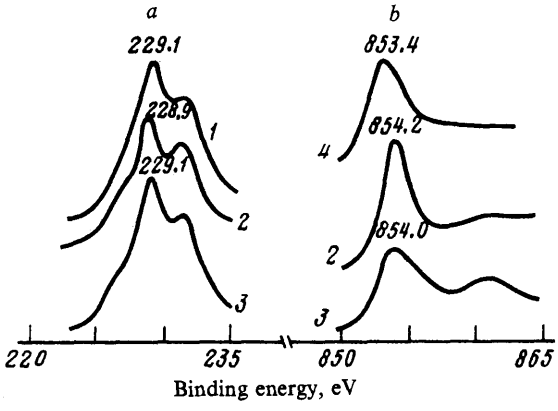


Figure 2. Profile of the *a*, Mo 3*d* and *b*, Ni 2*p* lines in the XP spectra of sulphide catalysts;[41] *1*, 4.5 Mo/Al_2O_3 (CM); *2*, (1.5 Ni, 4.5 Mo)/Al_2O_3 (CM); *3*, (1.2 Ni, 6.0 Mo)/Al_2O_3 (TC); *4*, 1.7 Ni/Al_2O_3 (CM).

The significant increase in E_b for Ni 2*p* and Co 2*p* in bimetallic catalysts in comparison with solid binary and applied sulphides (Table 1) was interpreted by us as a reduction in electron density on the Ni or Co atoms as a result of forming a new chemical compound, a SBMS, in which the Ni(Co) atoms are localised in the side face of $MoS_2(WS_2)$.[27,31,40] From the principles governing the change in E_b it is possible to assign a formal charge of +4 to this Ni(Co) atom. Closely similar values of E_b for Ni $2p_{3/2}$ are obtained for the $[Ni(WS_4)_2]^{2-}$ anion,[40,65] in which the Ni is in the centre of a square plane of S atoms.

3. Structure of dispersed particles of $MoS_2(WS_2)$ and the principle of the electrical neutrality of the molecule

As already mentioned above, the necessary structural unit on which the hydrogenolysis of thiophene can occur is a single patch of $MoS_2(WS_2)$ the linear size of which may vary from a few to several tens of angstroms. We now examine the structure of these highly disperse particles form the viewpoint of the principle of the electrical neutrality of the molecule. In the $(MoS_2)_x$ macromolecule all the valence bonds must be saturated when preserving the MoS_2 stoichiometry without changing the level of oxidation of Mo^{4+} and S^{2-}. In other words, in a macromolecule of any size the quantity of positive charges on the molybdenum atoms must be equal to the quantity of negative charges on the sulphur atoms. The excess (+) or (–) charges arising as a result of breaking valence bonds on the side face of a MoS_2 packet must be compensated by a corresponding quantity of charges opposite in sign. The problem of compensating the excess (–) charge on the terminal sulphur atoms was examined for the first time in 1980.[13]

The minimum structural unit determining the structure of a single MoS_2 patch is a trigonal prism made up of six S atoms in the centre of which is a Mo atom (Fig. 3). The formal excess charge of this cluster is 8 e^-, i.e. its chemical formula may be represented as $[MoS_6]^{2-}$. The macromolecule $(MoS_2)_x$ is formed by joining individual prisms along an edge, consequently a 'sandwich' is formed on joining three prisms, represented in projection from above as a regular hexagon. On the side face $(30\bar{3}0)$ of this hexagon there are two Mo atoms ($m = 2$) and on the $(0\bar{3}30)$ face one Mo atom ($n = m - 1 = 1$).

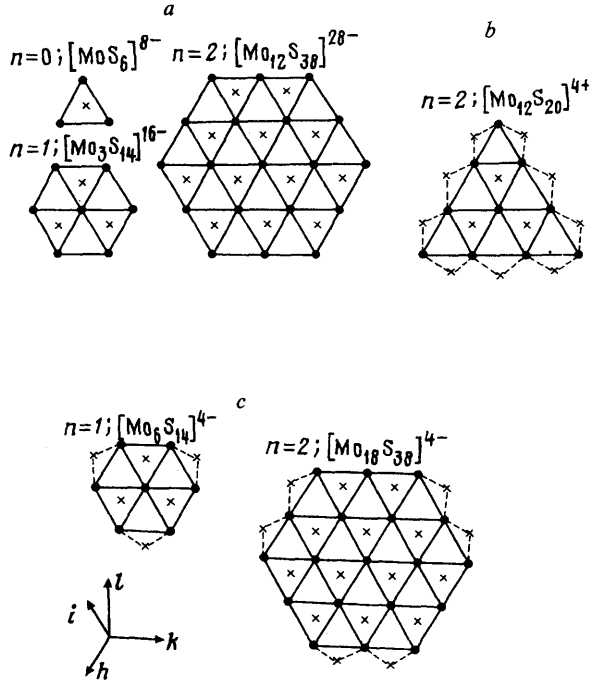


Figure 3. Formation of electrically neutral macromolecules of MoS_2 on putting into effect variants 1 (*a*), 2 (*b*) and 3 (*c*) (see text).

In the hexagon formed by three prisms there are 3 Mo and 14 S atoms which makes an excess charge of 16 e^-, i.e. the formula of the cluster is $[Mo_3S_{14}]^{16-}$. On increasing the length of the rib by one more Mo atom ($m = 3$, $n = 2$) the formula for the cluster will be

$[Mo_{12}S_{38}]^{28-}$. It is easy to show that in the general case a regular hexagon is described by the formula $[Mo_{(3n^2)}S_{2(3n^2+3n+1)}]^{(12n+4)-}$. With an increase in length of the rib the ratio of the sum of (–) charges on the S atoms to the sum of (+) charges on the Mo atoms in an infinitely large molecule $(MoS_2)_x$ will therefore be

$$\lim_{n\to\infty}\frac{4(3n^2+3n+1)}{12n^2}=1,$$

i.e. an infinitely large molecule is electrically neutral.

A significant excess of (–) charges will always exist in the case of a macromolecule of size $\leqslant 25$ Å ($n \leqslant 6$). An electrically neutral macromolecule may be formed by three different routes: 1) by adding protons to form S–H groups, 2) by removing excess S atoms with the formation of anionic vacant sites, 3) by adding additional Mo^{4+} atoms or other cations (Ni, Co, etc.).

We will examine these cases in more detail.

Variant 1. The adsorption of H_2 by bulk MoS_2 is well established experimentally and the presence of S–H groups has been confirmed spectroscopically.[67,68] The possibility of homolytic and heterolytic dissociation of dihydrogen on a MoS_2 surface has been shown by theoretical calculations.[69]

In the present case, $(12n + 4)$ protons are necessary to compensate the excess charge on the cluster the rib of which consists of n atoms of Mo which corresponds to the formula $H_{(12n+4)}Mo_{(3n^2)}S_{2(3n^2+3n+1)}$. This formula may be rewritten in the form $3n^2(MoS_2).2(3n + 1)H_2S$ from which it follows that the atomic ratio S:Mo is always greater than 2. Since this result contradicts numerous data according to which the ratio S:Mo < 2 and also the experimental data[67,68] on the quantity of H_2 adsorbed by MoS_2, it may be concluded that compensation of the (–) charge is probably not solely by addition of protons.

Variant 2. The possibility of removing peripheral S atoms with the formation of anionic vacant sites has been considered in many studies where the formation of adsorption centres and the activation of the reagents were examined (see, for example[70,71]). If the principle of the electrical neutrality of the macromolecule is followed then it is easy to show that to compensate for the (–) charge on a cluster the rib of which consists of n Mo atoms, it is necessary to remove all the S atoms on the side face $(10\bar{1}0)$ (Fig. 3, *b*). In this case the molecule is bordered by molybdenum atoms in the $(30\bar{3}0)$ plane and the quantity of S atoms remaining in the molecule is $(6n^2 - 4)$. Consequently the hexagon may be described by the formula $Mo_{(3n^2)}S_{(6n^2-4)}$, which in an infinitely large molecule

$\lim_{n\to\infty}\frac{6n^2-4}{3n^2}=2,$ corresponds to the formula MoS_2. A small excess of (+) charge is characteristic of clusters of a smaller size.

Variant 3. Extra cations, particularly Mo^{4+} may be added to the terminal S atoms on the $(10\bar{1}0)$ plane and occupy the regular positions of the MoS_2 lattice prescribed for Mo^{4+} ions during the growing process of the macromolecule (Fig. 3, *c*). In this case the formula of the macromolecule has the form $Mo_{(3n^2+3n)}S_{2(3n^2+3n+1)}$ which means that an infinitely large molecule is also described by the formula MoS_2. A small excess of (–) charges is observed in clusters of smaller size. Comparison of Figs. 3, *b* and 3, *c* show that variant 3 is a derivative of variant 2 with removal of angular Mo atoms and the corresponding quantity of S atoms.

The additional Mo^{4+} cations belonging to the side face $(30\bar{3}0)$ are coordinationally unsaturated. Following the principle of minimum free energy at the phase separation border, it may be proposed that the cations in question are able to shift from their regular positions towards the centre of the hexagon (Fig. 4), which may lead to the appearance of additional (+) charge on the peripheral $Mo^{(4+\delta)+}$ atoms. In our opinion this enables the small excess of (–) charge on small clusters to be compensated. It may also be proposed that these $Mo^{(4+\delta)+}$ cations are centres for adsorption and activation of donor molecules, i.e. they act as catalytically active centres.

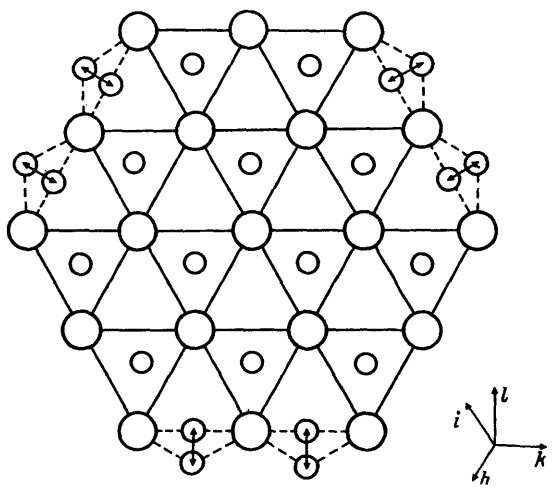


Figure 4. Displacement of cations from the regular positions of the lattice on the periphery of a MoS_2 patch.

In many respects a similar situation arises in the compensation of (–) charge on the terminal S atoms in the plane $(10\bar{1}0)$ after their coordination with Ni^{2+} or Co^{2+} cations. However since square-planar coordination[73–78] is characteristic for compounds of these metals with chelated sulphur-containing ligands then it is most probable that these cations occupy the centre of a square of S atoms in a plane $(10\bar{1}0)$ on the periphery of a $MoS_2(WS_2)$ patch (Fig. 4). With such coordination additional (+) charges on the Ni(Co) ions, corresponding to the formal oxidation level of 4+, are necessary to form electrically neutral fragments. A similar increase in charge was recorded by XP spectroscopy (see above). It is known[78] that reversible electron transfer reactions with the formation of stable products readily occur in square-planar complexes with S-containing ligands.

Evidently the compensation of the excess charge on the terminal S atoms by the addition to them of transition metal cations has a more general character. Thus after applying copper ions to a WS_2 surface a significant reduction was also detected in the electron density at the Cu atoms compared with the binary sulphide.[79] Even more, after applying Ni to the surface of both bulk and applied NbS_2 and ReS_2 (both these sulphides crystallise in the molybdenite

MoS_2 structure[80,81]) a reduction in the electron density on the Ni atoms compared with NiS was also recorded.[79] These observations serve as grounds for proposing that the coordinationally unsaturated electron-deficient atoms of Ni(Co) may act as centres for adsorption and activation of donor molecules.

4. The structure of the sulphide bimetallic species

In the previous section we came close to examining the structure of the active component of HDS catalysts known as the sulphide bimetallic species (SBMS).[27,72,82–86] The structural data forming the basis of this model were obtained by EXAFS [82] and by the X-ray method for the radial distribution of atoms (RDA).[60] According to this model the active component of the HDS catalyst is a uniform patch of $MoS_2(WS_2)$ on the side face $(10\bar{1}0)$ of which the Ni(Co) atoms are located (Fig. 5). In the SBMS the Mo(W) atoms are in the centre of trigonal prisms and are surrounded by six S atoms, the distances being Mo–S = 2.41 Å and W–S = 2.46 Å. The prisms are joined along an edge forming a 'sandwich' in which the distance Mo–Mo = 3.17 Å and W–W = 3.24 Å. All the values given for the interatomic distances are typical of bulk MoS_2 and WS_2.

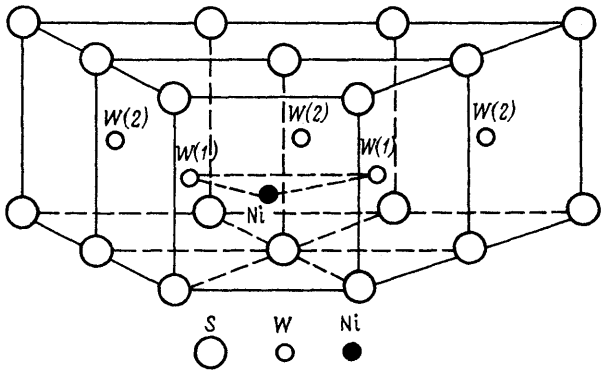


Figure 5. Stucture of the sulphide bimetallic species (SBMS), the active component of HDS catalysts.

When the Ni(Co) is located in the centre of a square of sulphur atoms in the plane $(10\bar{1}0)$, the distance Ni–S = 2.2 Å and Ni–W = 2.4 Å. Precisely the same values were found by EXAFS.[82] It must be emphasised that the distance Ni–S = 2.15–2.20 Å is typical for square-planar complexes with chelated S-containing ligands.[73–76] The short Ni–W distance = 2.4 Å suggests the formation of a direct metal–metal bond between the dissimilar atoms.

The closely similar values of the interatomic distances, particularly Co–S and Ni–S = 2.2 Å, were also found in other studies, however the Mo–Mo distance proved to be longer ~2.8 Å.[87,89] It was confirmed by XANES that the square-planar environment of the Ni atoms was transformed into trigonal-pyramidal after adsorption of a S-containing molecule.[88] It may be suggested that the increase in the Ni(Co)–Mo distance to 2.8 Å is explained by the fact that after adsorption of the donor molecule (H_2S in particular) onto Ni(Co) atoms forming part of the SBMS these atoms emerge from the plane $(10\bar{1}0)$ (Fig. 6). Such a situation is typical of pentacoordinated metal complexes. When the donor molecule occupies a pentacoordinate position in a square-planar complex a compound is formed in which the metal is in a square-pyramidal environment.[90]

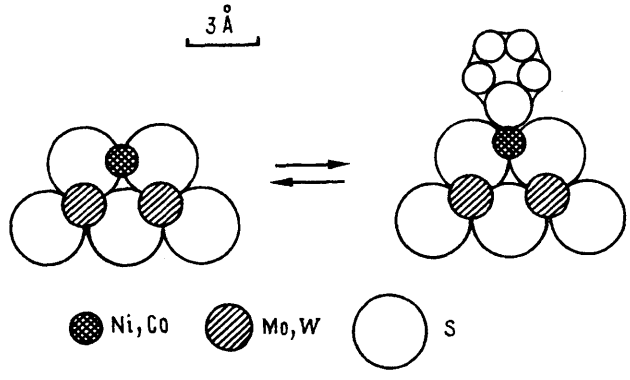


Figure 6. Adsorption of the thiophene molecule on SBMS.

IV. Reaction mechanism of the hydrogenolysis of thiophene

All the reaction mechanisms considered in the literature on the hydrogenolysis of the C–S bond are based on two main hypotheses.

1. The reaction is considered as a multistage oxidation–reduction process with the participation of anionic vacant sites of MoS_2 or Co–Mo–S phases.[8–19] Apparently one of the first mentions of the participation of anionic vacant sites of sulphide catalysts in the catalytic cycle appeared in 1969.[91] It may be suggested that this hypothesis arose from ideas on reaction mechanisms on oxide catalysts. Up to the present, fairly persuasive confirmation has been obtained of the participation of surface oxygen atoms of solid catalysts in the catalytic cycle.[92,93]

2. The active component of the catalyst is considered to be MoS_2, on the anionic vacant sites of which adsorption and activation of the S-containing molecule occurs. The Ni(Co) atoms are assigned the role of promoters. Various authors assess the role of promoters in a different way leading either to activation of hydrogen,[20] or to increase the number of anionic vacant sites,[22] or to the creation of qualitatively new types of vacant sites,[17,19,22] etc. The hypothesis on the distribution of roles between the active components and promoter is based, seemingly, on the following considerations. In the first place it is well known that addition of even small quantities of Ni(Co) to Mo(W) in the sulphide form leads to a sudden non-additive growth in activity, while addition of small quantities of Mo(W) to Ni(Co) sulphide causes only an insignificant increase in it. Secondly, modern methods, particularly electron microscopy, have shown the presence of $MoS_2(WS_2)$ particles in the catalysts (see part 1 of section III), while structures typical of Ni(Co) sulphides have not been detected.

The participation of anionic vacant sites in the catalytic cycle was also assumed on the basis of theoretical calculations on the reaction of thiophene with an MoS_2 surface.[94,95] The possibility of coordinating thiophene to an anionic vacant site through the S atom (η^1-coordination) and through the plane of the ring of the molecule (η^5-coordination) was examined in this way.

Table 4. Comparison of the amount of sulphur removed on TPR, the rate of exchange with $H_2{}^{35}S$ and the activity of sulphide catalysts in the hydrogenolysis of thiophene.[27,107]

Catalyst	Amount of sulphur removed on TPR in the range 25–500 °C, as % S content of the initial catalyst	Initial rate of isotopic hetero-exchange with $H_2^{35}S$ at 300 °C, g. at S/[g.at (Ni+M).s] × 10^3	Activity on thiophene hydrogenolysis at 300 °C, mole C_4H_4S/[g.at(Ni+M).s] × 10^4
Ni/SiO_2	100	–	2
Mo/SiO_2	35	42	5
$(Ni, Mo)/SiO_2$	41	36	60
W/SiO_2	26	–	3
$(Ni, W)/SiO_2$	31	25	123

However both of these suggestions are no more than hypotheses since there is no direct experimental confirmation and the indirect correlations are extremely inconsistent. We shall examine these hypotheses in more detail.

1. Participation of anionic vacant sites of $MoS_2(WS_2)$ in the catalytic cycle

Anionic vacant sites on the surface of sulphide particles may arise by the reaction of surface sulphur atoms with H_2 at elevated temperature and their removal as H_2S. The number of anionic vacant sites may be determined from the quantity of H_2S evolved in a temperature-programmed reduction (TPR) of the sulphide catalyst,[96,97] and also from the quantity of donor molecules adsorbed on the surface of sulphide catalysts after reducing them in H_2 at a particular temperature.[98–103] Both these procedures were used to construct correlation relationships. In some cases a correlation with catalyst activity in the hydrogenolysis of the C–S bond was detected[96–100] and in others it was absent or was not clearly displayed.[101–103]

To assess the mobility of oxygen in oxide catalysts and to study its role in catalysis, the method of hetero-exchange with oxygen in the gas phase has been widely used.[92,93] In the case of sulphide catalysts H_2S, labelled with the radioactive ^{35}S isotope, may serve as the appropriate test molecule.[104–106]

Correlations between catalytic activity and the mobility of surface S atoms were not detected by TPR or by $H_2{}^{35}S$ exchange methods on highly active sulphide catalysts.[27,107] After the addition of Ni to Mo(W) catalyst the rate of $H_2{}^{35}S$ exchange with the surface was reduced but the quantity of sulphur removed in the TPR process was practically unchanged and the activity of the catalyst was increased many times (Table 4).

A calculation of the enthalpy of the reaction of H_2 and sulphur atoms belonging to different faces of a single $MoS_2(WS_2)$ patch has been made by the interacting bond (IAB) method.[72] It turned out that to remove sulphur atoms from the basal plane $(000\bar{1})$ and from the side face $(0\bar{1}10)$ it was necessary to expend 335–398 and 92 kJ mol^{-1} respectively while the reaction of H_2 with S atoms in the plane $(10\bar{1}0)$ was characterised by a negative value of ΔH = 21–42 kJ mol^{-1}. This indicates that the removal of peripheral S atoms from plane $(10\bar{1}0)$ is energetically advantageous and consequently may occur even on forming a single $MoS_2(WS_2)$ patch.

As a result of forming an electrically neutral macromolecule (Fig. 3, *b*, *c*) the sulphur atoms which may be removed as H_2S are found in plane $(0\bar{1}10)$ and are coordinated with two Mo(W) atoms, i.e. for their removal ~92 kJ mol^{-1} is required. However the addition of S atoms to the vacant site formed is accompanied by a significant energy advantage. The enthalpy of this reaction is ΔH = –239 kJ mol^{-1}.[72] This indicates that under the conditions of the catalytic reaction the electrically neutral molecule must be thermodynamically stable since the reaction equilibrium is shifted strongly to the left.

$$S+H_2 \rightleftharpoons \square+H_2S.$$

A similar situation also arises in the case of the bimetallic catalysts. Calculations within the framework of IAB show[72] that it is necessary to expend 50–63 kJ mol^{-1} to remove sulphur atoms coordinating Ni(Co) atoms in the SBMS, while their addition to the vacancies formed is accompanied by an energy advantage of ~209 kJ mol^{-1}. Consequently in this case also the electrically neutral SBMS is a thermodynamically stable unit.

An important conclusion emerges from comparison of the enthalpy of the addition of S and removal of S from sulphide catalysts of various composition.[72] Since, according to Temkin's rule,[108] the rate of the two-stage catalytic process is maximal if the Gibbs' energies of both stages are approximately the same, the structure-forming sulphur atoms, i.e. those atoms which form the structure of the electrically neutral SBMS, may not participate in the catalytic cycle. Only those S atoms which have just one chemical bond with a metal atom may be catalytically active. This rule is better satisfied by the coordination of sulphur to the Ni or Co atoms than to Mo or W.

Examination of the thermodynamics of forming vacant sites on the surface of an electrically neutral SBMS places doubt on the possibility of their participation in the catalytic cycle. The absence of a correlation between the catalytic activity and the mobility of the surface sulphur atoms is inconsistent with this hypothesis.

2. The role of Ni(Co) and Mo(W) atoms in the activation of reacting molecules

The reductive desulphurisation of thiophene became apparent more than half a century ago[109] when it was discovered that benzene or toluene may be completely purified from thiophene contamination with Raney nickel. Subsequently the method of reductive desulphurisation of thiophene compounds was widely used in preparative organic chemistry both to establish the structure of thiophene derivatives and also for the synthesis of various saturated systems.[110–114] Raney cobalt is less suitable for these purposes.

The reductive desulphurisation of thiophene and its derivatives occurs on Raney nickel under very mild conditions. As a rule it takes place at room or elevated temperature (60–80 °C) using fairly inert solvents such as diethyl ether, ethanol, toluene, etc.[109–114] A necessary condition for high yield is the presence of hydrogen dissolved in the Raney nickel which is formed in the process of leaching out the Ni–Al alloy and is retained for a long time in large quantities in the bulk of the Raney nickel.[115] Usually the reaction is carried out in the absence of hydrogen in the gas phase and with an excess of Raney nickel. The reaction takes place fairly smoothly. Sulphur from the substrate molecule is irreversibly adsorbed onto the surface, deactivating it. The olefinic bonds are reduced with the evolution of aliphatic molecules into the gas phase. This reaction must be considered to be stoichiometric rather than catalytic[110,111] since it is necessary to remove the bound sulphur to complete a catalytic cycle. Seemingly this is impossible to accomplish under the conditions of the reaction since Ni sulphides are only reduced at a higher temperature.

Numerous experimental data convincingly point to a radical mechanism for the hydrogenolysis of a C–S bond on Raney nickel.[110,112] Fission of the C–S bond occurs after adsorption of the S-containing molecule with the formation of firmly bound sulphur and free radicals. The latter are saturated by the dissolved hydrogen and when this is absent the saturation of the free valencies occurs by dimerisation or disproportionation.[110]

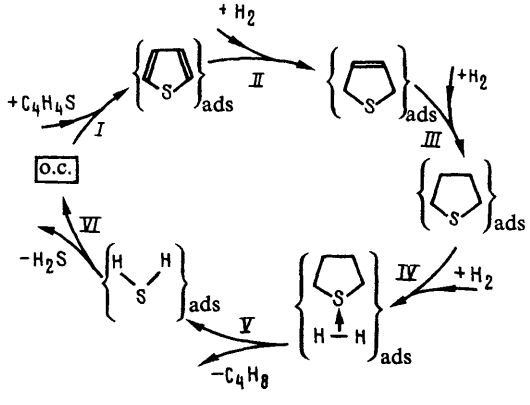
The desulphurisation reaction of dibenzothiophene (DBT) and its derivatives on Ni complexes, which also occurs under very mild conditions, is very representative.[116] The reaction of (2,2′-bipyridyl)-(1,5-cyclooctadiene)nickel(0) with DBT at ~60 °C is accompanied by the formation of only small quantities of diphenyl and its derivatives with nickel.[117] However if this complex of Ni(0) is first treated with $LiAlH_4$ in a molar ratio of 1:2 then the resulting complex will carry out the desulphurisation of DBT in quantitative yield.[116,118] These results indicate that nickel is extremely active in the fission of a C–S bond, however an excess of activated hydrogen is required to bring about the process.

A detailed study of the catalytic properties of Ni sulphides has shown[70] that they are inactive in H_2-D_2 exchange, in deuterium–hydrogen exchange reactions with olefins and in the hydrogenation of olefins at low temperatures. These catalysts begin to display activity only after reduction in H_2 at elevated temperatures. In addition the stoichiometric sulphides CoS, CoS_2, Co_9S_8 and Ni_3S_2 proved to be inactive in the hydrogenation of dienes.[119,120] However CoS in the absence of hydrogen accelerated the reaction of buta-1,3-diene with cyclohexa-1,3- and 1,4-dienes and also the disproportionation reaction of cyclohexadiene.[120] These data indicate the difficult activation of hydrogen on Ni and Co sulphides.

In contrast, MoS_2 is active in the hydrogenation of olefins and dienes at low temperature[118] and carries out the H_2-D_2 exchange reaction even at −40 °C.[121,122] Hydrogen is adsorbed in the dissociated form on MoS_2 and WS_2 with the formation of S–H groups.[67,68,123] From this it may be concluded that the activation of H_2 on $MoS_2(WS_2)$ occurs fairly readily.

The activation of hydrogen under mild conditions (25–75 °C, H_2 pressure 2 atm) is also effected on molybdenum complexes with S-containing ligands.[124–127] The resulting S–H groups readily hydrogenate olefinic and acetylenic hydrocarbons.[127]

On the other hand the heats of formation of MoS_2 (272 kJ mol^{-1}) and WS_2 (259 kJ mol^{-1}) are far greater than the heat of formation of NiS (71 kJ mol^{-1}).[128] Nickel sulphides readily lose sulphur in an atmosphere of H_2 and are reduced to the metal even at 300–400 °C while Mo and W disulphides are fairly stable at these temperatures.[27] In other words, the strength of the M–S bond in Mo or W sulphides is greater than in Ni sulphides.



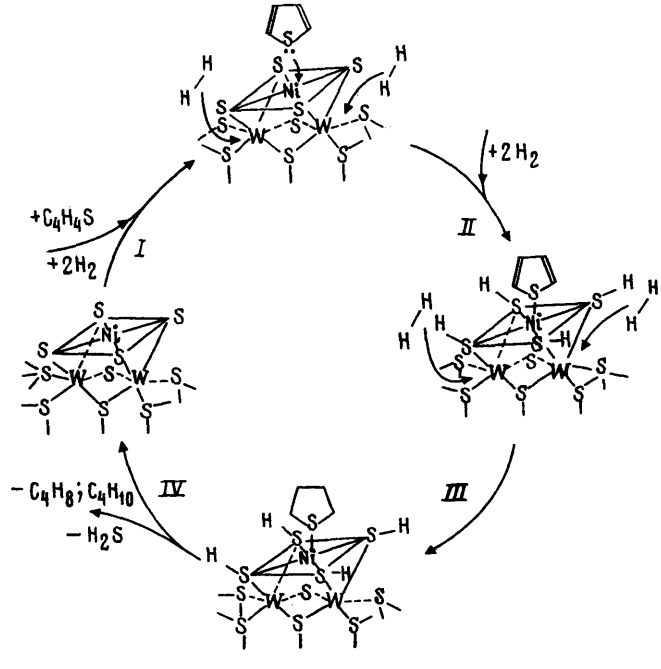
A catalytic cycle is shown for the hydrogenolysis of thiophene in six sequential stages, in each of which adsorption and activation of the reactants or desorption of the products occurs. The separation of the overall reaction into these stages is arbitrary since their number and sequence may be different. It is only important that the possible intermediates are strongly adsorbed on the catalyst and are not evolved into the gas phase during the entire catalytic cycle.[27,86] In spite of its arbitrary nature such a scheme for the conversion is convenient for examining the problem of the limiting stage of the reaction.

In the light of the arguments mentioned above one of the stages *II–IV*, in which activation of molecular hydrogen occurs, may be considered to be probably limiting for reaction on Ni(Co) sulphide catalysts. The stage for fission of the Ni–S(Co–S) bond and the desorption of H_2S into the gas phase (*VI*) seems to be rapid. On the other hand, stages *II–IV* are probably rapid on $MoS_2(WS_2)$ and the stage determining the rate of the whole process may, for example, be the removal of sulphur from the active centre (stage *VI*).

The clearly defined non-additive increase of the activity of bimetallic sulphide catalysts may be explained by the fact that those stages which determine the overall reaction rate on monometallic catalysts remain rapid. However for this it is necessary to assume that the adsorption of thiophene on Ni(Co) atoms occurs with the formation of a labile M–S bond and the ease of activation of H_2 on $MoS_2(WS_2)$ provides rapid hydrogenation of the thiophene ring. Then a different stage may become limiting, for example stage *V* in which fission of the C–S bond occurs.

3. Synchronous mechanism for the hydrogenolysis of thiophene in the coordination sphere of the SBMS

Analysis of the arguments mentioned above and the experimental data enable the following mechanism to be proposed for the hydrogenolysis of thiophene on a SBMS.



According to this mechanism the thiophene molecule is adsorbed on coordinationally unsaturated Ni(Co) atoms existing in a square-planar environment of S atoms. The deficiency of electron density on the Ni(Co) atoms enables coordination to them of an S atom, which in the thiophene molecule has an unshared electron pair. Simultaneously with the adsorption of thiophene on Ni(Co), activation of H_2 may occur in parallel and independently on Mo(W). The activated hydrogen may be passed on to the thiophene molecule, for example, via the S atoms coordinating the Ni(Co). However, other possible transfers of activated hydrogen are not excluded if the short metal–metal distance between the dissimilar atoms is taken into account, assuming the formation of a direct chemical bond. Seemingly the activation of hydrogen occurs continuously with its consumption in the hydrogenation of the thiophene ring. We propose that stages *I–III* for the activation of hydrogen and thiophene occur rapidly and stage *IV*, the fission of the C–S bond may be limiting after which the reaction products (H_2S, butenes, butane) are rapidly desorbed into the gas phase. The high rate for the process is provided by the synchronous interaction of reactants in the coordination sphere of the SBMS. A significant portion of the energy consumption on activating the reactants is compensated by the heat of adsorption and the hydrogenation energy of the thiophene ring, indicated by the low value of the activation energy $E_a = (59 \pm 8)$ kJ mol^{-1} (see Fig. 1).

Direct experimental confirmation of the proposed reaction mechanism has been obtained recently. It was shown by EXAFS *in situ* that the chemosorption of the selenophene molecule (the structural analogue of thiophene) on sulphide catalysts (Ni, Mo)/Al_2O_3 (MC) occurs only on the Ni and not the Mo atoms forming part of the SBMS.[129] Similar conclusions were reached previously.[88]

In order to answer the question of why thiophene is adsorbed by SBMS and H_2S is desorbed but the possible intermediate THF is not desorbed, the heats of adsorption of these molecules on SBMS of various composition were calculated within the framework of the IAB method.[130] The calculated heat of adsorption of H_2S was 48–52, of thiophene 88–94 and of THT 146–155 kJ mol^{-1}. The low value of the heat of adsorption of H_2S indicates the reversible nature of its adsorption under the reaction conditions and the possibility of displacing adsorbed hydrogen sulphide by thiophene. The significantly greater heat of adsorption of THT indicates that it is adsorbed practically irreversibly and the only possible variant of the catalytic cycle is hydrogenolysis of a C–S bond with desorption of hydrogen sulphide and hydrocarbons into the gas phase. Seemingly the main reason for the strength of the binding of THT to the active centre is the basicity of this S atom which is higher than that of thiophene and is caused by a reduction in the π-resonance energy on hydrogenating the aromatic thiophene molecule.

An additional argument in favour of the axial coordination of thiophene to the Ni(Co) atom (see Fig. 6) may be the existence of well-studied square-planar metal complexes with chelated macroligands.[131] The ability of square-planar complexes to undergo a reversible electron transfer reaction with the formation of stable products and the high electron-accepting ability of these complexes in relation to an organic donor have been well studied.[78,132]

The coordination of the thiophene molecule to a Ni(Co) atom in an SBMS is accompanied by a change in its coordination state. The adsorbed molecule adds on to the environment of the Ni(Co) to make a square pyramid which seemingly leads to a displacement of the Ni(Co) atoms from the centre of the square formed by the S atoms in the $(10\bar{1}0)$ plane of the SBMS (see Fig. 6). Such a displacement of atoms is very characteristic of square-planar metal complexes when they are transformed into pentacoordinated complexes after coordination of the donor ligands.[90] It is evident that the shift of Ni(Co) atoms is accompanied by a lengthening of the Ni(Co)–Mo distance. This effect has been observed in other studies.[87–89]

4. Other routes for converting thiophene

The synchronous mechanism for the hydrogenolysis of thiophene on SBMC enables the absence of the possible intermediates THT and butadiene from the gas phase to be explained. However they were recorded nevertheless in several cases when carrying out the reaction on one type of catalytic system. One of the most probable explanations for this discrepancy is the presence on the catalyst surface of other active centres, different from the SBMS, which may catalyse this reaction by a different route.

For some time past much attention has been paid to the study of the hydrogenolysis of the C–S bond on various faces of Mo, W and Ni single crystals.[24,25] The first stage of the hydrogenolysis of thiophene on Mo face (100) is fission of the C–S bond with evolution of butadiene into the gas phase.[133] The limiting stage of the reaction is the hydrogenation of sulphur adsorbed on the surface of the monocrystal.[134] At the same time propylene is the main product of THT hydrogenolysis and therefore THT cannot be an intermediate in the hydrogenolysis of thiophene.[133]

The desulphurisation of thiophene proceeds in a different way on a W surface (211).[135] The main product of the temperature-programmed desorption is propylene which indicates fission of a C–C bond at the α-carbon atom of the thiophene molecule. On the other hand with a Ni (111) surface, hydrocarbons C_{5+} are desorbed which implies dimerisation and possibly disproportionation of the reaction products.[136] However since the reaction took place in the absence of hydrogen,[135,136] one should speak of cracking and not hydrogenolysis in these cases.

Nevertheless the data on the reaction of thiophene with the surface of single crystals shows that the first stage of the process is fission of a C–S bond with subsequent saturation of the free valencies of radicals by reaction with H_2 or by recombination.

One way of clarifying the action mechanisms of solid catalysts is the study of the coordination of substrate molecules to the metal complex stabilised with different ligands. Although a large number of stable metal complexes of thiophene with various transition metals exist,[23,25] only a few of them include metals forming part of HDS catalysts.[137,138] A thiophene molecule coordinated to a metal through the S atom may be readily replaced by a weak ligand.

The preparation of THT by the catalytic hydrogenation of thiophene is not a simple problem. From a preparative point of view the ionic and electrochemical hydrogenation of thiophene are the most acceptable methods.[139] The hydrogenation of thiophene with molecular hydrogen is complicated by the rapid poisoning of the catalysts and by side reactions of hydrogenolysis of the C–S bond. Seemingly the most effective catalysts are based on noble metals and also rhenium sulphide.[140]

The appearance of THT among the hydrogenolysis products of thiophene on sulphide HDS catalysts may be linked with the formation of qualitatively new active centres. As has been shown[27,32,86] at a given level of activity of mono- and bimetallic sulphide catalysts based on Ni, Co, Mo and W prepared by various methods using various carriers, the hydrogenolysis of thiophene leads to the evolution only of H_2S, butenes and butane. The appearance of significant quantities of THT in the gas phase was observed under

the same conditions and on the same monometallic sulphide catalysts if, before carrying out the reaction, the catalysts are reduced in H_2 at 400 °C after sulphurisation in H_2S.[32] It was concluded from this that the responsible metal ions were in a low oxidation state after the reaction of hydrogenation of thiophene to THT. They may arise as a result of reduction of the catalyst surface either on carrying out the reaction in a non-stationary mode (for example, using pulse equipment in a H_2 stream), or with a deficient sulphur content in the raw material (for reoxidation of the catalyst surface), or in the presence in the catalyst of active centres different from the active centres of the HDS sulphide catalysts and not forming sulphides under the reaction conditions. It is more probable that the thiophene molecule is coordinated to that type of active centre not through the sulphur atom but by π-binding of the ring of the molecule.

V. Conclusion

Analysis of the principles for carrying out the hydrogenolysis of thiophene on highly active sulphide catalysts has enabled a new reaction mechanism to be proposed. The characteristic features of the proposed mechanism are as follows.

1. The hydrogenolysis of thiophene occurs within the coordination sphere of a sulphide bimetallic species without the participation of structure-forming sulphur atoms in the catalysis.

2. The adsorption and activation of the thiophene molecule is effected on Ni (or Co) atoms in the composition of the SBMS and the activation of H_2 occurs with the participation of Mo (or W) atoms.

3. The reaction occurs by a synchronous mechanism when the high rate of chemical conversion is provided by the synchronous interaction of reagents in the coordination sphere of the SBMS. In this way a high degree of compensation for the energy consumed on activating the reagents is achieved by the energy evolved on adsorption and hydrogenation of the thiophene ring.

The proposed mechanism for the hydrogenolysis of thiophene explains the occurrence of a synergistic effect. The clearly defined, non-additive increase in the chemical reaction rate on bimetallic in comparison with monometallic sulphide catalysts is explained by the formation of a new chemical compound, an SBMS, which combines the qualities of monometallic catalysts in relation to the activation of the reactants, viz. the activation of H_2 on $MoS_2(WS_2)$, the lability of the Ni(Co)–S bond and the transfer of the activated hydrogen to the adsorbed thiophene molecule by direct metal–metal reaction between the dissimilar atoms.

A synchronous mechanism for the interaction of reactants in the coordination sphere of a metal has been discovered most frequently in heterogeneous catalysis.[92] Thus, for example, partially and completely oxidised traditional molybdenum oxide catalysts, prepared through the synthesis of surface metal complexes, conduct the oxidation of H_2 and CO [141,142] and propylene[143] by a synchronous mechanism. Their activity and selectivity is appreciably higher than for the analogous catalysts prepared by the impregnation method. It may be suggested that the synchronous mechanism is more widespread in heterogeneous catalysis than has been considered until now. The main difficulty in detecting it is seemingly the non-uniformity of the chemical composition of the surface of solid catalysts, since in several cases the appearance of particular intermediates may be caused by an alternative reaction route having no direct relation to the mechanism being examined.

References

1. I B McKinley *Catalysis* (Edited by P H Emmett), Reinhold, New York, 1957, Vol. 5, p. 405
2. S C Schuman, H Shalit *Catal. Rev.*, 1970, **4** 245
3. O Weisser, S Landa *Sulphide Catalysis, Their Properties and Applications*, Academia, Prague, 1972, 506 pp
4. G C A Shuit, B C Gates *AIChE J.*, 1973, **19** 417
5. V H I De Beer, G C A Shuit *Preparation of Catalysts I* (Edited by B Delmon et al.), Elsevier, Amsterdam, 1976, p. 343
6. P C H Mitchell *Catalysis (London)* (Edited by C Kemball), 1977, Vol. 1, p. 204
7. F F Massoth *Adv. Catal.*, 1978, **27** 265
8. I F Le Page, I Cosuns, P Courti, et al. *Catalyse de Contact*, Technip, Paris, 1978, p. 441
9. B Gates, D J Ketzir, G Shuit *Chemistry of Catalytic Processes* (Translated into Russian), Mir, Moscow, 1978, p. 476
10. M I Loktev, A A Slinkin *Itogi Nauki i Tekhniki. Ser. Kinetika i Kataliz* (Results of Science and Technology. Series on Kinetics and Catalysis), 1980, **7** 3
11. P Grange *Catal. Rev.-Sci. Eng.*, 1980, **21** 135
12. E Furimsky *Catal. Rev.-Sci. Eng.*, 1980, **22** 371
13. P Ratnasamy, S Sivasanker *Catal. Rev.-Sci. Eng.*, 1980, **22** 401
14. P C H Mitchell *Catalysis (London)* (Edited by C Kemball), 1981, Vol. 4, p. 175
15. M Zdravzil *Appl. Catal.*, 1982, **4** 107
16. M L Vrinat *Appl. Catal.*, 1983, **6** 137
17. H Topsøe *Surface Science and Catalysis by Non-Metals* (Edited by I P Bonnele et al.), Reidel Publ. Co., New York, 1983, p. 329
18. R R Chianelli *Catal. Rev.-Sci. Eng.*, 1984, **26** 361
19. H Topsøe, B S Clausen *Catal. Rev.-Sci. Eng.*, 1984, **26** 395
20. B Delmon *Surf. Interface Anal.*, 1986, **9** 195
21. Yu I Ermakov *Usp. Khim.*, 1986, **55**(3) 499 [English translation in *Russ. Chem. Rev.*, 1986(3)]
22. M Zdravzil *Catalysis Today*, 1988, **3** 269
23. R J Angelici *Acc. Chem. Res.*, 1988, **21** 387
24. C M Friend, J T Roberts *Acc. Chem. Res.*, 1988, **21** 394
25. R Prins, V H J De Beer, G A Somorjai *Catal. Rev.-Sci. Eng.*, 1989, **31** 1
26. H L Hoffman *Hydrocarbon Process*, 1990, **69**(2) 53
27. A N Startsev, V A Burmistrov, Yu I Yermakov *Appl. Catal.*, 1988, **45** 191
28. V A Burmistrov, A N Startsev, Yu I Yermakov *React. Kinet. Catal. Lett.*, 1984, **24** 365
29. Yu I Yermakov, A N Startsev, V A Burmistrov *Appl. Catal.*, 1984, **11** 1
30. A N Startsev, S A Shkuropat *React. Kinet. Catal. Lett.*, 1990, **41** 175
31. A N Startsev. S A Shkuropat, V I Zaikovskii, et al. *Kinet. Katal.*, 1988, **29** 398
32. A N Startsev, S K Sengupta *Kinet. Katal.*, 1989, **30** 835
33. Y Kawaguchi, I G Dalla, F D Otto *Can. J. Chem. Eng.*, 1978, **56** 65
34. M Dobrovolszky, Z Nagy, Z Paal, P Tetenyi *Bull. Soc. Chim. Belg.*, 1984, **93** 659
35. A N Startsev *Khimiya i Tekhnologiya Topliv i Masel* (Chemistry and Technology of Fuels and Oils), 1991, No. 1, p. 32
36. Yu I Yermakov, B N Kuznetsov, V A Zacharov *Catalysis by Supported Complexes*, Elsevier, Amsterdam, 1981

37. Yu I Ermakov, V A Zakharov, B N Kuznetsov *Zakreplennye Kompleksy na Okisnykh Nositelyakh v Katalize* (Attached Complexes on Oxide Carriers in Catalysis), Nauka, Novosibirsk, 1980, 248 pp
38. Yu T Yermakov, B N Kuznetsov, A N Startsev, et al. *J. Mol. Catal.*, 1981, **11** 205
39. Yu I Ermakov, B N Kuznetsov, A N Startsev, et al. *Kinet. Katal.*, 1983, **24** 688
40. V N Rodin, B M Reddy, V V Rao, et al. *React Kinet. Catal. Lett.*, 1989, **40** 71
41. S A Shkuropat, E N Bogdanets, A N Kalinkin *React. Kinet. Catal. Lett.*, 1990, **41** 303
42. H Topsøe, B S Clausen, R Candia, et al. *Bull. Soc. Chim. Belg.*, 1981, **90** 1189
43. H Topsøe, B S Clausen, R Candia, et al. *J. Catal.*, 1981, **68** 433
44. C Wivel, R Candia, B S Clausen, et al. *J. Catal.*, 1981, **68** 453
45. B S Clausen, H Topsøe, R Candia, et al. *J. Phys. Chem.*, 1981, **85** 3868
46. B S Clausen, B Lengeler, R Candia, et al. *Bull. Soc. Chim. Belg.*, 1981, **90** 1249
47. M Boudart, J S Arrieta, R Dalla Betta *J. Am. Chem. Soc.*, 1983, **105** 6501
48. T G Parham, R P Merrill *J. Catal.*, 1984, **85** 295
49. N-S Chiu, S H Bauer, M F L Johnson *J. Catal.*, 1986, **98** 32
50. S M A M Bouwens, D S Koningsberger, V H J De Beer, D Prins *Bull. Soc. Chim. Belg.*, 1987, **96** 951
51. S M A M Bouwens, D S Koningsberger, V H J De Beer, R Prins *Catal. Lett.*, 1988, **1** 55
52. J Spens *Experimental High Resolution Electron Microscopy* (Translated into Russian), Nauka, Moscow, 1986
53. F Delannay, P Gajardo, P Grange, B Delmon *J. Chem. Soc., Faraday Trans. 1*, 1980, **76** 988
54. M A Apecetche, M Houalla, B Delmon *Surf. Interface Anal.*, 1981, **3** 90
55. J C Duchet, E M Van Oers, V H J De Beer, R Prins *J. Catal.*, 1983, **80** 386
56. V I Zaikovskii, L M Plyasova, V A Burmistrov, et al. *Appl. Catal.*, 1984, **11** 15
57. R Candia, O Sorensen, J Villadsen, et al. *Bull. Soc. Chim. Belg.*, 1984, **93** 763
58. M Breysse, M Cattenot, T Decamp, et al. *Catal. Today*, 1988, **4** 39
59. K Rikhter, Dissertation for Candidate of Chemical Sciences, Institute of Catalysis, Siberian Division of the Academy of Sciences of the USSR, Novosibirsk, 1973
60. E M Moroz, S V Bogdanov, S V Tsybulya, et al. *Appl. Catal.*, 1984, **11** 173
61. A F Wells *Structural Inorganic Chemistry* (Translated into Russian), Mir, Moscow, 1987, Vol. 2, p. 495
62. V I Nefedov *Rentgenoelektronnaya Spektroskopiya Khimicheskikh Soedinenii* (X-Ray Electron Spectroscopy of Chemical Compounds), Khimiya, Moscow, 1984
63. R L Chin, D M Hercules *J. Phys. Chem.*, 1982, **86** 3079
64. I Alstrupt, I Chorkendorff, R Candia, et al. *J. Catal.*, 1982, **77** 397
65. W Eltzner, M Breysse, M Lacroix, M Vrinat *Polyhedron*, 1986, **5** 203
66. J P R Vissers, V H J De Beer, R Prins *J. Chem. Soc., Faraday Trans. 1*, 1987, **83** 2145
67. C J Wright, C Sampson, D Fraser, et al. *J. Chem. Soc., Faraday Trans. 1*, 1980, **76** 1585
68. R B Moyes *Hydrogen Effects in Catalysis*, Basel–New York, 1988, p. 583
69. A B Anderson, Z Y Al-Saigh, W Keith Hall *J. Phys. Chem.*, 1988, **92** 803
70. K I Tanaka, T Okuhara *Catal. Rev.-Sci. Eng.*, 1977, **24** 24
71. K I Tanaka *Adv. Catal.*, 1985, **33** 99
72. Yu I Yermakov, A N Startsev, V A Burmistrov, et al. *Appl. Catal.*, 1985, **18** 33
73. J A McCleverty *Prog. Inorg. Chem.*, 1968, **10** 49
74. R Eisenberg *Prog. Inorg. Chem.*, 1970, **12** 295
75. E Diemann, A Müller *Coord. Chem. Rev.*, 1973, **10** 79
76. A A G Tomlinson *Coord. Chem. Rev.*, 1981, **37** 221
77. V M Bry'ko *Ditiokarbamaty* (Dithiocarbamates), Nauka, Moscow, 1984
78. V E Shklover, S S Nagapetyan, Yu T Struchkov *Usp. Khim.*, 1990, **59**(7) 1179 [English translation in *Russ. Chem. Rev.*, 1990(7)]
79. V N Rodin, B M Reddy, V V Rao, et al. *React. Kinet. Catal. Lett.*, 1989, **40** 71
80. V L Kalikhman, Ya S Usmanskii *Usp. Fiz. Nauk*, 1972, **108** 503
81. K Traere *Bull. Soc. Chim. Fr.*, 1965, **5** 1284
82. D I Kochubei, M A Kozlov, K I Zamaraev, et al. *Appl. Catal.*, 1985, **14** 183
83. A N Startsev *Geterogennyi Kataliz v Khimiya Geterotsiklicheskikh Soedinenii* (Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds), Riga, 1987, p. 161
84. A N Startsev *Proc. IX Indian Nat. Sympos. Catal.*, Madras, 1988, Pos. 15
85. A N Startsev *Proc. VI Intern. Sympos. Relat. Homog. Heter. Catal.*, Pisa, 1989, Pos. B5
86. A N Startsev *Kinet Katal.*, 1990, **31** 869
87. S M A M Bouwens, D C Konigsberger, V H J De Beer, et al. *Catal. Lett.*, 1990, **5** 273
88. W Niemann, B S Clausen, H Topsøe *Catal. Lett.*, 1990, **4** 355
89. S M A M Bouwens, J A R Van Veen, D C Koningsberger, et al. *J. Phys. Chem.*, 1991, **95** 123
90. R R Holmes *Prog. Inorg. Chem.*, 1984, **32** 199
91. J M J C Lipsch, G C A Schuit *J. Catal.*, 1969, **15** 179
92. G K Boreskov *Geterogennyi Kataliz* (Heterogeneous Catalysis), Nauka, Moscow, 1986
93. G K Boreskov *Catalysis: Science and Technology* (Edited by J R Anderson, M Boudart), Springer-Verlag, Berlin–Heidelberg–New York, 1982, Vol. 3, p. 39
94. J Joffre, P Geneste, D A Lerner *J. Catal.*, 1986, **97** 543
95. M C Zonnevylle, R Hoffmann, S Harris *Surf. Sci.*, 1988, **199** 320
96. N K Nag, D Fraenkel, J A Moulijn, B C Gates *J. Catal.*, 1980, **66** 162
97. B Scheffer, N J J Dekker, P J Mangnus, J A Moulijn *J. Catal.*, 1990, **121** 31
98. S J Tauster, K L Riley *J. Catal.*, 1981, **67** 250
99. T A Bodrero, C H Bartolomew, K C Pratt *J. Catal.*, 1982, **78** 253
100. J W Gasseling, H Schaper, J P De Jonge, W H J Stark *Appl. Catal.*, 1987, **32** 337
101. K S Chang, F E Massoth *J. Catal.*, 1980, **64** 332
102. J Bachelier, J C Duchet, D Cornet *Bull. Soc. Chim. Belg.*, 1981, **92** 1301

103. W Zmierczak, G Murali Dhar, F E Massoth *J. Catal.*, 1982, **77** 432
104. H R Lukens, R G Meisenheimer, J N Wilson *J. Phys. Chem.*, 1962, **66** 469
105. K C Campbell, M L Mirza, S J Thompson, G Webb *J. Chem. Soc., Faraday Trnas. 1*, 1984, **80** 1689
106. J Freel, J G Larson, J F Adams *J. Catal.*, 1985, **96** 544
107. A N Startsev, E N Artamonov, Yu I Yermakov *Appl. Catal.*, 1988, **45** 183
108. M I Temkin *Kinet. Katal.*, 1984, **25** 299
109. J Bougault, E Cattelain, P Chabrier *Bull. Soc. Chim. Fr.*, 1940, **7** 781
110. W A Bonner, R A Grimm *The Chemistry of Organic Sulfur Compounds* (Edited by B Kharasch, G Y Neyers), Pergamon Press, Oxford, 1966, p. 35
111. A I Meyers *Heterocycles in Organic Synthesis*, Wiley-Intersci., New York, 1974
112. Ya L Gol'dfarb (Editor) *Novye Napravleniya Khimii Tiofena* (New Directions in Thiophene Chemistry), Nauka, Moscow, 1976
113. D H R Barton, W D Ollis *Comprehensive Organic Chemistry* (Translated into Russian), Khimiya, Moscow, 1985, Vol. 9
114. H Hauptmann, W F Walter *Chem. Rev.*, 1962, **62** 347
115. P Fouilloux *Appl. Catal.*, 1983, **8** 1
116. J J Eisch, L E Hallenbeck, K I Han *J. Am. Chem. Soc.*, 1986, **108** 7763
117. J J Eisch, L E Hallenbeck, K I Han *J. Org. Chem.*, 1983, **26** 2963
118. J J Eisch, K R Im *J. Organomet. Chem.*, 1977, **139** C51
119. M George, R B Moyes, D Ramanarao, P S Wells *J. Catal.*, 1978, **52** 486
120. K Tanaka, K Tanaka, K Miyahara *J. Catal.*, 1979, **59** 423
121. T Okuhara, K Tanaka, K Miyahara *J. Catal.*, 1977, **48** 229
122. K Tanaka, T Okuhara *J. Catal.*, 1982, **78** 155
123. C J Wright, D Fraser, R B Moyes, P P Wells *Appl. Catal.*, 1981, **1** 49
124. M Rakowski DuBois, M C VanDerveer, D L DuBois, et al. *J. Am. Chem. Soc.*, 1980, **102** 7456
125. M Rakowski DuBois *J. Am. Chem. Soc.*, 1983, **105** 3710
126. M McKenna, L L Wright, D J Miller, et al. *J. Am. Chem. Soc.*, 1983, **105** 5329
127. C J Casewit, M Rakowski DuBois *J. Am. Chem. Soc.*, 1986, **108** 5482
128. T A Pecoraro, R R Chianelli *J. Catal.*, 1981, **67** 430
129. A N Startsev, S A Shkuropat, V V Kriventsov, et al. *Mendeleev Commun.*, 1991, **1** 6
130. N N Bulgakov, A N Startsev *Mendeleev Commun.*, 1991, **1** 97
131. M Hanack, S Deger, A Lange *Coord. Chem. Rev.*, 1988, **83** 115
132. M M Ahmad, A E Underhill *J. Chem. Soc., Dalton Trans.*, 1983, 165
133. A J Gellmann, D Neiman, G A Somorjai *J. Catal.*, 1987, **107** 92
134. A J Gellmann, M E Bussell, G A Somorjai *J. Catal.*, 1987, **107** 103
135. R E Preston, B Benziger *J. Phys. Chem.*, 1985, **89** 5010
136. G R Schoofs, R E Preston, J B Benziger *Langmuir*, 1985, **1** 5010
137. J H Eekhof, H Hogeveen, R M Kellogg, E Klei *J. Organomet. Chem.*, 1978, **161** 183, 361
138. H J Wasserman, G J Kubas, R R Ryan *J. Am. Chem. Soc.*, 1986, **108** 2294
139. L I Belen'kii, V P Gul'tyai *Khim. Geterotsikl. Soedin.*, 1981, (6) 723
140. A V Mashkina *Geterogennyi Kataliz v Khimii Organicheskikh Soedinenii Sery* (Heterogeneous Catalysis in the Chemistry of Organic Sulphur Compounds), Nauka, Novosibirsk, 1977, 344 pp
141. B N Kuznetsov, O N Kimkhai, D Gutchick, et al. *Z. Anorg. Allg. Chem.*, 1982, **493** 149
142. D Gutshik, O N Kimkhai, B N Kuznetsov, et al. *Kinet. Katal.*, 1980, **21** 436
143. A A Efremov, A B Khandros, A A Davydov, G K Boreskov *Kinet. Katal.*, 1979, **20** 1215

Translated from *Uspekhi Khimii* **61** 356–383 (1992) U.D.C. 66.097+548.734+539.26

X-Ray diffraction study of carriers and deposited metallic catalysts

E M Moroz
Institute of Catalysis, Siberian Division of the Russian Academy of Sciences

ABSTRACT. The possibilities of applying some X-ray diffraction methods in the study of multicomponent highly disperse systems are examined. Such methods include the method based on the radial distribution of atoms (RDA), full-profile X-ray diffraction analysis (FPA), and the method involving the determination of substructural characteristics (MDSC). Examples of the determination of the structural and substructural characteristics of the most important catalyst carriers as well as deposited and non-deposited metallic catalysts are presented.

The bibliography includes 129 references.

Contents

I. Introduction 188
II. The possibilities of X-ray diffraciton methods in the study of multicomponent highly disperse systems 188
III. Structural and substructural characteristics of catalyst carriers 193
IV. Structural and substructural characteristics of deposited and non-deposited monometallic catalysts 196
V. Determination of the phase composition of deposited bimetallic catalysts 198
VI. Conclusion 200

I. Introduction

Despite the widescale use of X-ray diffraction methods in materials science, the application to the study of catalysts is mainly limited to qualitative and quantitative phase analyses of well crystallised coarsely disperse (crystallite size in the range 50–1000 Å) systems. In his concluding remarks in a well known monograph devoted to methods for the study of catalysts, Lambert[1] indicates eight criteria in terms of which the effectiveness of the method should be estimated: (1) the need to use centralised or local laboratory equipment; (2) speed of analysis; (3) the possibility of studying catalysts in the course of their operation or after use; (4) destructiveness or non-destructiveness of the method; (5) the universality of the method (sensitivity in relation to various chemical elements, suitability for the study of deposited and non-deposited catalysts); (6) the possibility of obtaining useful information in the presence of a large amount of contaminants formed during the operation of the catalyst; (7) cost; (8) thickness of the layer of the specimen investigated.

Evidently, from this standpoint, X-ray diffraction methods are entirely effective, but, since it is assumed that they yield information mainly about the structural and substructural characteristics of the bulk phase of the specimen, inadequate attention has been devoted to them. The authors of monographs in which the structural features of catalysts are discussed, for example, Lambert[1] and Anderson,[2] as a rule do not dwell on the X-ray diffraction methods for their investigation. At the Ist European Conference on Powder Diffraction held in March 1991 in Munich, a small number of experimental studies on highly disperse materials were presented,[3–9] only three of which[7–9] were devoted to the study of catalysts. Nevertheless, X-ray diffraction methods occupy a place among the series of physical methods for the study of catalysts, especially deposited catalysts, because they make it possible to obtain information simultaneously about the dispersity and phase composition of the active component and the carrier and about their structural characteristics and the degree of their interaction.

Examination of the usual parameters of the diffraction patterns of well crystallised substances, such as the positions, intensities, and form of the diffraction maxima, for the investigation of highly disperse multicomponent catalytic systems yields little information. Special X-ray diffraction methods for the investigation of highly disperse materials, based on the integral analysis of the curve for the X-ray scattering intensity, namely the method based on the radial distribution of atoms (RDA), the methods based on the determination of substructural characteristics (MDSC), and full-profile X-ray analysis (FPA), are being developed at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences. This review deals with the fundamental possibilities of the methods developed and presents the results of their use in order to obtain structural and substructural characteristics of the principal catalysts carriers (aluminium oxides and carbon materials) as well as deposited and non-deposited metallic catalysts having different chemical compositions.

II. The possibilities of X-ray diffraction methods in the study of multicomponent highy disperse systems

1. Methods based on the radial distribution of atoms

Mainly liquids (solutions and liquid metals) and amorphous and vitreous materials have been studied experimentally by the RDA method (see, for example, Refs. 10–13). Procedures for the interpretation of data and for the analysis of errors of different kinds have been examined theoretically.[14–21] Catalysts have been studied by the RDA method in a number of investigations.[13,22–29] Many catalysts of different chemical composition have been investigated in the Laboratory of Structural Research Methods at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences. This review presents the results of the investigation of catalyst carriers and metallic catalysts.

The X-ray diffraction RDA method is based on the relation between the atomic density (ρ) radial distribution function and the intensity of the coherent scattering of X-rays $i(s)$ in the diffraction experiment:

$$4\pi r^2\rho(r)=4\pi r^2\rho_0+(2r/\pi)\int_{s_{min}}^{s_{max}} i(s)s\sin(sr)ds, \quad (1)$$

$$\rho_0=\sum_{A=1}^{m}(n_AK_A)^2dL/M,$$

$$i(s)=\left[I(s)/N-\sum_{A=1}^{m}n_Af_A^2(s)\right]\Big/f_e^2(s),$$

where $\rho(r)$ is the spherically symmetrical atom distribution function, d the pyknometric density, L the Avogadro number, M the molecular weight, $I(s)$ the coherent component of the scattered diffraction beam, r the radius-vector of the inverse lattice, $\rho_0(r)$ the average density obtained for a completely random distribution of atoms, i.e. in the absence of interference, K the effective number of electrons, f_e the atomic unit factor, and N the number of atoms in the agglomeration.

In the case of binary systems, where the atoms of one system (phase) form separate groups since they are surrounded only by atoms of the same system, the formula has the following general form:[30,31]

$$\rho(r)=C_A\rho_{AA}(r)+C_B\rho_{BB}(r)+2C_AC_B\rho_{AB}, \quad (2)$$

where ρ_{AA}, ρ_{BB}, and ρ_{AB} are the partial RDA functions and C_A and C_B are the concentrations of individual phases.

It is useful to use Eqn. (2) instead of Eqn. (1) for comparable values of C_A and C_B. In deposited metallic catalysts, the concentration of the metal is low relative to the carrier ($C_B \ll C_A$), so that Eqn. 1 can be used.

For the calculation of the RDA curves, it is essential to have at one's disposal certain experimental and reference characteristics of the test substance. Such experimental data are (1) the set of data for the intensity of scattering by the specimen; (2) the set of data for the intensity of phonon scattering; (3) information about the thickness of the specimen and the pressing density (these quantities are important for systems consisting of light atoms); (4) chemical composition of the specimen ($n_A...n_m$) per molecule; (5) pyknometric density.

Data from reference sources include (1) the number of electrons in the atoms; (2) the absorption coefficients of the atoms for the given X-ray irradiation; (3) radiation wavelength; (4) atomic factors of the atoms. The RDA curves are plotted in terms of the variables $4\pi r^2\rho$ and $f(r)$, where r is expressed in Ångstroms and the electron density ρ in electron^2 Å^{-3}.

The quantitative parameters of the structure are the equilibrium interatomic distances (the values of r to which correspond the electron density peaks), the coordination numbers Z (determined from the areas of the coordination peaks), the averge quadratic atomic shifts (determined from the widths of the coordination peaks), as well as the distance over which the correlation in the disposition of atoms disappears [the distance r starting from a certain value $\rho(r) = \rho_0$]. The experimental areas of the coordination peak corresponding to the given distance r can be compared with the theoretical values calculated from the formulae

$$\Pi_T=2n_AZ_{AB}K_AK_B;\ \Pi_T=n_AZ_{AA}K_A^2, \quad (3)$$

where n_A is the number of atoms of kind A, which depends on the chemical composition, and Z_{AB} the coordination number, i.e. the number of atoms of kind B in the spherical shell bounded by the distances r and $r + d$ from the centre of the atom of kind A.

When the reliability criteria concerning the normalisation of the intensity curves hold and there is only a slight deviation from the series of approximations involved in the derivation of the principal formulae (the isotropic nature of the accumulation of atoms, the homogeneity of the medium, and infinite extent of the volume ensuring a statistically equiprobable environment of the atoms), the positions of the coordination peaks on the RDA curves are determined to within $\Delta r/r = \pm 0.5\%$ and the accuracy of the determination of the areas is to within ±5%.

Analysis of the RDA curves makes it possible not only to obtain the standard information described above but also to estimate the size of the crystallites when the latter is less than 30 Å. The determination is based on the fact that the form of the interference function for a high dispersity of the crystallites depends on their size. The form of the peaks on the scattering intensity curve and their resolution vary as a function of size.[32,33] For example, if the size of the metal crystallite with a face-centred cubic (FCC) lattice is 30 Å, then only 24 out of the 35 diffraction peaks are resolved. A change in the scattering intensity curve leads to a change in the RDA function. The coordination numbers in spherical particles of a metal with a face-centred cubic structure, whose diameters were multiples by factors of 3, 5, 7, etc. of the diameters of the individual atoms, have been evaluated by a statistical calculation.[34] With decrease in the size of the particles, there is a steady decrease in the area of the coordination peaks. For a particular size, there are consistent ratios of the areas. This feature has been used to estimate the sizes of highly disperse particles.[35–41] For a platinum particle diameter of 8 Å, the area of the first coordination sphere is half the value calculated for an infinite crystal, while the area of the second sphere is smaller by 30%; for a diameter of 30 Å, these areas are smaller by 15 and 25% respectively.

A characteristic feature of the calculation of the RDA curves by Moroz[20] is double normalisation (with respect to the far region of angles and with respect to the areas under the scattering intensity curves) and the use of experimental scattering factors. Criteria were developed for the reliability of the RDA curves as regards the normalisation of the X-ray scattering intensity and the intermediate parameters of the calculation.[20,42]

Experimental errors leading to failure of the reliability criteria were analysed, including the errors in the measurement of the intensity over a wide range of angles and at a single point (incorrect allowance for the contribution of the background and Compton scattering, the presence of fluorescent emission) and also the errors in the specification of the chemical composition.[20]

At the same time, procedures were developed for taking into account the contribution of the carrier to the overall X-ray scattering intensity curve and the RDA curve for the catalyst. Comparison of the curves for the intensity of the scattering of X-rays by the catalyst and the carrier is difficult owing to the different depths of the "working layer", because the catalyst contains as a rule a highly absorbing component. These disadvantages can be avoided if corrections are introduced in the analysis of the scattering intensity

curves for the background, polarisation, and absorption, and when the change to electronic units is made. The change to electronic units for the scattering intensity curve is an intermediate stage in the calculation of the RDA function and the construction of the difference intensity curve (DIC) then becomes possible.[20,42]

The determination of the dispersity of the active component in highly disperse deposited catalysts (D < 30 Å) is based on the analysis of the difference RDA curves. In principle, scattering intensity data are obtained by the RDA methods in the same way as in the usual precision measurements: the scattered X-ray intensity is measured over a wide range of angles with similar accuracies using monochromatic radiation. Short-wavelength molybdenum radiation with λK_{α_1} = 0.71 Å is usually employed. The intensity is measured for angles up to 2θ = 160°, which corresponds to $S_{max} = 4\pi \sin\theta_{max}/\lambda$ = 17.41 Å.

The use of a monochromator leads to the loss of up to 80% of the intensity. The monochromator, ensuring a better relation between the signal and the background, does not transmit Compton (incoherent) scattering for angles θ > 20°. For smaller angles, the monochromator transmits the entire Compton scattering, but in this region the Compton scattering itself is small.[27,43]

Conditions for an automated experiment with computer calculations have been described. The experiment lasts ~50 h and requires the stable operation of the apparatus (diffractometers of the DRON-3,4 or HZG-4C, B, A type are usually employed). The successful application of the RDA method requires that the following conditions be maintained:

1. The structure of the system components under consideration must be simple; the set of different interatomic distances must be small and the coordination numbers must be large.
2. Heavy atoms, whose percentage content is high, must be present in the system.
3. The components must have a perfect structure (absence of defects and vacancies). Analysis of the RDA curves does in fact make it possible to discover the presence of imperfections in the structure as a result of the comparison of the observed and calculated curves.
4. Accurate chemical analysis is essential.
5. A model of the postulated structure is needed.

The RDA method examined has been used successfully in the study of highy disperse systems of different chemical composition. However, the rigorous requirements which must be met by the experiment (monochromatisation, correct allowance for incoherent scattering, duration of the experiment) and by the preliminary treatment of data (careful normalisation of the scattering curves) and the ambiguity of the interpretation of the RDA curves limit the possibilities of this method in normal X-ray laboratories.

A high-speed method for the determination of atomic radial distribution functions, based on the *a priori* assumption that the functions of the background incoherent and independent gas scattering are monotonic, is being developed at present. This method does not require the measurement of the background and the knowledge of the intensity of the Compton scattering. The structure-sensitive part of the intensity curves is isolated with the aid of the cubic B-spline minimised by the method of least squares.[44] The method has been tested on polycrystalline silver and palladium.[45] The Fourier analysis of the structure-sensitive part of the intensity curve is used to obtain radial distribution functions by a procedure similar to that used in the Fourier transformation of the function of the long-range fine structure of the X-ray absorption spectrum in the EXAFS method, used to obtain structural information.[46,47] The proposed method makes it possible to accelerate and simplify the procedure involving the collection and treatment of experimental data (the experiment can be carried out without a monochromator, with a β-filter, and the normalisation of the intensity curves is also not needed). However, it cannot be used to establish the structural parameters of unknown materials, because it does not permit the determination of the absolute values of the coordination numbers. This method can be employed to analyse the changes in the structural characteristics in a series of specimens.

2. The method based on the full-profile X-ray analysis

About 20 years ago, a new effective method for the interpretation of powder diffraction data, called the Rietveld method,[48] appeared in neutron diffraction. It was subsequently used also in X-ray diffraction.[49–52]

The FPA method is based on the minimisation of the difference between the experimental and calculated diffraction patterns at any point on the X-ray diffraction pattern profile.

The function

$$\Phi = \sum_i^N W_i (y^e - y^t)^2,$$

is minimised by the methods of least squares. Here y^e and y^t are respectively the experimental and calculated intensities at the ith point of the profile, w_i is the weighting function, and N the number of points on the profile. Next, a sequence of corrections to the parameters of the specified model, converging to zero, is calculated. The summation in terms of the matrix elements of the least squares method is carried out over all the points on the profile included in the calculation. A series of matrices with the specified weighting factor are added to the matrix thus constructed. These matrices take into account the limitations to the ranges of variation of the interatomic distances and the equality of the bond lengths between various atoms, atoms in special positions being included in the calculation.[53] Since a non-linear relation between the parameters is fitted by a linear relation in the least squares method, it is essential to carry out several refining cycles.

The unreliability factors are used to estimate the reliability of the model:

$$R_p = \sum_i^N |Y_i^e - kY_i^t| \Big/ \sum Y_i^e \quad \text{(profile-based factor)}$$

and

$$R_I = \sum_i^N |I_i^e - kI_i^t| \Big/ \sum I_i^e \quad \text{(intensity-based factor)}$$

The factor R_P is found by summation over all the points of the profile and R_I by summation over the intensities of the diffraction lines. R_P usually exceeds R_I by a factor of two, while R_I is in its turn greater than the unreliability factor R_F, used in the single crystal method, by a factor of 1.5–2.

We used a computer program written in FORTRAN for the BESM-6 computer,[53,54] which includes the program published by Clark, et al.[55]

The entire X-ray diffraction pattern can be represented as a linear combination of the profiles of individual peaks. The overall intensity at each point on the pattern is described by the expression

$$Y_i^t = k \sum_j^N Y_j \Omega_{ij} + Y_i^\Phi,$$

where Ω_{ij} is the peak shape function, k the reduction coefficient, Y_i^b the background at the ith point, and Y_j the intensity of the jth reflection.

A line diagram based on the specified model is used for the construction of the theoretical profile (this requires the knowledge of the unit cell parameter, the symmetry space group, and the atomic coordinates).

The theoretical intensity is calculated by the formula

$$I_{hkl}=F_{hkl}^2 LPGn,$$

where L, P, and G are the Lorentz, polarisation, and geometrical factors respectively, n is the repeatability factor, and F_{hkl}^2 the structure factor. The structure factor is calculated in a general form in accordance with the formula

$$F_{hkl}^2=\left[\sum_{j=1}^{N} f_j\mu_j T_j \exp 2\pi i(hx_j+ky_j+lz_j)\right]^2$$

where x_j, y_j, and z_j are atomic coordinates, f_j is the atomic factor, μ_i the multiplicity of the atoms, T_j the thermal multiplier, and h, k, and l are the reflection indices.

Next, the line diagram is smeared by the function of the profile, which has parameters depending on the reflection angle. The neighbouring reflections contribute to the intensity at each point on the diffraction pattern. The main difficulty in the application of the Rietveld method involves the description of an individual profile of a reflection, since, in contrast to neutron diffraction, where Pearson's *VII* functions are used successfully, a similar unique theoretically well-founded function has not yet been proposed in X-ray diffraction. This is associated with the fact that the diffraction peaks corresponding to different reflection angles have different shapes and the experimental dependence of the peak half-width on the angle θ is not monotonic owing to effects caused by the real structure of the polycrystalline material (microdistortion, smallness of the coherent scattering regions, anisotropy, packing defects).[50,56–58] The majority of investigators[56,59–61] assume that a single profile is described most successfully by the generalised Pearson function:

$$P_{ij}=2\left(\frac{2^{1/m}-1}{\pi}\right)^{1/2}\frac{\Gamma(m)}{\Gamma(m-1/2)}H_j^{-1}\left[1+4\frac{(2\theta_i-2\theta_j)^2}{H_j^2}(2^{1/m}-1)\right]^{-m},$$

where Γ represents gamma-functions, H_j is the peak half-width (the width of the peak at the level of half its height); the power exponent m may be refined.

In our calculations, we used the version with $m = 2$ whereupon the Pearson function becomes a modified Lorentz function:

$$ML(2\theta_i, 2\theta_j)=\frac{2^{1/2}-1}{\pi H_j}\left[1+\frac{4(2^{1/2}-1)}{H_j^2}(2\theta_i-2\theta_j)^2\right]^{-2}.$$

According to Vainshtein's formula,[14] the dependence of H_j on θ_j has the form

$$H_j^2 = u\tan^2\theta + v\tan\theta + w.$$

The parameters u, v, and w are found from individual reflections and are refined.

In the FPA method, there are also other approaches, in particular the synthesis of the diffraction profile on the basis of specified instrumental, spectroscopic, and physical experimental parameters.[62] All the calculations are carried out in terms of Fourier coefficients, which ensures sufficient accuracy and speed. This approach made it possible to determine not only the structure but also the substructure parameters of substances.[63]

The FPA method is useful in the solution of many problems involving the refinement of structures whose type is already known. Such problems include the distribution of isomorphous impurities, the ordering of defects, the distribution of cations in spinels and other compounds, etc.[64–70] However, examples of the application of this method in the determination of unknown structures of new compounds also exist.[71–73]

The following structural parameters can be determined by the FPA method: (1) the atomic coordinates in fractions of the cells x, y, and z; (2) the overall thermal parameter (Q); (3) individual isotropic thermal factors of the ith atom; (4) the coefficient of the occupation of a given site by the ith atom (n_i); (5) the scaling coefficient (k).

In addition, a series of profile parameters, determining certain characteristics of the specimen and of the recording, can be refined: (1) the line half-width parameters u, v, and w; (2) the overall shift of the X-ray diffraction pattern relative to the origin z; (3) the lattice parameters A, B, C, α, β, and γ; (4) the asymmetry parameter P; (5) the texture parameter G; (6) the ratio of the intensities of the radiation components K_{α_1} and K_{α_2} (after passage through the monochromator, $I_{K_{\alpha_1}}$ and $I_{K_{\alpha_2}}$ may not be 2).

The experimental data obtained by the FPA method as well as the RDA method consist of measurements for individual points. The scanning step is determined by the line width (usually 0.01–0.05°). The use of Soller slits is obligatory. For a reliable determination of the profile parameters, it is recommended that individual peaks and non-doublet K_β radiation be employed.[67]

3. The method involving the determination of substructural characteristics

The method involving the determination of substructural characteristics (sizes of crystallites and their microdistortions, parameters determining the size distribution of crystallites), based on the harmonic analysis of the diffraction peak profiles, can be applied to systems of virtually any chemical composition in which the size of the crystallites is 30–1000 Å. An important feature is the fact that the substructural characteristics listed above refer directly to the component investigated (metal, oxide, salt, etc.) in the system under consideration.

The role of all the experimental factors influencing the profile of the diffraction maximum, such as the width of the slits on the collimator in the tube and in the counter, the focussing conditions etc. has been examined in detail.[74,75]

For a clear-cut differentiation of the profiles of the diffraction lines for the phase investigated, it is essential to carry out precision measurements of the line intensity at each point, which is achieved by scanning over the points with accumulation of a large number of counts. The lines are focussed using the 1:2:0.25 slit on the goniometer and monochromatised non-doublet CuK_β radiation (the monochromator is a flat graphite plate) in the range of angles exceeding by a factor of ~5 the half-width of the diffraction maximum. This is necessary in order to avoid additional errors associated with the numerical analysis of a profile of complex shape. The wide range of scanning angles ensures a satisfactory

determination of the line "tails", which is essential for the accurate determination of the Fourier coefficients. The correct determination of the profile of the instrumental line is very important.[76] Corondum (α-Al_2O_3) or silver black are chosen as reference standards. Their line profiles are described by the function

$$b^2 = u\tan^2\theta + v\tan\theta + w,$$

where u, v, and w are constants and θ is the Wulff–Bragg angle.

The substructural characteristics of deposited catalysts must be determined in four stages. The first stage consists in the separation of the diffraction maxima of the active component from the background due to the presence of the carrier. In the course of such treatment, the catalyst and carrier intensity curves are normalised and the background due to the carrier can be fitted by a polynomial. In the case of a single-phase system (for example, a metallic black) the problem simplifies and involves the usual separation of the background from the diffraction maximum.

The second stage reduces to the isolation from the experimental curve of the intensity of the profile associated with the physical broadening of the line (allowance for the instrumental line width). The third stage involves the finding of the fraction of the physical broadening of the line associated solely with the fine dispersity of the system (allowance from microdistortions). Warren's method is used for this purpose.[77] The method involving the expansion in Fourier series of the functions describing the profiles of the diffraction maxima of the reference standard and the test specimen is used in the second and third stages.

The parameters of the size distribution of the crystallites or the distribution function are found in the fourth stage. The profile of the diffraction maximum depends in principle on the crystallite size distribution function. However, according to Guinier,[78] the distribution of the lengths of sections in the crystallite (chords) perpendicular to the reflecting plane can be determined directly from the X-ray line profiles. It has been suggested[79] that the *hkl* line profile, determined by the reflection from crystallites, coincides with the profile of the diffraction line which arises in the presence of a set of parallel and incoherent linear sections. The ratios of the lengths of these sections must be the same as those of the chords of the grains perpendicular to the reflecting [h, k, l] plane. According to Bertaut's formula,[79] the intensity of the diffraction maximum is

$$I(x) = \int_0^\infty \frac{\sin^2 \pi A m x}{(\pi A x)^2} q(m)\, dm,$$

where $x = \theta - \theta_y$ is the angular scattering relative to the centre of gravity of the lines for the angle θ, $q(m)$ the function of the probability of the distribution of the lengths m of the chords perpendicular to the reflecting plane of the lattice in the set of crystallites, $A = (2\cos\theta)/\lambda$, θ is the Wulff–Bragg angle, and λ the radiation wavelength. The use of this equation presupposes that only the part of the physical broadening caused by the small size of the crystallites enters into the diffraction maximum profile. The profile is deduced from Fourier coefficients and normalised:

$$f_N(x) = f(x) \Big/ \int_{-\infty}^{\infty} f(x)dx.$$

The normalised function has a number of properties.[80] Thus, for $x = 0$ (at the maximum), we have $f_N(0) = 1/\beta = DA$, where $D = \lambda/2\beta\cos\theta$ is the average effective size of the crystallites (according to the Selyakov–Scherrer procedure) and β is the integral half-width of the line profile. The normalised function $f_N(x)$ is related to the function $I(x)$ by the expression

$$I(x) = (M_1/A) f_N(x),$$

where M_1 is the first moment of the chord length distribution function $q(m)$. The moment of any order of the chord length distribution function

$$M_n = \int_0^\infty m^n q(m)\, dm, \qquad M_2 = I(0)$$

can be expressed in terms of M_1:

$$M_{n+2} = (n+1)(n+2) M_1 \int_0^\infty m^n h(m)\, dm,$$

where $h(m)$ is the cosine component of the Fourier transformant $f_N(x)$.

Thus, knowing the diffraction maximum profile, it is possible, in principle, to determine the parameters characterising the size distribution of the crystallites, because the moments of the chord distribution curve can be determined on the basis of these data. The function itself can be deduced from the moments of the distribution curve. The quantity $V = M_2 - M_1^2$ characterises the variance of the distribution. In a study[8] using various methods of describing the distribution, such as the δ-function, the Gaussian function, the overall logarithmic distribution, and the lognormal distribution, it has been shown that the last distribution describes correctly the distribution of the chords in metallic particles on different carriers. The quality of the fit is characterised by the reliability coefficient. In our investigation,[81] it was also suggested that the chords present in the set of crystallites obey the lognormal distribution law (LND):

$$q(m) = \frac{1}{\sigma\sqrt{2}\,\pi m} \exp - \left(\frac{\ln m - \ln \mu}{2\sigma^2} \right).$$

The parameters μ and σ of the distribution can be obtained from the moments of the distribution curve $q(m)$ by means of the formula

$$\mu = M_1^2/\sqrt{M_2}, \quad e^{\sigma^2} = M_2/M_1^2.$$

A computer program was devised to interpret the experimental data. The following input information is used: (1) the intensities of two X-ray lines, of the specimen and the reference standard, the initial and final scanning angles, the scanning steps for the specimen in the reference standard, and the number of Fourier coefficients which must be calculated; (2) the range of the expansions; (3) the positions of the line maxima (either the position itself is specified or the centre of gravity is calculated); (4) the lattice parameter and Young's modulus. Young's modulus is required for the calculation of the microdistortions using the two lines corresponding to reflections from the [h, k, l] plane in different directions.

The calculated output data are as follows: (1) the Fourier coefficients of the initial lines of the specimen and the standard, the Fourier coefficients of the true physical broadening of each line, and the Fourier coefficients of the broadening due to the block structure

and microdistortions; (2) the curves deduced for the true physical broadening and the block structure normalised with respect to area; (3) the moments of the chord size distribution curve; (4) the distribution of the microdistortions; (5) the average particle size calculated from the Selyakov–Scherrer formula using the integral half-width of the function of the broadening induced by the block structure; (6) the positions of the centres of gravity of the initial lines.

Knowing the LND parameters μ and σ, it is possible to find (1) the most probable size of the crystallites m_0, (2) the average size of the crystallites in the bulk phase m, and (3) the area of the surface formed by the set of crystallites.

Thus the method involving the determination of substructural characteristics, based on the harmonic analysis of the diffraction peak profiles, yields information about the sizes of the crystallites, which exceed by a factor of 10^3 the wavelength, the microdistortions of the crystallites equilibrated in the bulk phase, and the parameters determining the size distribution of the crystallites. An important case of the breakdown of order in the crystal is that of the planar disorder. This is particularly important for close-packed structures or structures made up of planar networks superimposed in accordance with a definite law. The deviations from the general law governing the deposition of layers relative to one another in such structures influence significantly the diffraction line profiles.[76,78]

In principle all the characteristics obtained by the method considered, apart from the size of the microdistortions, can be determined with the aid of an electron microscope. However, the electron microscope method is local in scope and requires the availability of a large statistical set of data. Furthermore, the electron beam can affect small particles with a low melting point. The surface area of metals on carriers can also be determined by the chemisorption method. However, it is subject to a series of limitations determined by the assumptions underlying it. The application of this method presupposes the selective nature of the adsorption, the knowledge of the stoichiometric coefficient for the chemisorption of the adsorbate, and the availability of information about the number of surface metal atoms. The method involving the determination of substructural characteristics is usually employed to establish the size of the crystallites and of the microdistortions equilibrated within the bulk of the crystallite. We were able to supplement this information by data concerning the size distribution of crystallites.[81–83]

III. Structural and substructural characteristics of catalyst carriers

1. Aluminium oxides

(a) Low-temperature forms

The dehydration of the initial aluminium hydroxides above 473 K gives rise to the formation of different low-temperature forms of the oxides, depending on the nature of the hydroxides: amorphous, χ, γ, ρ, and η. In terms of their structure, these oxides are defective spinels, in the structure of which 21.33 cations are distributed among 24 cationic sites. In conformity with the requirements of stoichiometry and electroneutrality, they are described by the general formula $Al_{8/3}\square_{1/3}O_4$. The differences between the forms are manifested by the distribution of vacancies among the cationic sites. It has been suggested that the vacancies in γ-Al_2O_3 are located preferentially in octahedra, while those in the η-forms are in tetrahedra.[84–89]

The diffraction patterns of the low-temperature forms of aluminium oxide, obtained from pseudoboehmite, bayerite, and gibbsite, differ only slightly from one another. Characteristic regions exhibiting differences in the diffraction pattern correspond to each form. Analysis of these differences constitutes the basis of quantitative phase analysis.[20,90,91]

The RDA curves for the low-temperature forms differ from one another less than the corresponding scattering intensity curves (the RDA curve for the amorphous phase obtained from the deposited hydroxide is an exception).[20,92–94] This indicates the similarity of their structures and the equality of the interatomic distances and of the coordination numbers in the first coordination spheres.

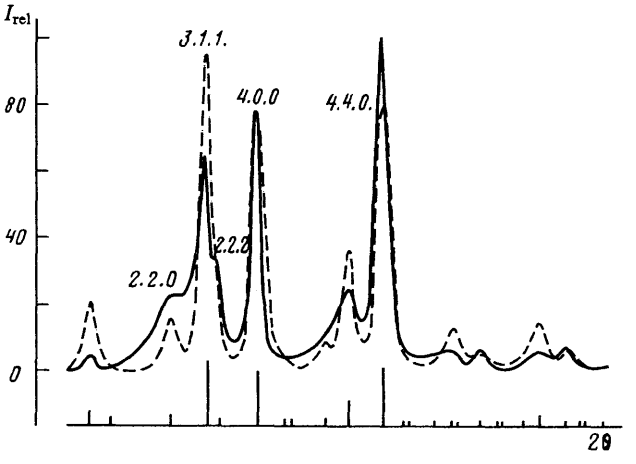


Figure 1. Fragments of the experimental (continuous line) diffraction pattern of η-Al_2O_3 and the pattern calculated on the basis of the defective spinel model with vacancies (dashed curve).[96]

We investigated by the FPA method the structures of the low-temperature oxides obtained from boehmite, pseudoboehmite, and bayerite.[95,96]

Models of defective spinels with different distributions of vacancies were used as the initial models for the calculation of the diffraction patterns: in octahedra—$Al[Al_{13.33}\square_{2.67}]O_{32}$ and in tetrahedra—$Al_{5.33}\square_{2.67}[Al_{16}]O_{32}$. The calculations were carried out within the framework of the space group $Fd3m$ with the origin of coordinates at a tetrahedral cation. Fig. 1 presents the experimental diffraction pattern of η-Al_2O_3 and the pattern calculated on the basis of the spinel with vacancies model. Evidently the most intense experimental line is 4.4.0, whereas according to the calculation the most intense line should be 3.1.1. Furthermore, the experimental intensity of the 2.2.2 line is appreciably higher than the calculated intensity. The difference between the calculated and experimental densities is also significant: the calculated density is 3.62 g cm^{-3}, while the experimental densities range from 3.35 to 3.42 g cm^{-3} for different forms. The unreliability factor R is about 40% for both models described by the general formula $Al_{21.23}\square_{2.67}O_{32}$. A change in the distributon of vacancies between the tetrahedral and octahedral sites does not reduce R.

In the real structures of the low-temperature oxides, an appreciable proportion of the anions exist as OH^- groups. Having included these groups in the structure, it is possible to describe the oxides by the general formula $Al_2O_3.nH_2O$, where $0 < n < 0.6$. According to this formula, the ratio of the numbers of cations and oxygen atoms is altered and this makes it possible to consider formally another spinel structure with a greater number of cationic vacancies. By varying the number of these vacancies in the range from 2.67 to 6.5, which corresponds to a number of water molecules between 0 and 0.6, it is possible to reduce the R factor to ~30% for the optimum number of vacancies of about 5. Variation of the distribution of vacancies among the cationic sites within the limits indicated does not reduce the R factor.

The space group $Fd3m$ permits the existence of two pairs of cationic sites when the origin of coordinates is selected at the point $\bar{4}3m$: it is possible to select the coordinates A(0; 0; 0) or A*(0.5; 0.5; 0.5) for the eightfold site (tetrahedra) and B(0.625; 0.625; 0.625) or B*(0.125; 0.125; 0.125) for the sixteenfold site (octahedra). The use of only the coordinates A* and B* is equivalent to a shift of the origin of coordinates, which naturally does not alter the R factor. A model of the type $A^*_{x_1}A_{x_2}B^*_{y_1}B_{y_2}O_{32-z}(OH,...)_z$ was examined. It follows from steric considerations that the use of type A* coordinates is possible only when the four nearest octahedral cations B are removed simultaneously. The disposition of the cations B* requires in its turn the removal of two nearest cations A displaced relative to one another by a vector with the coordinates 0.25; 0.25; 0.25. The B* atom is then located at the centre of the vector.

Several models of the structures of the low-temperature oxides were calculated. The data for modelling the η-Al_2O_3 structure are presented in Table 1, which also indicates the unreliability factors and the calculated densities. It follows from the Table that the lowest unreliability factor corresponds to the structural formula

$$A^*_{1.5}A_{6.75}B^*_{1.0}B_{10.0}O_{32-z}(OH,\ldots)_z,$$

where A and B are the spinel cationic sites and A* and B* are the non-spinel cationic sites.

Table 1. Modelling of the η-Al_2O_3 structure.

Parameter	1	2	3	4
x_1	–	–	–	1.5
x_2	5.66	8.0	7.75	6.75
y_1	–	–	–	1.0
y_2	16.0	13.66	11.5	10.0
R	45.6	44.7	34.1	10.1
d, g cm^{-3}	3.60–3.70		3.33–3.35	

Note. The following notation has been adopted for the models: 1, $A_{5.66}\square_{2.33}B_{16}O_{32}$; 2, $A_8B_{13.66}\square_{2.33}O_{32}$; 3 and 4, $A^*_{x_1}A_{x_2}B^*_{y_1}B_{y_2}.O_{32-z}(OH,...)_z$.

Table 2 presents the structural formulae and data for the distribution of cations in the low-temperature oxides. It is striking that anionic modification of the low-temperature oxide (inclusion of OH groups in the anionic skeleton) entails cationic modification (new positions of the aluminium cations). Such compounds are referred to as "protospinel" compounds.[97]

Table 2 shows that the fraction of tetrahedral cations is almost the same in all the forms (0.4–0.46). The greatest number of filled tetrahedra (8.5) combined with the smallest number of filled octahedra (10.0) occurs in the $\gamma_{\pi/\sigma e}$-Al_2O_3 form. In terms of the ratio of the numbers of tetrahedra and octahedra the oxides can be arranged in the series $\gamma_{\pi/\sigma e} > \eta > \gamma_{\sigma e}$.

Table 2. Structural formulae and the distribution of cations in low-temperature aluminium oxides.

Form of oxide	Fraction of tetrahedra (T)	Fraction of octrahedra (O)	T/O	A+B	A*+B*	$\frac{A+B}{A^*+B^*}$
$\gamma_{\sigma e}$	0.40	0.60	0.66	14.5	3.75	3.9
$\gamma_{\pi/\sigma e}$	0.46	0.54	0.85	15.75	2.75	5.7
η	0.43	0.57	0.75	16.75	2.5	6.7

Note. The following forms of the oxides were examined:

$\gamma_{\sigma e} - A^*_{1.75}A_{5.50}B^*_{2.0}B_{9.0}O_{22.75}(OH,\ldots)_{9.25}$;

$\gamma_{\pi/\sigma e} - A^*_{1.75}A_{6.75}B^*_{1.0}B_{9.0}O_{23.5}(OH,\ldots)_{8.50}$;

$\eta - A^*_{1.50}A_{6.75}B^*_{1.0}B_{10.0}O_{23.75}(OH,\ldots)_{6.25}$.

Thus on the basis of the real diffraction pattern and using the method of the full-profile analysis, we established that the low-temperature forms γ- and η-Al_2O_3 cannot be described as spinel-type structures with a statistical or regular distribution of vacancies. If the space group $Fd3m$ is adopted as a basis, then the above forms can be regarded as structures in which two allowed tetrahedral and two allowed octahedral sites are filled statistically. Each form has its own characteristic number of anions consisting of hydroxy-groups or other residual groups of the type NO_3^-, Cl^-, etc.

The OH groups were regarded[98] as the structural elements of the low-temperature forms, but it was assumed that there are vacancies in the cationic sublattice: $Al_{20}\square_4O_{28}(OH)_4$. Using the general Debye formula for the scattering intensity and comparing the synthesised and experimental diffraction patterns, Espinat, et al.[99] confirmed the validity of the model of γ-Al_2O_3 described above.

(b) High-temperature forms

The high-temperature δ- and θ-forms of aluminium oxide are also used widely as carriers for catalysts of high-temperature processes. They are produced from γ- and η-Al_2O_3 by dehydration at temperatures above 1100 K. It has been shown by the RDA method[94] that, together with the loss of OH groups, dehydration involves a rearrangement of the structures associated with a decrease and increase in the filling of the octahedral and tetrahedral cationic sites respectively. Under these conditons, new cationic sites, uncharacteristic of the low-temperature forms, are filled. The high-temperature aluminium oxides differ in the filling of the cationic sites and are described by the general formula $E_RA^*_{x_3}A_{x_4}B^*_{y_3}B_{y_4}O_{32-f}(OH,...)_f$, where $R + x_3 + x_4 + y_3 + y_4 < 21.33$ and f is the number of structural OH and other groups. The

formation of the δ- and θ-forms can be regarded as a result of the structural compensation for the partial removal of hydroxy-groups and other anionic "impurities" during the complete dehydration of the hydroxides to anhydrous α-Al_2O_3.

(c) Promoted aluminium oxides

The refinement of the structures of the low-temperature aluminium oxides made it possible to put forward a hypothesis concerning the mechanism of the formation of the solid solutions and non-stoichiometric spinels obtained when cations and anions are introduced. Since all the ionic sites in the structures of the oxides are characterised as regards their positions in the cell and the degree of their filling, it is possible to construct models of the hydroxide oxide compounds modified by cations and anions.

The polymorphic transformations occurring on aluminium oxides have been investigated[100–106] and the phase compositions and structures of the low-temperature oxides promoted by divalent and trivalent cations (Mg^{2+}, Ni^{2+}, Cu^{2+}, Cr^{3+}) have been analysed. It has been shown[102–104] that the low-temperature solid solutions are formed in these systems as a result of the filling of the vacancies in the bulk-phase structure of the spinel and by the substitution of certain tetrahedral and octahedral sites in the structure of the protospinel. The substitution of aluminium by a divalent cation in the protospinel structure, without a distinct preference for an octahedral or a tetrahedral environment, leads to the breakdown of the electroneutrality of the Al_2O_3 molecule. The excess charge can then be compensated either by an increase in the number of hydroxy-groups in the anionic skeleton (on formation of mixtures of hydroxides by coprecipitation) or by the removal of some of the anions, i.e. OH^- and NO_3^- (during heat treatment). In both cases, a general disordering of the structure, in particular of the anionic skeleton, is observed, which is manifested by a frequently noted broadening of the diffraction maxima. Another way of compensating for the excess charge is also possible. This can be achieved if the cations occupy preferentially the tetrahedral sites and involves a rearrangement of the cationic skeleton. Such rearrangement can be attained by the migration of aluminium from the A* and B* sites to the A and B sites respectively and the disposition of the divalent cations in the A sites. This results in the formation of a normal spinel of the type AB_2O_4. The location of the divalent cation in a tetrahedral site A does not require structural compensation, because it corresponds to the arrangement typical for a spinel. In such systems an increase in temperature does not entail the formation of the intermediate δ- and θ-forms of Al_2O_3.

The distribution of cations in the structure of an alumino-magnesium spinel with a non-stoichiometric composition was refined[107] by the FPA method. The magnesium and aluminium cations were detected at sites uncharacteristic of a spinel. These cations are regarded as point defects. It was established by the method involving the determination of substructural characteristics that the dominant type of defects in the specimen is packing defects caused by half-dislocations, whose concentration is virtually identical with the concentration of the detected point defects. The presence in the specimen of specific extended defects, whose orientation is identical with that of the half-dislocation vector, was confirmed by high-resolution electron microscopy. The non-stoichiometric aluminomagnesium spinel was investigated by a version of the FPA program, in which provision is made for the possibility of refining individual profile parameters of the diffraction peaks. The solution of this problem can also be assisted by the application of the versions used in other studies.[68,108]

2. Carbon carriers for catalysts

Carbon materials are widely used as sorbents, but recently porous carbon materials have come to be used also as carriers for metallic catalysts and as catalysts themselves. The study of the structural and substructural characteristics of these materials is extremely important for the elucidation of their adsorption and texture characteristics in order to achieve an understanding of the chemistry of their surfaces. The carbon materials investigated include Sibunit, Altunit, activated charcoals (from Saran plastic and birchwood), acetylenic carbon black, and brown coal semicoke.[20,109–111]

The following characteristics were determined for Sibunit: degree of crystallinity K = 0.65, fraction of aromatic carbon A = 1.0, degree of three-dimensional order γ = 0.3, size of crystallites in the plane of aromatic layers L_a = 35 Å, size of crystallites in the direction at right angles to the plane of aromatic layers (thickness of packets of layers) L_c = 40 Å. The size distribution of the particles was determined for Altunit by X-ray diffraction, which yielded a variance of the distribution V = 230 Å^2, the average particle size L = 20 Å, and the most probable particle size m_0 = 10 Å. It was established that microdiffraction does not occur in Altunit. It was suggested that Silbunit has a graphite-like structure, while Altunit has a diamond-like structure. The interatomic distances r and coordination numbers were calculated for these structures and were determined from the RDA curve (Tables 3 and 4).

Table 3. Structural characteristics of Sibunit.[20]

r, Å		C.N.	
expt.	calc.	expt.	calc.
1.44	1.42	2.2	3
2.44	2.46	6.0	6
2.90	2.84	3.6	3
3.36	3.37	2.5	2
–	3.66	—	12
3.78	3.76	13.1	6
–	4.17	diffuse	12
4.29	4.26	peaks	6
–	4.41	ditto	12
4.88	4.92	"	6

Table 4. Structural characteristics of Altunit.[20]

r, Å		C.N.	
expt.	calc.	expt.	calc.
1.58	1.54	2.4	4
2.54	2.52	11.4	12
3.02	2.96	10.1	12
3.46	3.57	3.0	6
3.90	3.89	10.0	12
4.38	4.37	22.0	24
4.78	4.63	16.0	16
5.22	5.28	24.0	24
5.74	5.64	24.3	24

Examination of Tables 3 and 4 showed that Tibunit has a somewhat disordered graphite structure while Altunit has the diamond structure. A globule 35 Å in diameter is a coherently scattering element in Sibunit, which corresponds to ~100 unit cells. The layered structure is retained in such a globule, but the interlayer distance along the c axis has increased owing to the azimuthal disorientation of the graphite networks. Together with the three-dimensionally ordered crystalline carbon, the specimen contains also carbon in the form of two-dimensional hexagonal formations, i.e. the entire carbon is aromatic (A = 1).

The diamond structure of Altunit is characterised by an increased unit cell parameter a (Δa = 0.007 Å). This change is apparently associated with the high dispersity of the material (the size of the crystallites is ~20 Å). An important characteristic of Altunit is the absence of microdistortions equilibrated in the bulk of the crystallite. The [size] distribution of the particles in this material is fairly narrow.

Carbon carriers also include activated charcoals differing in their porous structure: Saran and birchwood charcoals, brown coal semicoke, and acetylenic carbon black.[112] The Saran charcoal has the most perfect structure; the highest degree of three-dimensional order (γ = 0.3) and high degrees of aromaticity and crystallinity are characteristic of this material. The RDA curves for the above carbon materials show that the Saran charcoal is also distinguished by a more pronounced long-range order than, for example, acetylenic carbon black, which exhibits a weak three-dimensional order and a low aromaticity and crystallinity.

IV. Structural and substructural characteristics of deposited and non-deposited monometallic catalysts

The development of X-ray diffraction methods for the study of highly disperse systems and refinement of the structures of catalyst carriers have made it possible to carry out precision analyses of highly disperse metal–carrier systems. In the course of such investigations, it was essential to answer the question whether the metal–carrier system is additive and whether it is permissible to use the structural and substructural characteristics of highly disperse non-deposited metals (blacks) in the study of deposited particles. Can blacks serve as reference standards for the construction of difference RDA curves? What is the role of the carrier in the stabilisation of the active component?

Table 5. Substructural characteristics of metal blacks.[81,82]

Crystallographic direction	L, Å		$10^{-2} \cdot V$, Å^2		m_0, Å		$10^3 \cdot \varepsilon$	
	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd
[111]	38	370	9.8	111	16	330	3.8	1.2
[100]	38	215	4.8	50	22	180	3.8	1.4

The study of the structural and substructural characteristics of highly disperse and non-deposited metals (Pt, Ir,[35,81] Pd,[82] and Ni[112]) showed that, as the size of the crystallites decreases from 700 to 40 Å, the coordination peaks (CP) on the RDA curves are broadened and their area diminishes. The mean square displacements of the atoms relative to the equilibrium position are ~3% of the shortest distance. Analysis of the RDA curves showed that the blacks exist in a polydisperse state, i.e. the coordination peak areas on these curves do not exhibit an unambiguous dependence on dispersity. The substructural characteristics of the non-deposited metals depend significantly on the average size L of the crystallites (Table 5): for large values of L, a wider size distribution of the crystallites is observed, mainly in the direction of the growth of the particles [111], while small particles are isotropic. Small crystallites are distinguished by greater microdistortions, which alter the structural characteristics—the unit cell parameter (by 3×10^{-3} Å) and the coordination numbers.[35]

The substructural characteristics of the non-deposited and deposited highly disperse metals were compared for aluminoplatinum catalysts and platinum blacks.[83] Model catalysts containing 3.8 wt.% Pt on γ-Al_2O_3 and blacks heat-treated at different temperatures were used as the objects of study. Table 6 shows that the black and the non-deposited aluminoplatinum catalyst, heat-treated at the same temperature (773 K), are characterised by significantly different average sizes of the crystallites and variances of the size distributions of the particles. The size distribution of the platinum particles in the non-deposited catalyst is narrower.

Table 6. Comparison of the substructural characteristics of highly disperse deposited and massive metals.[83]

Specimen, heat treatment temperature	Pt, wt.%	S_{sp}, m^2 g^{-1}	Substructural characteristics			Microdistortions, $10^3\varepsilon$
			L, Å	$V \cdot 10^{-2}$, Å^2	m_0, Å	
Pt/Al_2O_3, 773 K	3.8	88±8	46	3.7	35	–
Pt/Al_2O_3, 1103 K	3.8	1	160	96	100	–
Pt black, 773 K	–	6±2	150	154	70	1.4
Pt black, 333 K	–	–	38	9.8	20	3.8

The structural characteristics of the non-deposited metals were obtained by the RDA method. Table 7 indicates the interatomic distances and the coordination peak areas as well as the sizes of the crystallites (L) for aluminoplatinum catalysts containing 2.4 and 7 wt.% Pt on γ-Al_2O_3. Analysis of the Table shows that only a certain proportion of platinum is present in the face-centred cubic structure of the metal and varies within the range 0.5–0.7. The ratios of the coordination peak areas corresponding to different coordination spheres (26:58:62:102 and 112:245:234:465) for catalysts with platinum contents of 2.4 and 7 wt.% respectively are close to the theoretical ratios 1:2:2:4. This shows that the metal particles are ordered and well crystallised.

Thus it follows from the comparison of the substructural and structural characteristics of the non-deposited and deposited metals that the carrier influences significantly the state of the metallic highly

disperse particles: the structure of the deposited particles is closer to ideality (the changes in the interatomic distances and coordination numbers characteristic of the blacks are not observed and there are no microdistortions). It becomes clear why the affinity of the adsorption isotherms on the deposited catalysts holds only when the crystallised black is used as the reference standard:[113] the metal on the carrier surface apparently exists in a micro-single crystal state, i.e. the similarity of the adsorption properties is a consequence of the identity of the structural and substructural characteristics.

Table 7. Theoretical and experimental interatomic distances (r) and coordination numbers for deposited aluminoplatinum catalysts.

Coordination sphere	C.N.	2.4% Pt/γ-Al_2O_3				7% Pt/γ-Al_2O_3			
		r, Å		CP area, el.^{2}		r, Å		CP area, el.^{2}	
		calc.	theory	calc.	theory	calc.	theory	calc.	theory
I	12	2.78	2.78	54	26	2.78	2.80	170	112
II	24	4.80	4.80	108	58	4.80	4.78	340	245
IV	24	6.21	6.20	108	62	6.21	6.16	340	234
VI	48	7.34	7.40	216	102	7.34	7.34	680	465
P_e/P_c^*		0.51				0.69			
L, Å		30				40			

*P_e/P_c is the ratio of the experimental and calculated coordination peak areas.

Comparison of the structural and substructural characteristics of the deposited and non-deposited metals shows that highly disperse blacks cannot serve as reference standards for the construction of the difference RDA curves in the study of the phase composition of deposited catalysts.

Catalysts containing 1.5–30 wt.% of platinum, iridium, and palladium on γ-, χ-, η-, and θ-Al_2O_3 [36–38,40,114–117] and on carbon carriers[39] were also investigated, the dispersity of the active component was estimated, and data were obtained for the phase compositions of the catalysts at different stages of their preparation. The dispersity and composition of the active component depend on the conditions in the preparation of the catalyst: when they are prepared by the method involving the impregnation of carriers with a solution of the metal-containing component, the temperature and composition of the gas phase play a significant role. After impregnation with a chlorine-containing substance and drying in air, a complex between the carrier and the $(MCl)_6^{2-}$ anion is formed in the catalyst, some of the chloride ions in the complex being replaced by hydroxy-groups. Activation by oxidative treatment at 723 K leads to the decomposition of the complex and an interaction phase, incorporating the metal ion, arises between the carrier and the active component. This phase has a spinel-like structure.[36,115] Metal ions are not distributed statistically on the surface of the carrier but are incorported in its structure. The reduced catalysts contain not only the metallic phase but also the interaction phase.

Fig. 2*a* presents fragments of the diffraction scattering intensity curves on the η-Al_2O_3 carrier and the 10 wt.% Ir/η-Al_2O_3 catalyst as well as the difference intensity curve (DIC). On the latter, there is a diffraction maximum due to iridium (0.2.2) (2θ = 69°2′) and the maximum (4.4.0) of the protospinel phase, the unit cell parameter of which has increased by 0.01 Å compared with that of the carrier. The position of the 0.2.2 line coincides with the theoretical position calculated for the iridium single crystal with a face-centred cubic latice. The RDA curve was plotted on the basis of the difference intensity curve (Fig. 2*b*). Together with the peaks corresponding to the interatomic distances in the face-centred cubic lattice of iridium (r = 2.7, 3.84, 4.70, 5.43, 6.07, 7.18 Å), the RDA curve contains a peak due to the protospinel interaction phase (r = 3.3, 4.2, 5.2, etc. Å). The amount of iridium incorporated in the form of ions in the interaction phase is determined by the overall content of the deposited metal, the structure of the carrier, and the temperature and composition of the gaseous medium. For a large iridium content in the ionic form, the specimens exhibit an enhanced chemisorption capacity in relation to hydrogen, which is associated with the additional adsorption of hydrogen on the modified carrier.[37,38]

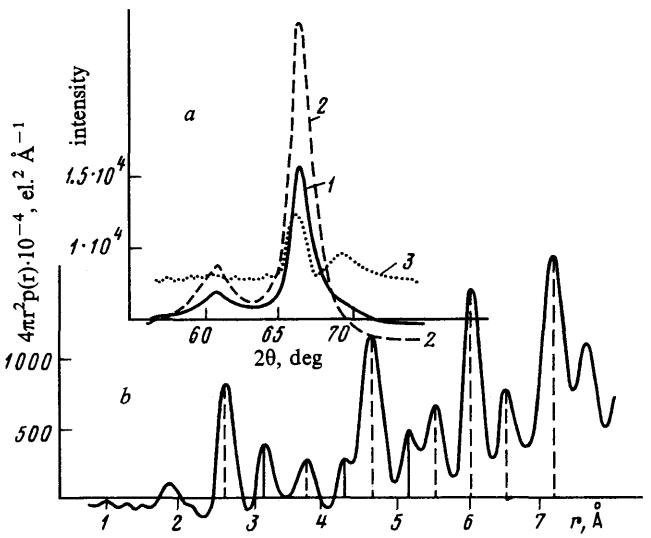


Figure 2. Fragments of the curves for the diffraction scattering of X-rays by the 10% Ir/η-Al_2O_3 catalyst (curve *1*) and the carrier (curve *2*) (in counts) and the difference intensity curve (curve *3*) (in electronic units) (*a*) as well as the difference RDA curve calculated from the difference intensity curve[42] (*b*).

The study of different deposited metallic catalysts showed[20] that in the general case the metal can exist in the following states: (a) as metallic particles distributed on the carrier surface; (b) as oxide particles or as an oxide film on the surfaces of large crystallites; (c) as the phase due to the interaction with the carrier, which is formed on activation (heat treatment with air) of the catalyst. The existence of these states and their thermal stability together with diffusional atom (particle) migration processes influence one of the most important characteristics of the deposited catalyst—the dispersity of the active component.

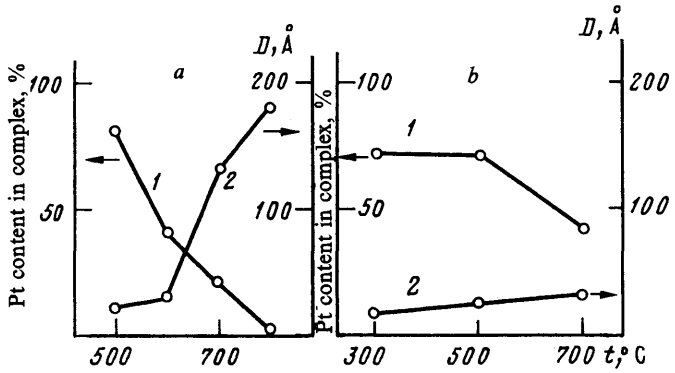


Figure 3. Dependence of the amount of Pt^+ (line *1*) and the Pt^0 particle size (line *2*) on the heat treatment temperature of the aluminoplatinum catalyst in oxidising (*a*) and reducing (*b*) gaseous media.[129]

Table 8. Certain characteristics of platinum catalysts on various carriers.

Carrier	Specific surface of carrier $m^2\ g^{-1}$	Pt^0/Pt^+	*L*, Å
γ-Al_2O_3	140	0.6	30
η-Al_2O_3	350	0.5	30
θ-Al_2O_3	70	0.4	30
SiO_2	300	1.0	100
C	600	0.4	30
$ZnAl_2O_4$	12	1.0	350

Fig. 3 presents the dependences of the sizes of the platinum crystallites *D* in the aluminoplatinum catalyst and of the amount of platinum incorporated in the interaction phase on the temperature in various gaseous media. In an oxidising medium (Fig. 3*a*), an antiparallel relation is observed between the amount of Pt^+ in the carrier structure and the dispersity of the metallic particles distributed on the surface. Evidently, the decomposition of the spinel-like phase results in the concentration of atoms on the surface and in the sintering of the active components. The decrease in the amount of platinum bound to the carrier apparently lowers the number of sites where the metallic particles are fixed on the carrier surface, which entails the sintering of these particles. A similar explanation was given, for example, in a study[118] of the role of ions as "energy traps" for metallic particles. In a reducing medium (Fig. 3*b*), a decrease in the amount of platinum bound to the carrier does not cause a sharp alteration of the sizes of the crystallites, because above 773 K an increase in the dispersity of the active component due to the dissolution of hydrogen in platinum is observed.[114] During phase transformations in the carrier, the interaction phase also decomposes, this being accompanied by the appearance of highly disperse metallic particles.[38] The Pt^0 and Pt^+ active centres exhibit definite catalytic activity: Pt^0 is active in the cyclohexane dehydrogenation reaction and Pt^+ is active in the dehydrocyclisation of n-heptane.[119,120] Table 8 presents the results of the comparison of the platinum impregnation catalysts deposited on sections of the carrier differing in their chemical nature and in their specific surfaces.

The Table shows that the amount of metal incorporated in the interaction phase is determined not by the surface area of the carrier but by its structure. The bulk-phase structure of the carrier determines also the number of reactive groups which can participate in the formation of the sites where highly disperse zerovalent metal particles are fixed.

V. Determination of the phase composition of deposited bimetallic catalysts

It is fairly difficult to obtain information about the structure of highly disperse bimetallic deposited catalysts, because mainly a comparative method is used for this purpose: the RDA curves for the carrier, the active component with the carrier, and the modifying element with the carrier are compared with the RDA curves for the bimetallic catalyst. The results of the X-ray diffraction study are therefore mainly qualitative and concern the phase composition. We shall consider the study of platinum–rhenium, platinum–tin, and nickel–tin catalysts.

1. Platinum–rhenium catalysts

Platinun–rhenium catalysts on γ-Al_2O_3, obtained by the impregnation method, were investigated by Ushakov, et al.,[121] who compared specimens containing only platinum, only rhenium, and a combination comprising 2 wt.% Pt + 0.8 wt.% Re. Analysis of the difference curves showed that (1) in both the bimetallic and aluminorhenium catalysts there is no metallic rhenium phase; (2) the areas of the coordination peaks for the platinum structure in the bimetallic catalyst are smaller than in the aluminoplatinum catalyst; (3) the areas of the coordination peaks for the carrier structure in the bimetallic system increase for the octahedral distances (Fig. 4). This permitted the conclusion that the rhenium in the bimetallic catalyst is present in the oxidised state (during preparation, the carrier interacts with rhenium ions) and the dispersity of platinum increases.

Analysis of the diffraction patterns recorded accurately by a procedure involving the accumulation of 2×10^5 counts did not reveal the shift of the diffraction maxima characteristic of the platinum–rhenium alloy. Platinum–rhenium catalysts on silica gel, obtained by the method involving the successive impregnation of the carrier with NH_4ReO_4 and H_2PtCl_6 solutions and the deposition of the organometallic complexes $[Re(OC_2H_5)_3]_3$ and $Pt(\pi\text{-}C_4H_7)_2$, were also investigated.[122]

Fig. 4 presents the RDA curves for the two specimens investigated. Im the impregnation specimen, the active component exists in a fairly coarsely disperse state: all the coordination peaks correspond, as regards their areas and positions, to the structures of the metallic rhenium and platinum, the Pt–Re alloy phase not being observed. The RDA curve for the catalyst obtained by the immobilisation of the platinum particles on the rhenium ion-modified silica gel surface has only the first coordination peak of the face-centred cubic structure of platinum. Hence it follows that platinum crystallises in a highly disperse state (the crystallite diameters are ~6 Å). The state of rhenium can be inferred from the coordination peak at r = 2.48 Å. This value of r corresponds to the

Re–Re distance in the trinuclear rhenium complexes used for the deposition of low-valence ions on the silica gel surface. The conclusions reached were confirmed by other physical methods (EXAFS, X-ray photoelectron spectroscopy, chemisorption).[123]

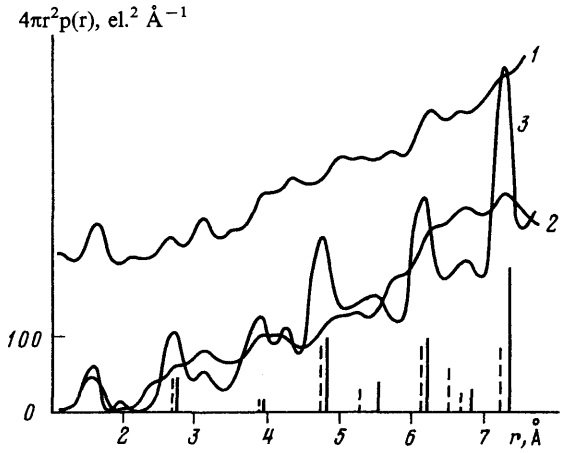


Figure 4. RDA curves for the SiO_2 carrier (curve *1*) and the platinum–rhenium catalysts obtained from organometallic compounds (curve *2*) and by the impregnation method (curve *3*).[123]

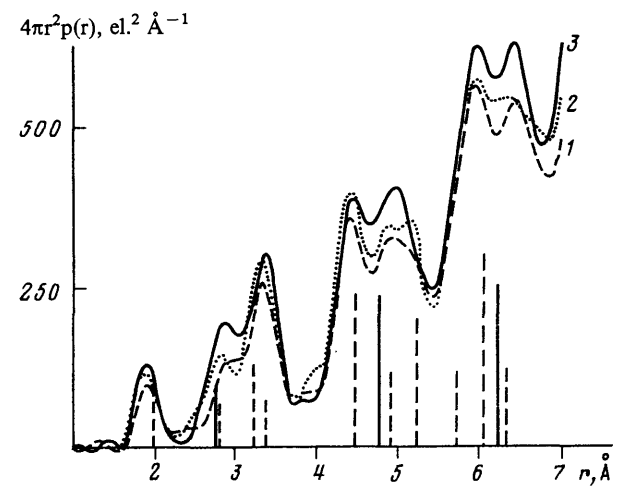


Figure 5. RDA curves for the γ-Al_2O_3 carrier (curve *1*), the aluminotin catalyst (curve *2*), and the aluminoplatinum–tin catalyst (curve *3*).[124]

2. Platinum–tin catalysts

In the course of the development of a thermostable and selective catalyst for the aromatisation of paraffinic hydrocarbons,[124,125] it was observed that the aromatising activity and stability of the catalysts synthesised by the interaction of platinum tetrachloride with low-valence tin ions stabilised on the aluminium oxide surface is appreciably higher than that of the reference catalyst prepared by the impregnation method. In order to elucidate the causes of the modifying effect of tin, a study was made of specimens containing 2.5 wt.% Sn and 2.6 wt.% Pt + 3.9 wt.% Sn on γ-Al_2O_3. The form of the RDA curves (Fig. 5) indicates the absence of the metallic tin phase and of Pt–Sn alloys.

The dispersity of the crystalline platinum phase is high (the size of the crystallite is ~10 Å) and tin is incorporated in the carrier surface, forming a spinel-like phase (the areas of the coordination peaks corresponding to the A–B, B–O, and B–B distances increase). Mössbauer spectroscopic data also confirmed that tin does not form an alloy with platinum but is present in the carrier structure. The effective charge on the platinum atoms decreases in the presence of Sn^{2+} ions (X-ray photoelectron spectroscopic data), which alters the adsorption and catalytic properties of platinum. The coordinatively unsaturated tin ions on the carrier surface are centres for the stabilisation of platinum atoms. The increase in the energy of the interaction of the active component with the carrier is indicated by the thermal stability of the active phase (the dispersity of platinum is close to the limiting value and persists for a long time up to a reduction temperature of ~873 K).

When silicon oxide modified by tin acetate is used as the carrier,[126] the phase composition of the active component is different: part of the tin (~$^1/_3$) is reduced to the zerovalent state, forming the Pt_3Sn alloy, while the remainder is bound chemically to the SiO_2 surface. Thus the state of tin on silica gel is different than on γ-Al_2O_3. The catalytic properties are likewise different: the catalysts on γ-Al_2O_3 propagate the hydrogenolysis and aromatisation reactions at temperatures above 673 K and are inactive up to this temperature in benzene and cyclohexane hydrogenation reactions, whereas catalysts on SiO_2 are active in the former reaction already at 373 K and in the latter at 523 K.

The platinum–tin catalysts on a zinc–aluminium spinel are used for the single-stage dehydrogenation of lower paraffins to diolefins in water vapour at atmospheric pressure.[127] The study of the genesis of the phase composition of a catalyst containing 0.4–1 wt.% Pt + 1–5 wt.% Sn at all stages of their preparation showed that the gaseous medium used in the preliminary heat treatment affects significantly the composition of the catalyst. Reduction directly after drying of both monometallic and bimetallic catalysts (H_2, 848 K) leads to the formation of inactive intermetallic compounds with zinc (ZnO enters into the composition of the carrier as an excess phase), the composition of these compounds being determined by the ZnO content. After activation in an oxidising medium with water vapour, the X-ray diffraction patterns of the platinum–tin and monometallic platinum catalysts show the platinum lines corresponding to the normal unit cell parameter. Tin is then present in an oxidised state. With increase in the zinc content, there is also an increase in the dispersity of platinum (the particle size diminishes from 130 to 60 Å) and there is also a decrease in the fraction of well crystallised platinum. After activation, there is no interaction of the active components with one another and with the carrier and the SnO_2 and Pt phases are present on the carrier surface.

A solid solution of tin in platinum with a face-centred cubic lattice is formed during the dehydrogenation reaction. For the ratios Pt:Sn = 1:3 and 1:5, the intermetallic compound Pt_3Sn with a primitive cubic cell is formed, whereas in the presence of a high platinum content the PtSn and $PtSn_2$ alloys are produced.

An important feature of the catalysts investigated is that the platinum–tin alloys are stable only in the reaction medium and are produced solely when acted upon by the latter. The regeneration of

the catalyst (elimination of carbonaceous deposits) leads to the decomposition of the alloys. However, when a new dehydrogenation cycle is carried out, the platinum–tin alloys are reformed already in the first minutes.

The role of the modifying additive is interesting. The tin in the platinum catalysts deposited on a spinel can play a dual role—it can serve either as a promoting agent, increasing appreciably the activity and selectivity of platinum in the lower paraffin dehydrogenation reaction (alloys containing $\leqslant 25$ at.% of tin, having the platinum structure, are then formed in the catalyst) or behaves as a catalytic poison (on formation of alloys with a high tin content). Similar results were obtained for catalysts deposited on a magnesium–aluminium spinel.

3. Nickel–tin catalysts

The addition of tin to aluminonickel catalysts alters significantly the mode of reaction of unsaturated hydrocarbons: nickel catalysts accelerate the hydrogenolysis reaction, while nickel–tin catalysts on γ-Al_2O_3 exhibit an aromatising activity at high temperatures, which is typical of the Pt/Al_2O_3 catalysts.[124]

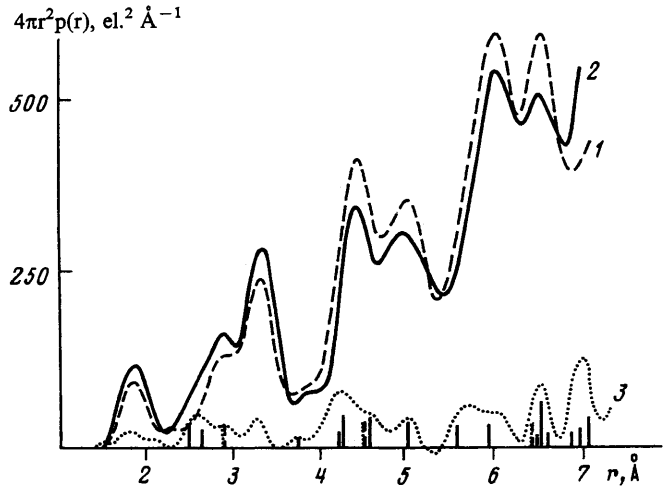


Figure 6. RDA curves for the γ-Al_2O_3 carrier (curve *1*) and the aluminonickel–tin catalyst (curve *2*) as well as the difference RDA curve (curve *3*).[128]

Diffractometric studies[128] of nickel–tin catalysts (1.7 wt.% Ni + 3.5 wt.% Sn on aluminium oxide) showed that the α-Sn phase with a particle size of 50 Å and a metallic nickel phase are formed in the specimens reduced at 823 K. Metallic nickel phases with a face-centred cubic structure (r = 2.50, 4.30, 5.56, and 6.58 Å), metallic α-Sn phases (r = 2.97, 3.17, 4.57, and 6.49 Å), and metallic nickel phases with a hexagonal structure (r = 2.66, 3.75, 4.33, 4.60, 5.08, and 5.93 Å) are detected on the difference RDA curve (Fig. 6). The stabilisation of the last structure is known to require the obligatory presence of admixtures of other metals. Indeed, data concerning the effect of temperature on the relative magnetisation of nickel–tin catalysts show that their Curie point is lower by 40 K than for the catalyst without the additive. This confirms the formation of a nickel–tin alloy (containing 2% of tin). X-Ray spectroscopic data and analysis of the Mössbauer spectra also confirm the presence of a Ni–Sn alloy in the catalysts investigated, but the Mössbauer spectroscopic data indicate also the presence of Sn^{2+} in the carrier structure. The RDA curves also have maxima corresponding to the interatomic distances in the phase in which the tin interacts with aluminium oxide (r = 1.76 and 3.30 Å). The surface Sn^{2+} ions on the carrier are apparently centres for the stabilisation of highly disperse alloy particles.

VI. Conclusion

Thus, despite the apparently small amount of information contained in the initial diffraction data (the diffraction peaks are small, diffuse, and frequently superimposed on another), an appropriate formulation of the experiment with interpretation of the results by modern computer techniques makes it possible to obtain a lot of useful data on the phase composition (RDA method) and the structural (FPA method) and substructural (RDA and MDSC methods) characteristics of the test objects.

During the last decade, the long-range fine structure of the X-ray absorption spectra of a given chemical element (EXAFS spectroscopy) began to be studied widely in the investigation of the structure of its local environment.[46,47] This method has many advantages over the X-ray RDA method: (1) selectivity, associated with the possibility of obtaining independent RDA curves for the local environment of each chemical element in the specimen; (2) the possibility of determining not only the interatomic distances and coordination numbers but also the kind of atoms in the vicinity of the specified atom. A powerful source of X-rays (synchrotron radiation) is usually employed in this method, which makes it highly sensitive and rapid. Such a source can be used also in the X-ray diffraction method. However, the EXAFS method is inferior to the X-ray diffraction RDA method in that the information obtained with its aid concerns mainly 1–2 coordination spheres in the structure, which significantly hinders the analysis of the structural characteristics. On the other hand, one obtains by the EXAFS method interatomic distances which are not absolute but involve a phase shift. Problems arise also in the determination of the coordination numbers.

Despite the existence of a number of difficulties concerning also the very principles of the EXAFS method and the procedures used to extract structural information, at the present time it is widely employed in the study of catalysts.[47] The data for metallic deposited catalysts obtained by this method in the main agree with the results obtained previously by the X-ray diffraction RDA method. It is apparently useful to combine the two methods.

References

1. R M Lambert *Characterisation of Catalysts* (Edited by J M Thomas, R M Lambert) (Translated into Russian), Mir, Moscow, 1983, 294 pp.
2. J R Anderson *Structure of Metallic Catalysts* (Translated into Russian), Mir, Moscow, 1978, p. 398
3. V Valvoda *First European Powder Diffraction Conference: Abstracts*, Münich, 1991, p. 7

4. M Gamarnik *First European Powder Diffraction Conference: Abstracts*, Münich, 1991, p. 38
5. N Mattern *First European Powder Diffraction Conference: Abstracts*, Münich, 1991, p. 41
6. L G Shabelnikov *First European Powder Diffraction Conference: Abstracts*, Münich, 1991, p. 60
7. J F Faudon, G Bergeret, A Renouprez *First European Powder Diffraction Conference: Abstracts*, Münich, 1991, p. 117
8. E M Moroz, V A Ushakov, S V Bogdanov *First European Powder Diffraction Conference: Abstracts*, Münich, 1991, p. 118
9. K Richter, B Peplinski, P Doppler *First European Powder Diffraction Conference: Abstracts*, Münich, 1991, p. 128
10. R F Skryshevskii *Strukturnyi Analiz Zhidkostei i Amorfnykh Tel* (Structural Analysis of Liquids and Amorphous Bodies), Vys. Shkola, Moscow, 1980, 328 pp.
11. A N V Temperley, J S Rowlinson, G S Rushbrooke *Physics of Simple Liquids. Experimental Studies* (Translated into Russian), Mir, Moscow, 1971, 308 pp.
12. Yu G Poltavtsev *Struktura Poluprovodnikovykh Rasplavov* (The Structure of Semiconductor Melts), Metallurgiya, Moscow, 1984, 176 pp.
13. R Mozzi, B E Warren *J. Appl. Crystallogr.*, 1969, **2**(7) 149
14. B K Vainshtein *Kristallografiya*, 1957, **2** 29
15. R Hoseman, S N Bagchi *Direct Analysis of Diffraction by Matter*, Amsterdam, 1962, p. 111
16. Ya I Stetsiv *Kristallografiya*, 1973, **18** 484
17. V G Nagornyi, D K Khakimov, A N Avdeev *Kristallografiya*, 1973, **20** 900
18. F A Brusentsev *Matematicheskie Metody Resheniya Nekotorykh Zadach Fiziki Tverdogo Tela i Strukturnoi Khimii s Ispol'zovaniem ETsVM* (Mathematical Methods for the Solution of Certain Problems in Solid State Physics and Structural Chemistry Using Computers), Naukov Dumka, Kiev, 1973, p. 239
19. J T Randall *Diffraction of X-Rays and Electrons by Amorphous Solids, Liquids and Gases*, London, 1964, 240 pp.
20. E M Moroz, Doctoral Thesis in Chemical Sciences, Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1989, 333 pp.
21. L I Tatarinova *Struktura Tverdykh Amorfnykh i Zhidkikh Veshchestv* (The Structure of Solid Amorphous and Liquid Substances), Nauka, Moscow, 1983, p. 151
22. A J Leonard, P N Semaille, J J Fripiat *Proc. British Ceramic Solid*, 1969, **13** 109
23. P Ratnasamy, A J Leonard *Catal. Rev.*, 1972, **6** 293
24. P Ratnasamy, A J Leonard, L Rodrique, J J Fripiat *J. Catal.*, 1973, **29** 374
25. P Ratnasamy, A J Leonard *J. Phys. Chem.*, 1972, **76** 1838
26. P Gallezot, A Bienenstock, M Boudart *Nouv. J. Chim.*, 1978, **2** 263
27. K G Rikhter, Candidate's Thesis in Chemical Sciences, Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1973, 144 pp.
28. K G Rikhter, S V Ketchik, L G Simonova, M S Borisova *Kinet. Katal.*, 1975, **16** 1298
29. K G Rikhter, E M Moroz, E A Levitskii, V I Kolomiichuk *Kinet. Katal.*, 1975, **16** 1578
30. N C Halder, R J Metzger, C N Wagner *J. Chem. Phys.*, 1966, **45** 1259
31. D T Keeting *J. Appl. Phys.*, 1963, **34** 923
32. C W Grigson, E Barton *Brit. J. Appl. Phys.*, 1966, **17** 1019
33. C W Grigson, E Barton *Brit. J. Appl. Phys.*, 1967, **18** 175
34. V N Kolomiichuk *Metody Issledovaniya Kataliticheskikh Sistem* (Methods for the Study of Catalytic Systems). Vol. 1. *Rentgenografiya Katalizatorov* (X-Ray Diffraction of Catalysts) (Edited by V N Kolomiichuk), Izd. Inst. Katal. Sib. Otd. Akad. Nauk SSSR, Novosibirsk, 1977, p. 67
35. E M Moroz, S V Bogdanov, V A Ushakov *React. Kinet. Catal. Lett.*, 1978, **9** 109
36. E M Moroz, V A Ushakov, G R Kosmambetova, et al. *Kinet. Katal.*, 1988, **29** 1446
37. E M Moroz, S V Bogdanov, N E Buianova, O S Kovrizhina *Kinet. Katal.*, 1978, **19** 1029
38. E M Moroz, S I Bogdanov, V A Ushakov, E A Levitskii *Kinet. Katal.*, 1979, **20** 173
39. K G Rikhter, E A Levitskii, V N Kolomiichuk, E M Moroz *Kinet. Katal.*, 1975, **16** 1578
40. O N Kimkhai, B N Kuznetsov, N A Pashkovskaya, et al. *React. Kinet. Catal. Lett.*, 1977, **6** 393
41. E M Moroz, A A Tripol'skii, Yu A Ryndin, E N Kuznetsov *Kinet. Katal.*, 1977, **18** 1531
42. E M Moroz, V A Ushakov, S V Bogdanov, V A Gusev *Metody Issledovaniya Kataliticheskikh Sistem* (Methods for the Study of Catalytic Systems). Vol. 1. *Rentgenografiya Katalizatorov* (X-Ray Diffraction of Catalysts) (Edited by V N Kolomiichuk), Izd. Inst. Katal. Sib. Otd. Akad. Nauk SSSR, Novosibirsk, 1977, p. 53
43. H Krebs, H J Gruber *Z. Naturforsch., A*, 1967, **22** 96
44. P E Kolosov *Kataliz v Neftekhimii i Neftepererabotke: Regional'naya Shkola-Seminar Molodykh Uchenykh. Omsk* (Catalysis in Petrochemistry and Petroleum Processing: Regional School-Seminar for Young Scientists. Omsk), Omsk, 1990, p. 91
45. P E Kolosov, E M Moroz *Kinet. Katal.* (in the press)
46. D I Kochubei *Usp. Khim.*, 1986, **55**(3) 418 [English translation in *Russ. Chem. Rev.*, 1986(3)]
47. D I Kochubei, Yu A Babanov, K I Zamaraev, et al. *Rentgenospektral'nyi Metod Izucheniya Struktury Amorfnykh Tel: EXAFS-Spektroskopiya* (X-Ray Spectroscopic Method for the Study of the Structures of Amorphous Susbtances: EXAFS Spectroscopy), Nauka, Novosibirsk, 1988, 306 pp.
48. H M Rietveld *J. Appl. Crystallogr.*, 1969, **2** 65
49. R A Young, P E Mackie, R B von Dreel *J. Appl. Crystallogr.*, 1977, **10** 262
50. C P Khatak, D E Cox *J. Appl. Crystallogr.*, 1977, **10** 405
51. L D Calvert, E J Gobe, Y Page *Acta Crystallogr.*, 1981, **37** 314
52. R A Young, D B Wiles *Adv. X-Ray Analysis*, 1981, **24** 1
53. S D Kirik, S V Borisov, V G Fedorov *Zh. Strukt. Khim.*, 1981, **22**(2) 130
54. S D Kirik, I S Yakimov *Trudy Instituta Tsvetnykh Metallov* (Transactions of the Institute of Non-ferrous Metals), Krasnoyarsk, 1985, p. 20
55. C Clark, D K Smith, G G Jonson *Bull. Exper. Stat. Pensylvania*, 1973
56. A Albinati, B T Willis *J. Appl. Crystallogr.*, 1982, **15** 361
57. G S Pawley *J. Appl. Crystallogr.*, 1980, **13** 630
58. S V Tsybulya, L P Solov'eva *Apparatura i Metody Rentgenovskogo Analiza* (Apparatus and Methods for X-Ray Analysis), Leningrad, 1988, No. 38, p. 46

59. L P Solov'eva, S V Tsybulya, V A Zabolotnyi *Trudy Seminara "Rentgenostrukturnyi Analiz Polikristallov". Rostov-na-Donu* (Proceedings of the Seminar on "X-Ray Diffraction Analysis of Polycrystalline Materials". Rostov-on-don), Izd. Kalmytskogo Univ., Rostov-on-Don, 1986, p. 81
60. C J Howard *J. Appl. Crystallogr.*, 1982, **15** 615
61. A Brown, J M Edmonds *Adv. X-Ray Analysis*, 1980, **23** 361
62. V A Kogan, M F Kupriyanov, E G Fesenko *Kristallografiya*, 1988, **33** 1368
63. V A Kogan, M F Kupriyanov *First European Powder Diffraction Conference. Abstracts*, Münich, 1991, p. 16
64. G Caglioti, A Paoletti, F P Ricci *Nucl. Instrum.*, 1958, **3** 223
65. A N Hewat *J. Phys. Chem.*, 1973, **6** 2559
66. B W Lucas *Acta Crystallogr., Sect. B*, 1979, **35** 1038
67. B Moraveck, P Montgolfier, A J Renouprez *J. Appl. Crystallogr.*, 1977, **10** 184
68. A Glazer, S Mabud *Acta Crystallogr.*, 1978, **34** 1060
69. V A Ushakov, E M Moroz *Kinet. Katal.*, 1985, **26** 968
70. H Bosman *Acta Crystallogr.*, 1970, **26** 649
71. G Burchard, W Rudolff *Z. Anorg. Allg. Chem.*, 1978, **445** 79
72. A Mangeli *Reactiv. Solids. Proc. 8th Intern. Symp. Göteborg*, 1976, New York, 1977, p. 1
73. L P Solov'eva, S V Tsybulya, I P Olen'kova, L N Plyasova *Zh. Strukt. Khim.*, 1984, **25**(5) 177
74. I V Smushkov, V F Tkachenko *Monokristally, Stsintillyatory i Organicheskie Lyuminofory* (Single Crystals, Scintillators, and Organic Phosphors), Izd. Kharkov. Gos. Univ., Kharkov, 1967, No. 2, p. 43
75. E M Moroz, Candidate's Thesis in Physical-Mathematical Sciences, Institute of Catalysis of the Siberian Divison of the USSR Academy of Sciences, Novosibirsk, 1971, 146 pp.
76. V I Iveronova, G P Revkevich *Teoriya Rasseyaniya Rentgenovskikh Luchei* (Theory of X-Ray Scattering), Izd. Moskov. Gos. Univ., Moscow, 1978, p. 129
77. B E Warren *Advances in Metal Physics* (Translated into Russian), Metallurgizdat, Moscow, 1963, Vol. 5, p. 172
78. A Guinier *X-Ray Diffraction of Crystals* (Translated into Russian), Fizmatgiz, Moscow, 1961, 392 pp.
79. E Bertaut *Acta Crystallogr.*, 1950, **3** 14
80. H Spindler, P Orban, B Westphal *Kristalle und Technik*, 1977, **17** 517
81. E M Moroz, S V Bogdanov, et al. *Kinet. Katal.*, 1984, **25** 171
82. S V Bogdanov, E M Moroz, S V Tsybulya *Kinet. Katal.*, 1984, **25** 1203
83. S V Bogdanov, E M Moroz, P G Tsyrul'nikov, et al. *Kinet. Katal.*, 1988, **29** 498
84. B C Lippens, J J Steggerda *The Structure and Properties of Adsorbents and Catalysts* (Translated into Russian), Mir, Moscow, 1973, 190 pp.
85. B C Gates, J R Kutzer, G C A Schuit *Chemistry of Catalytic Processes* (Translated into Russian), Mir, Moscow, 1981, 307 pp.
86. C A Spitler, S S Pollack *J. Catal.*, 1981, **69** 241
87. H P Rooksby *X-Ray Methods for the Study of Argillaceous Minerals and Their Structures* (Translated into Russian), Mir, Moscow, 1965, 405 pp.
88. S Yamaguchi *Z. Anal. Chem.*, 1974, **270** 191
89. A J Leonard, D Semaile, J J Fripiat *Proc. Brit. Ceram. Soc.*, 1969, **13** 103
90. E M Moroz, T D Kambarova *Metody Issledovaniya Kataliticheskikh Sistem* (Methods for the Study of Catalytic Systems). Vol. 1. *Rentgenografiya Katalizatorov* (X-Ray Diffraction of Catalysts) (Edited by V N Kolomiichuk), Izd. Inst. Katal. Sib. Otd. Akad. Nauk SSSR, Novosibirsk, 1977, p. 110
91. R A Shkrabina, Yu K Vorob'ev, E M Moroz, et al. *Kinet. Katal.*, 1981, **22** 1080
92. Yu K Vorob'ev, R A Shkrabina, E M Moroz, et al. *Kinet. Katal.*, 1981, **22** 1595
93. V A Ushakov, E M Moroz *Kinet. Katal.*, 1985, **26** 963
94. V A Ushakov, E M Moroz *Kinet. Katal.*, 1985, **26** 1200
95. E M Moroz, V A Ushakov, S B Bogdanov *15th Congress and General Assembly of International Union of Crystallography. Collected Abstracts.* Bordeau (France), 1990, p. 371
96. V A Ushakov, E M Moroz *React. Kinet. Catal. Lett.*, 1984, **24** 113
97. G B Erenburg, V P Fateeva, A I Min'kov, et al. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.*, 1981, **1**(2) 54
98. S Soled *J. Catal.*, 1983, **81** 252
99. D Espinat, F Thevenot, K Malkio *12th European Crystallographic Meeting. Abstracts*, Moscow, 1989, Vol. 3, p. 280
100. V N Kuklina, E A Levitskii, E M Plyasova, et al. *Kinet. Katal.*, 1972, **13** 1269
101. A S Ivanova, V A Dzis'ko, E M Moroz, et al. *Kinet. Katal.*, 1985, **26** 429
102. E M Moroz, V N Kuklina, V A Ushakov *Kinet. Katal.*, 1987, **28** 699
103. V A Dzis'ko, A S Ivanova, L M Plyasova, S V Ketchik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 983
104. E M Moroz, O A Kirichenko, V A Ushakov, E A Levitski *React. Kinet. Catal. Lett.*, 1985, **28** 9
105. R A Shkrabina, E M Moroz, E A Levitskii *Kinet. Katal.*, 1981, **22** 1293
106. T F Limar', Yu A Kagan, L A Shepelenko, N T Kisel' *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1972, **8** 500
107. S V Tsybulya, L P Solov'eva, G N Kryukova, E M Moroz *Zh. Strukt. Khim.*, 1991, **32**(3) 18
108. L Lutterotti, P Scardi *J. Appl. Crystallogr.*, 1990, **23** 246
109. Yu I Yermakov, V F Surovikin, G V Plaksin, et al. *React. Kinet. Catal. Lett.*, 1987, **33** 435
110. V L Kuznetsov, M N Aleksandrov, I V Zagoruiko, et al. *Carbon*, 1991, **29** 665
111. P A Simonov, E M Moroz, V A Likholobov, G V Plaksin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1478
112. E M Moroz, S D Mikhailenko, A K Dzhunusov, A B Fasman *React. Kinet. Catal. Lett.*, 1991, **43** 63
113. N E Buyanova, O F Zapreeva, A P Karnaukhov, et al. *Kinet. Katal.*, 1977, **18** 736
114. V A Ushakov, E M Moroz, K G Rikhter, et al. *Dokl. Akad. Nauk SSSR*, 1974, **219** 158
115. V A Ushakov, E M Moroz, P A Zhdan, et al. *Kinet. Katal.*, 1978, **19** 744
116. V A Ushakov, E M Moroz *React. Kinet. Catal. Lett.*, 1985, **27** 351
117. E M Moroz, S D Mikhailenko, A K Dzhunusov, et al. *Kinet. Katal.*, 1990, **31** 1506

118. Yu I Ermakov *Nanesennye Metallicheskie Katalizatory Prevrashcheniya Uglevodorodov* (Deposited Metallic Catalysts of the Reactions of Hydrocarbons), Izd. Inst. Kataliza Sib. Otd. Akad. Nauk SSSR, Novosibirsk, 1978, Part 1, p. 90
119. M D Smolikov, A S Belyi, A Nizovskii, et al. *React. Kinet. Catal. Lett.*, 1988, **37** 437
120. A S Belyi, M D Smolikov, N M Ostrovskii, V K Duplyakin *React. Kinet. Catal. Lett.*, 1988, **37** 457
121. V A Ushakov, E M Moroz, N R Bursian, et al. *Kinet. Katal.*, 1979, **20** 177
122. A N Startsev, T M Moravskaya, B N Kuznetsov, et al. *Nanesennye Metallicheskie Katalizatory Prevrashcheniya Uglevodorodov* (Deposited Metallic Catalysts of the Reactions of Hydrocarbons), Izd. Inst. Kataliza Sib. Otd. Akad. Nauk SSSR, Novosibirsk, 1978, Part 2, p. 157
123. Yu I Ermakov, B N Kuznetsov, A N Startsev *Nanesennye Metallicheskie Katalizatory Prevrashcheniya Uglevodorodov* (Deposited Metallic Catalysts of the Reactions of Hydrocarbons), Izd. Inst. Kataliza Sib. Otd. Akad. Nauk SSSR, Novosibirsk, 1978, Part 2, p. 195
124. Yu A Ryndin, E M Moroz, B N Kuznetsov, et al. *Nanesennye Metallicheskie Katalizatory Prevrashcheniya Uglevodorodov* (Deposited Metallic Catalysts of the Reactions of Hydrocarbons), Izd. Inst. Kataliza Sib. Otd. Akad. Nauk SSSR, Novosibirsk, 1978, Part 2, p. 239
125. V K Duplyakin *Nanesennye Metallicheskie Katalizatory Prevrashcheniya Uglevodorodov* (Deposited Metallic Catalysts of the Reactions of Hydrocarbons), Izd. Inst. Kataliza Sib. Otd. Akad. Nauk SSSR, Novosibirsk, 1978, Part 1, p. 74
126. B N Kuznetsov, A N Startsev, V K Duplyakin *Nanesennye Metallicheskie Katalizatory Prevrashcheniya Uglevodorodov* (Deposited Metallic Catalysts of the Reactions of Hydrocarbons), Izd. Inst. Kataliza Sib. Otd. Akad. Nauk SSSR, Novosibirsk, 1978, Part 2, p. 43
127. N A Pakhomov, R A Buyanov, G R Kotel'nikov, et al. *VII Sovetsko-Yaponskii Seminar po Katalizu: Doklady. Irkutsk* (The VIIth Soviet-Japanese Seminar on Catalysis: Reports. Irkutsk), Irkutsk, 1983, p. 172
128. E M Moroz, B N Kuznetsov, A N Startsev, et al. *Nanesennye Metallicheskie Katalizatory Prevrashcheniya Uglevodorodov* (Deposited Metallic Catalysts of the Reactions of Hydrocarbons), Izd. Inst. Kataliza, Sib. Otd. Akad. Nauk SSSR, Novosibirsk, 1978, Part 2, p. 219
129. E M Moroz *Fizikokhimiya Ul'tradispersnykh Sistem* (Physical Chemistry of Ultradisperse Systems), Nauka, Moscow, 1987, p. 85

Translated from *Uspekhi Khimii* 61 384–414 (1992) U.D.C. 621.039+539.194.01

The theory of the equilibrium isotope effects of hydrogen

D A Knyazev, N F Myasoedov, A V Bochkarev
Timiryazev Moscow Agricultural Academy
Institute of Molecular Genetics, Russian Academy of Sciences, Moscow

ABSTRACT. The present state of the theory of the equilibrium isotope effects of hydrogen has been examined using a new approach developed by the present authors, namely the coordinate analysis of isotope effects. The mathematics of the theory have been described briefly. The conditions under which the isotopic effect is localised have been formulated. The relationship of the isotope effects in protium–deuterium and protium–tritium replacements has been refined. Particular attention has been made to clear methods for interpreting the parameter $\ln\beta$, making it possible to reveal the relationship between the isotope effect and intramolecular properties, and to systematise isotope effects on the basis of concepts having a clear physical significance. The isotope effects for the principal classes of hydrogen compound have been analysed and systematised. The factors determining the magnitude and nature of the variation in the equilibrium isotope effect have been established.

The bibliography contains 66 references.

Contents

I. Introduction 204
II. Basic postulates of the theory of equilibrium isotope effects of hydrogen 204
III. Theoretical methods for interpreting isotope effects 208
IV. Analysis of quantitative data on the β-factors of hydrogen compounds 214

I. Introduction

The use of deuterium and tritium as isotopic tracers makes it possible to solve research problems in the most varied branches of physics, chemistry, and biology. These studies must take account of chemical isotope effects,[1] which may be anomalously large for the isotope pairs protium/deuterium and more particularly protium/tritium. The differences in the chemical behaviour of protium, deuterium, and tritium are themselves used as an effective means of studying the molecular and dynamic aspects of chemical and cellular mechanisms.[1] This approach is based on the fact that the equilibrium isotope effects are determined by the specific features of the chemical bonds and the structural characteristics of molecules. The prediction of the separation coefficients of the hydrogen isotopes in chemical exchange systems remains an important problem.

The statistical thermodynamics of isotope effects must solve three main problems: 1, the establishment of the quantitative relationship between isotope effects and the geometric parameters and force field of a molecule; 2, the interpretation of available experimental material on this basis in terms of molecular structure; and 3, the prediction of the magnitude of isotope effects in systems which have not been studied experimentally. From the viewpoint of statistical thermodynamics, the isotopic replacement of hydrogen is the most interesting general case, since hydrogen effects are large and can be measured accurately. Moreover, the theoretical results obtained for hydrogen replacement are applicable to the replacement of the atoms of all other elements. In addition, the extremely large amount of data that has been accumulated on hydrogen effects can be used to analyse the thermodynamics of isotopic exchange.

II. Basic postulates of the theory of equilibrium isotope effects of hydrogen

The theory of equilibrium isotope effects is based on statistical thermodynamics and the theory of molecular vibrations. In the present work, we shall restrict ourselves to an examination of the isotope effects of hydrogen in the harmonic oscillator–rigid rotator approximation. This is related to the fundamental fact that the decisive contribution to the isotope effect at room temperature is made by the harmonic vibrational component of the isotopic differences in the thermodynamic functions, so that all the basic regularities in the isotope effects can be explained in the above approximation. Allowance is made for anharmonicity only by introducing a correction, which may alter the numerical values slightly but which cannot lead to the appearance of qualitatively new phenomena.

1. Chemical isotopic exchange. Calculation of the separation coefficient

The term equilibrium chemical isotope effect denotes the deviation of the distributions of isotopes between chemical forms (components of the system) in the state of thermodynamic equilibrium from those corresponding to equal probabilities. The isotopic exchange of hydrogen atoms between the components AH_n and BH_m (A and B are arbitrary molecular residues, and m and n the numbers of equivalent hydrogen atoms of a given type) involves molecular exchange reactions of the type[2]

$$AH_{n-i+1}D_{i-1}+BH_{m-j}D_j \rightleftharpoons AH_{n-i}D_i+BH_{m-j+1}D_{j-1}, \qquad (1)$$

and also homomolecular isotopic exchange reactions. Each of these reactions is characterised by its own individual equilibrium constant. The isotope effect is revealed in the equilibrium constants of reactions (1) deviating from the equal-probability isotope distribution.

The quantity used as a measure of the thermodynamic isotope effect is the separation coefficient α, defined for the replacement of protium by deuterium as

$$\alpha_{D/H} = \frac{([D]/[H])_A}{([D]/[H])_B} \quad (2)$$

To calculate the separation coefficient α by statistical thermodynamics it is necessary to establish its relationship to the equilibrium constants of reactions (1). The separation coefficient α is given by the equation:[2,3]

$$\alpha = \beta_{A^*/A}/\beta_{B^*/B}, \quad (3)$$

where A* and B* are the heavy isotopic forms of the molecules A and B.

The quantity $\beta_{A^*/A}$ (the "β-factor") [the term "ratio of the reduced partition functions" and the notation $(s/s')/f$ are also used] characterises the thermodynamic non-equilibrium distribution of the isotopes only in the molecule of the given substance A. The physical significance of the $\beta_{A^*/A}$-factor is that it is the equilibrium constant of the hypothetical isotopic exchange reaction between the substance AH_n and the ideal monatomic gas D.

The β-factor is a basic concept in the theory of isotope effects. The advantage of using the β-factors is that the calculated values of the β-factors of molecules and Eqn. (3) can be used to calculate the separation coefficients of the systems which they form. The concept of the β-factor is also convenient for analysing isotope effects in terms of molecular structure, since it makes it possible to restrict the examination to one molecule.

In a number of cases a molecule contains hydrogen in different non-equivalent groups. Thus the molecule of propionic acid CH_3CH_2COOH contains three groups of hydrogen atoms: the three hydrogen atoms of the methyl group, the two hydrogen atoms of the methylene group, and the hydrogen atom of the carboxyl group. The hydrogen atoms of these groups differ from the viewpoint of their chemical behaviour, and each group must be characterised by its own individual value of the β-factor. It is possible in principle to have intramolecular (intrastructural) isotope effects, that is the isotopic enrichment of individual groups by intramolecular exchange. Intrastructural effects are valuable as a means of study in those cases where it is possible to be confident that true equilibrium has been established (for example in geochemical systems). When true equilibrium has been established with respect to several non-equivalent groups, the separation coefficient can be estimated using the concept of the overall β-factor of the molecule (β_Σ), proposed by Galimov; the method for calculating β_Σ from the β-factors of individual groups has been described.[4]

2. Isotope effects and the theory of molecular vibrations

From the viewpoint of mechanics, an n-atom molecule is a system of n material points of mass m_i connected by elastic forces. This system has $N = 3n$ degrees of freedom, of which $3n-6$ correspond to vibrations ($3n-5$ for a linear molecule). In the harmonic approximation, the frequencies of these vibrations are given by the matrix equation

$$\hat{G}\hat{F}\hat{L} = \hat{L}\hat{\Lambda}, \quad (4)$$

where $\hat{G}$ is the kinetic energy matrix, expressed in terms of the generalised momenta, and $\hat{F}$ the potential energy matrix in generalised coordinates. The elements of the matrix $\hat{G}$ (the so-called kinematic coefficients) can be calculated if the geometric parameters of the molecule and the masses of the atoms are known. The elements of the matrix $\hat{F}$ (the force constants) are the values of the second derivatives of the potential energy with respect to the generalised coordinates at the point corresponding to the equilibrium geometric configuration of the molecule. The matrix Λ is the diagonal matrix of the eigenvalues of the matrix $\hat{G}\hat{F}$, which with an accuracy corresponding to a constant coefficient are equal to the squares of the frequencies of the vibrations ($\lambda_i = C\nu_i^2$, where C is a constant which depends on the chosen dimensions). The matrix $\hat{L}$ (the so-called matrix of the modes of the vibrations) is the matrix of the eigenvectors of the matrix $\hat{G}\hat{F}$, and is the matrix for changing from generalised to normal coordinates. The generalised coordinates usually employed to solve Eqn. (4) are the so-called natural vibrational coordinates, that is the deviations of the geometric parameters of the molecule (bond lengths and valence and dihedral angles) from their equilibrium values.

To take better account of the symmetry and specific features of the molecule, it is usual to introduce as coordinates the deviations from the equilibrium values of all the bonds and valence angles in the molecule (complete system of natural coordinates). The number of coordinates is then greater than the number of vibrational degrees of freedom. In this case, zero frequencies appear in the solution of the vibrational problem.

The natural vibrational coordinates make it possible to relate the vibrational-spectroscopic properties of a molecule to the concepts of the classical theory of chemical structure, such as the chemical bond, molecular fragments, their properties, etc. In particular, the force constants expressed in natural coordinates have the property of transferability, that is they change little in series of similar molecules.

In isotopic replacement, the potential energy of a molecule and hence the force constant matrix remain unchanged (to a high approximation), and changes take place only in the kinematic coefficients, which depend on the masses of the atoms. For replacement by a heavier isotope, the vibrational frequencies can only decrease. The sums and products of the frequencies of the vibrations of the isotopic forms of a molecule are related by various rules.[5]

3. Calculation of ln β in the harmonic approximation

In practice, it is more convenient to deal not with the β-factor itself but with its logarithm. The value of ln β in the harmonic oscillator–rigid rotator approximation is calculated using the equation:[3]

$$\ln\beta = \sum_{i=1}^{N}\ln\beta_i = \frac{1}{l}\sum_{i=1}^{N}\ln\left[\left(\operatorname{sh}\left(\frac{u_i}{2}\right)\Big/u_i\right)\Big/\left(\operatorname{sh}\left(\frac{u_i^*}{2}\right)\Big/u_i^*\right)\right] = \frac{1}{l}\left\{\sum_{i=1}^{N}\ln\frac{u_i^*}{u_i} - \frac{1}{2}\sum_{i=1}^{N}(u_i^*-u_i) + \sum_{i=1}^{N}\ln\frac{1-\exp(-u_i)}{1-\exp(-u_i^*)}\right\}.$$

Here and subsequently, $u_i = hc\nu_i/kT$ represents the dimensionless so-called reduced frequencies, h is Planck's constant, c the velocity of light, ν_i the vibrational wavenumbers, cm^{-1}, N the number of vibrational degrees of freedom of the molecule, and l the number of atoms replaced; the superscript "*" indicates that the corresponding

quantity is associated with the heavy isotopic form. The last two terms on the right-hand side of Eqn. (5) reflect the contribution made to $\ln\beta$ by the vibrational degrees of freedom of the molecule; the second term, with an accuracy corresponding to a certain factor, is the difference in the energies of the zero-point vibrations, and the third term reflects the contribution of vibrational excitation. The first term on the right-hand side of Eqn. (5) reflects the contribution of translational and rotational motion, and is expressed in terms of the vibrational frequencies using the Teller–Redlich theorem.[6]

4. Analysis of the accuracy of the basic assumptions

The accuracy of Eqns. (3) and (5) is determined by the accuracy of the assumptions forming the basis of the theoretical premises from which they are derived, primarily the Born–Oppenheimer approximation and the harmonic oscillator–rigid rotator approximation. Deviations from the Born–Oppenheimer approximation lead to the appearance of the so-called "electronic isotope effect", which has been studied in detail.[7–10] It is revealed to the greatest extent for ions, and also for the simplest molecules. Thus for the gas-phase reaction

$$D^+ + H_2 \rightarrow H^+ + HD\,,$$

the electronic isotope effect is 15% of the value of the equilibrium constant at 300 K.[7] For the gas-phase reaction

$$D_2 + 2HCl \rightleftarrows H_2 + 2DCl\,,$$

this error in K_{equil} is 3.3%.[11] In other systems in which the deviations can be related unambiguously to the electronic isotope effect, such high values have not been observed. For most molecules at temperatures around 300 K, the separation of the electronic component of the isotope effect in the Born–Oppenheimer approximation does not introduce a significant error.

When considering the separation of, and separate allowance for, the contributions of the vibrational and rotational motion, it should be noted that the influence of this assumption on the accuracy has been studied in detail. All possible corrections related to this assumption have been calculated for molecular hydrogen and a number of simple hydrogen-containing molecules,[12] and it has been shown that the influence of this factor does not exceed 1% of $\ln\beta$. The correction for the effect of quantisation of the rotation, and the correction for the contribution of the nuclear–spin component,[13] are significant only for molecular hydrogen and only at low temperatures ($T < 100$ K).

The anharmonicity of the vibrations must be considered, since vibrations involving the hydrogen atom have the greatest anharmonicity. A special study[14] of this question showed that the anharmonicity does not in fact make such significant differences to the value of $\ln\beta$ as usually assumed. In particular, if $\ln\beta_{D/H}$ is calculated using the so-called frequencies "corrected for anharmonicity", then the result differs by not more than 6.5% from the value obtained using the experimentally observed frequencies. The difference between the wavenumbers "corrected for anharmonicity" and the observed values may reach 200 cm^{-1} (for the O–H and N–H stretches). The small difference in the values of $\ln\beta$ for such a large difference in the wavenumber is related to the fact that, in accordance with Eqn. (5), there is partial compensation of the systematic shift of the wavenumbers for the two isotopic forms.

A similar result is obtained by comparing $\ln\beta$ calculated using Eqn. (5) with the value obtained by direct summation with respect to the vibrational–rotational energy levels.[15] It is necessary to avoid calculating the separation coefficient using $\ln\beta$ values obtained in different approximations, since in this case compensation will not take place, and the error in the value of α may be considerable.

Particular mention must be made of the error introduced by the ideal gas approximation (that is when no account is taken of the phase state of the substance). For hydrogen compounds, this question is related, apart from anything else, to the tendency of many of them to associate by hydrogen bond formation, accompanied by changes in the geometry and force field of the molecule. The values of α calculated theoretically for an ideal gas may differ from the values measured experimentally in the liquid or solid phases. It is of interest to estimate the magnitude and sign of this error for different chemical exchange systems involving hydrogen-containing molecules.

The change in the logarithm of the β-factor of a substance with change in the phase state is equal to the logarithm of the separation coefficient for the phase transformation. Neglecting the correction for non-ideal character and other small corrections, for the chemical isotopic exchange reaction

$$AH + BD \rightleftarrows BH + AD$$

we have

$$\ln\alpha_l - \ln\alpha_g = \ln\beta^l_{AH/AD} - \ln\beta^l_{BH/BD} - \ln\beta^g_{AH/AD} + \ln\beta^g_{BH/BD} = \ln(p_{AH}/p_{AD}) - \ln(p_{BH}/p_{BD})\,. \quad (6)$$

Equations taking account of the small corrections have been published.[16]

Sufficient data on the equilibrium vapour pressure above isotopic forms are now available to make possible their evaluation.[17] Eqn. (6) shows that the maximum error from neglect of the phase effect arises when for the exchanging forms A and B the distillation effects have different signs, for example when for form A the vapour pressure $p_{AH} > p_{AD}$ and for B, $p_{BH} < p_{BD}$. In this case the two contributions in the right-hand side of Eqn. (6) have the same sign.

The group of compounds for which $p_D > p_H$ consists mainly of substances which are not associated in the liquid phase, but also substances which are associated both in the vapour and in the liquid (organic acids and hydrogen fluoride). Thus for $CHCl_3$ at 283 K, the ratio p_D/p_H is 1.016, and for other similar substances the value calculated for one atom being replaced at room temperature is even smaller. For compounds which form hydrogen bonds only in the liquid, usually, $p_H > p_D$; the greatest isotopic vapour-pressure difference is shown by alcohols and hydroperoxides. For t-butyl hydroperoxide, $\ln(p_H/p_D) = 0.08$ at 300 K (highest known value). Combined with the above value for chloroform, this gives $\ln\alpha_l - \ln\alpha_g = 0.10$. Since for the chloroform–t-butyl hydroperoxide system the logarithm of the separation coefficient is small (~ 0.1), we find that the relative error in the determination of $\ln\alpha$ for this case is more than 100%. At the same time it must be borne in mind that, usually, the separation coefficients for systems of practical importance are large, and for them the error is smaller than that given above. Since for each specific class of substance the sign of the error is known and its approximate value can be estimated, it is obvious that the calculation of the β-factors for the gas phase combined with data on the vapour pressure of the isotopic forms of

model classes of compound can be used to estimate the separation coefficient in condensed phases with an accuracy sufficient for practical purposes.

Another important assumption made in the derivation of Eqns. (3) and (5) is the so-called rule of the geometric mean, analysed below. Here it may be noted that for all compounds except molecular hydrogen, the error introduced by departure from this rule does not exceed 1% (at 300 K).

When considering reactions involving the isotopic forms of molecular hydrogen when homomolecular exchange takes place, however, the departures from this rule are large, and Eqns. (3) and (5) cannot be used. In this case it is necessary to take separate account of all reactions of type (1) and reactions of homomolecular exchange with corresponding constants. The required equations have been published.[18,19]

Before analysing numerical data on $\ln\beta_{D/H}$, the following summary is appropriate. It was noted above that the accuracy of the harmonic oscillator–rigid rotator approximation and the rule of the geometric mean is ~2%. The absolute values of the vibrational frequencies are determined experimentally for the gas phase with an accuracy of ~1 cm^{-1}. At the same time, published data give estimates of the accuracy of the frequencies of 1–35 cm^{-1}. This is related to the fact that many spectra have been obtained for condensed phases; moreover, various wavenumbers are not observed experimentally, and are estimated using approximate isotope rules.

The values of the error in $\ln\beta_{D/H}$ given subsequently in the Tables include only the error in the initial vibrational frequencies, and were obtained from the equation:

$$\delta \ln\beta = \sum_{i}^{N}\left(\frac{\partial \ln\beta}{\partial\nu_i}\delta\nu_i + \frac{\partial \ln\beta}{\partial\nu_i^*}\delta\nu_i^*\right).$$

The values given for ν_i and $\delta\nu_i$ are the most reliable recommended published values.[20,21]

In most cases the errors in the $\ln\beta$ data are smaller than those given below. Cases where the vibrational frequencies are determined with large errors are encountered, however. Thus the calculation of $\ln\beta_{D/H}$ from published[20] frequencies for $HDCO/H_2CO$ gives the value 1.99, and for D_2CO/H_2CO the value 2.13, whereas according to the rule of the geometric mean the difference between them should not exceed 1%. According to data from other sources,[22] the value of 2.13 is close to the true value, so that the published[20] frequencies for HDCO are incorrect.

Thus to guarantee reliability of the error in $\ln\beta$, we have taken for $\delta\nu_i$ the largest values of the estimate of the error in the frequencies given in the works cited.[20,21] The influence of errors in the original data on the error in the β-factor has been studied by other workers.[23,24] Calculation of the error in $\ln\beta_{D/H}$ on the basis of an estimate of the inaccuracy of the vibrational frequencies gives an error of about 2%, which corresponds to the error of the harmonic approximation. From this it is apparently meaningless to speak of a value of $\ln\beta_{D/H}$ with an accuracy of better than 1%. The values of $\ln\beta$ obtained from experimental spectroscopic data are therefore given below to two decimal places. We are interested, however, not only in the actual numerical values of α for specific systems but also in the correlations between $\ln\beta$ and the parameters of the force field and the structure of the molecule. In the theoretical analysis, therefore, the values of $\ln\beta$ are given with an extra significant figure.

5. Relationship between the equilibrium isotope effects for proton–deuterium and protium–tritium replacement

In recent years, tritium has been used increasingly as an isotopic tracer in research work. The trend, observed in the eighties, towards the preferential use of stable isotopes compared with radioactive tracers has not affected the use of tritium, which continues to increase rapidly. It is therefore often necessary to have data on the β-factors of the tritiated forms of compounds. In most cases these data are not available, since spectroscopic studies are carried out mainly using the deuteriated forms.

This gives considerable interest to the problem of the relationship between the values of the equilibrium isotope effects with respect to different atoms, that is the problem of calculating the magnitude of the tritium effect from the known deuterium effect, and *vice versa*.

For different molecules, the ratio

$$\gamma = \ln\beta_{T/H}/\ln\beta_{D/H}\ , \qquad (7)$$

is almost constant.[25–27] A detailed analysis of Eqn. (7) has been carried out.[28,29] It has been shown that γ depends on the factors on which $\ln\beta$ depends, that is the geometry of the molecule, the masses of its atoms, and the force field (that is on its nature), and on temperature. By varying the parameters of a molecular model it is always possible in principle to obtain the maximum and minimum theoretical limits of γ (lower limit 1.33, upper 1.44). It should be emphasised that the published observation[25,28,29] that the value of γ for real molecules is constant and is related not to the properties of Eqn. (7) but to the fact that the values of the masses of the atoms and the force constants in real molecules lie in fairly narrow ranges.

The analysis[28,29] of the behaviour of the ratio γ for a representative large number of molecules has established that γ is highly characteristic with respect to the type of bond (that is to the nature of the atom directly joined to the hydrogen being replaced).

Table 1. Recommended values of γ for molecules of different types at different temperatures.

Molecule	*T*, K			
	100	200	300	400
H*F	1.435	1.429	1.423	1.416
H*Cl	1.436	1.427	1.417	1.407
H*Br	1.436	1.426	1.414	1.402
H*I	1.436	1.424	1.410	1.396
HOH*	–	1.412	1.407	1.400
CH_3OH*	1.418	1.410	1.402	1.396
CH_3SH*	1.419	1.407	1.396	1.386
H_2*O	1.434	1.426	1.418	1.418
H_2*S	1.419	1.407	1.396	1.385
H_2*Se	1.442	1.428	1.415	1.402
H*CN	1.417	1.409	1.403	1.396
C_2H_4*	1.418	1.407	1.397	1.389
NH_3*	1.432	1.422	1.413	1.404
PH_3*	1.433	1.418	1.405	1.394
AsH_3*	1.432	1.415	1.401	1.388
SbH_3*	1.428	1.409	1.394	1.381
CH_4*	1.421	1.409	1.398	1.388
SiH_4*	1.419	1.402	1.388	1.377
GeH_4*	1.420	1.402	1.388	1.376
SnH_4*	1.420	1.401	1.386	1.373

Note. The asterisk indicates the atom being replaced.

In addition, γ also depends on the number of equivalent atoms being replaced (it increases with increase in this number). The influence of other factors is insignificant.

Since γ is characteristic, the most correct method of finding $\ln\beta_{T/H}$ is by direct calculation from $\ln\beta_{D/H}$ using the relationship $\ln\beta_{T/H} = \gamma\ln\beta_{D/H}$. The recommended values of γ for molecules of different types are given in Table 1, compiled using published data.[29] The contributions to $\ln\beta$ from individual frequencies do not necessarily satisfy Eqn. (7). Moreover, Eqn. (7) can be used as a criterion of the correctness of regarding molecular fragments as individual molecules, and also for verifying the reliability of data on the vibrational frequencies of D- and T-forms.

Thus the use of Eqn. (7) makes it possible, for isolated molecules, to restrict the study to only the deuterium or only the tritium equilibrium isotope effect.

III. Theoretical methods for interpreting isotope effects

1. Approximate representations of the β-factor

Although Eqn. (5) is fairly convenient for calculations, it is not suitable for interpreting the data obtained in the study of isotope effects. This is related primarily to the fact that the vibrational frequencies depend on all the characteristics of a molecule, and not only on the characteristics of the atom being replaced and its immediate environment. The association of a frequency with a given vibrational coordinate, reflected in its assignment, is in general provisional. Each vibration involves a change in not one but all of the natural coordinates (bonds and angles), and each coordinate makes its own contribution to the form of a given vibration. An assignment is usually made with respect to the natural coordinates making the greatest contribution to the given vibration. The distribution of the contributions depends on the masses of the atoms, and the assignment of the frequencies often changes on deuteriation. For this reason it cannot be expected that the contributions of the ith pair of vibrational frequencies to $\ln\beta$, denoted $\ln\beta_i$ in Eqn. (5), will effectively describe the dependence of $\ln\beta$ on the nature of the molecule. It is more correct to interpret the quantity $\ln\beta$ in terms of the structural elements of molecules, that is the bonds between the atoms and the valence and dihedral angles, and this requires appropriate representations.

There are now more than 30 published papers dealing with the development of methods for interpreting isotope effects on the basis of the approximate representation of $\ln\beta$ as an analytical function of the force field and the geometry of the molecule. Historically, the first such representation was the expansion of $\ln\beta$ with respect to the force constants, carried out by Bigeleisen and co-workers.[3,30] This approximation is too crude for the study of most characteristics of isotope effects, so that it was necessary to develop more complex methods of interpretation, primarily the approximation of $\ln\beta$ by polynomials, proposed by Bigeleisen and Ishida,[31–33] and its improved versions.[34–38]

The most general form of the Ishida–Bigeleisen representation is the equation:

$$\ln\beta = \sum_{j=1}^{M} W_j A_j \sum_{i=1}^{N} (u_i^{2j} - u_i^{*2j}), \qquad (8)$$

where u_i represents the reduced frequencies. The sum with respect to i in this equation, with an accuracy corresponding to a temperature-dependent coefficient, is equal to $\Delta\,\mathrm{tr}(\hat{G}\hat{F})^i$, so that $\ln\beta$ is clearly expressed in terms of the geometric parameters and force constants. The numbers A_j are the Bernoulli coefficients, and W_j represents the so-called "modulating factors". The appearance of the coefficients W_j in the expansion (8) is related to the need to increase the rate of convergence of this series; for this purpose, the authors cited resort to scaling of the reduced frequencies by dividing them by the highest frequency in the spectrum of the molecule being considered.

An unsatisfactory feature of the polynomial approximation is its indeterminacy, which is revealed, in particular, by the fact that the relative values of the contributions to $\ln\beta$ from different molecular parameters depend on the value taken as u_{max} in the analysis of $\ln\beta$ for a large number of molecules, and more particularly on the chosen number of terms in the expansion of M.

Bigeleisen and co-workers[33,39] used another method of interpretation, which they called the method of "total effects". The method can be described as follows. The value of $\ln\beta$ for the molecule is calculated using data on its geometry and force field. One of the force constants is then put equal to zero, and a new value of $\ln\beta$ is calculated. In practice, this cannot be done directly, because of the appearance of imaginary frequencies, and the value of $\ln\beta$ with a zero force constant is estimated by extrapolation. The difference between the total value of $\ln\beta$ and the value obtained with a force constant equal to zero is taken as the contribution made to $\ln\beta$ by this constant. This contribution is then associated with the corresponding coordinate (bond, angle, coordinate interaction). Thus the value of $\ln\beta$ in the method of "total effects" is represented as the sum of the products of the crude estimates of the partial derivatives of $\ln\beta$ with respect to the force constant and the finite increase in the argument (in the present case the actual force constant). The proposed method is clearly one of the forms of the crude approximation of $\ln\beta$ as a function of the molecular parameters, so that it does not differ fundamentally from the method of orthogonal polynomials. From our viewpoint, it is less satisfactory than the method of orthogonal polynomials primarily because it has been less developed theoretically. The accuracy of the method of "total effects" for the replacement of protium by deuterium is not very high, and for molecules of medium complexity having out-of-plane vibrations it is equal to 4–6% at 300 K.

Another approach is that of Wolfsberg and co-workers.[40,41] This approach represents the application of perturbation theory to the calculation of $\ln\beta$, where the quantity taken as the zeroth approximation $\ln\beta_0$ is obtained by neglecting all the non-diagonal terms in the matrices $\hat{G}$ and $\hat{F}$. The basic principle of the method is that $\ln\beta_0$ is represented as the sum of contributions with respect to the "zeroth" frequencies ν_{0i} and ν^*_{0i}, each of which (since the matrix of the zeroth approximation $\hat{G}_0\hat{F}_0$ is diagonal) can be associated with a corresponding vibrational coordinate (bond, angle, etc.). For this, naturally, the values of the zeroth approximation $\ln\beta_0$ must be close to the exact value of $\ln\beta$ (that is the matrix $\hat{G}\hat{F}$ should not contain significant non-diagonal elements).

The concept of "zeroth frequencies" ν_{0i} leads to serious methodological difficulties. Thus for the methane molecule, the use of the complete system of natural coordinates gives ten "zeroth frequencies" ν_{0i}, whereas this molecule has only nine vibrational degrees of freedom. This difficulty arises as a result of the methodological inconsistency of the Wolfsberg method. In fact, since $\ln\beta$ is represented in terms of the geometry and force field, this

method still uses the concept of the contributions of the vibrational frequencies.

The methods considered, for all their differences, reduce to the representation of $\ln\beta$ as a simple algebraic function, which after transformation is reduced to the form of a power series with respect to the molecular parameters, for example the force constants. The series is terminated after account has been taken of the first few terms.

It has been shown[42] that all expansions of this type are "non-physical", that is from the coefficients of this series and from the calculated contribution made by a molecular parameter, nothing can be said about the contribution which this parameter in fact makes to $\ln\beta$. This is related to the fact that the value of the derivative of $\ln\beta$ with respect to the parameter, obtained from the expansion, depends decisively on the number of terms of the expansion taken into account.

This conclusion follows from Eqn. (5) itself, in which the molecular parameters appear via the frequencies ν_i. The latter are described by the branches of a multiple-value function $\nu_i = [\lambda_i(\zeta_1,...,\zeta_N)]^{1/2}$, where ζ represents the molecular parameters, the dependence on which is being considered. In this case, however, in accordance with the theory of power series, the radius of convergence of the power expansion of $\ln\beta$ cannot be greater than the distance from the point at which the derivative is calculated to the nearest branch point of the function $[\lambda_i(\zeta_1,...,\zeta_N)]^{1/2}$. The positions of these unique points have been studied for a number of molecules,[42] and it has been shown that the change in the assignment of frequencies with change in a parameter takes place close to them. Thus attempts to expand $\ln\beta$ in a Taylor series are not promising; if however approximate power expansions are used, then with increase in the accuracy and hence in the number of terms taken into account, this expansion approaches a Taylor series; since this series is diverging, the terms of higher powers make increasing contributions to $\ln\beta$, distorting the structure of the contributions of the molecular parameters and concealing the real reason for the variability of $\ln\beta$. This was previously noted[43] for the expansion in series of orthogonal polynomials.

Since it is impossible to construct a universal analytical expansion of the β-factor, there remain two possibilities: either to construct transcendental universal expansions suitable for the analysis of particular cases, or to represent $\ln\beta$ directly as the sum of the contributions of structural elements using numerical methods.

2. Representation of $\ln\beta$ as an infinite transcendental series

An accurate representation of $\ln\beta$ in the harmonic approximation as the sum of the terms of an infinite series of functions which are clearly and simply determined by the force constants, the geometry, and the masses of the atoms of the isotopic forms of the molecule has been proposed.[44,45] The representation has the form

$$\ln\beta = \sum_{p=1}^{\infty} \ln\beta_p = \sum_{p=1}^{\infty} \frac{1}{l} \ln \cdot$$

$$\cdot \left[1 + \frac{(\varkappa/p)^2\Delta\sigma_1 + (\varkappa/p)^4\Delta\sigma_2 + \ldots + (\varkappa/p)^{2N}\Delta\sigma_N}{1 + (\varkappa/p)^2\sigma_1^* + (\varkappa/p)^4\sigma_2^* + \ldots + (\varkappa/p)^{2N}\sigma_N^*}\right]. \qquad (9)$$

The quantities σ_p are equal to the sums of all the principal minors of pth order of the matrix $\hat{G}\hat{F}$, $\sigma_i = \sigma_i^* + \Delta\sigma_i$, $\varkappa = h/4\pi^2kT$.

The expansion (9) converges for all positive u_i. The existence of a simple equation for estimating the error for a restricted number of terms taken into account, the fact that the signs of the logarithmic terms are constant, and the rapid decrease in the contributions of these terms with increase in p distinguishes the expansion (9) from familiar approximate expansions. Eqn. (9) has been used successfully[44-46] to analyse the regularities of the behaviour of $\ln\beta$.

3. The representation of the vibrational component of $\ln\beta$ as the sum of the contributions of structural elements of the molecule

As noted above, it is most correct to interpret the quantity $\ln\beta$ in terms of the contributions of the structural elements, that is the bonds between atoms and the valence and dihedral angles.

A clear and accurate representation of the differences in the heat capacities and internal energies of isotopic forms as the sums of the contributions with respect to the vibrational coordinates corresponding to the above structural elements has been proposed.[47] A similar representation of the isotopic difference in the vibrational components of the entropies and the vibrational component of $\ln\beta$ has also been proposed.

To construct this representation we note that the logarithm of the β-factor, with an accuracy corresponding to an additive constant, is the difference, divided by kT, between the free energies for the two isotopic forms of the molecule AX_l and AX_l^*, calculated for one atom being replaced:

$$\ln\beta_{AX_l/AX_l^*} = \frac{1}{l}\left[\frac{F_{AX_l} - F_{AX_l^*} + F_X - F_{X^*}}{kT}\right]. \qquad (10)$$

Here, $(F_X - F_{X^*})kT$ is the difference between the free energies of the isotopes of the hypothetical monatomic gas X (which is constant for a given type of isotopic replacement).

For the difference between the internal energies of the isotopic forms we can write:

$$\Delta U = U^* - U = kT^2\left(\frac{\partial \ln(Q^*/Q)}{\partial T}\right), \qquad (11)$$

where Q is the partition function. Adopting the Born–Oppenheimer approximation and the harmonic oscillator–rigid rotator approximation, we have $Q = Q_tQ_rQ_v$ (subscripts; t = translational, r = rotational, v = vibrational motion). The translational and rotational motions do not contribute to the isotopic difference in the energies. Thus their zero-point energy (the energy at the absolute zero) is equal to zero, and the ratios Q^*/Q for the translational and rotational partition functions are independent of temperature, and the derivatives of these ratios with respect to T are equal to zero. Thus the difference in the internal energies of the isotopic forms is equal to the difference in the vibrational energies.

Substituting in Eqn. (11) the expression for Q_v taking account of the energy of the zero-point vibrations gives[47]

$$\Delta U = \sum_{i=1}^{N}\left[\frac{hc\nu_i^*}{2}\operatorname{cth}\frac{hc\nu_i^*}{2kT} - \frac{hc\nu_i}{2}\operatorname{cth}\frac{hc\nu_i}{2kT}\right] = E^* - E, \qquad (12)$$

where E is the vibrational energy of the molecule in the harmonic approximation. We now introduce the system of natural vibrational coordinates corresponding to the above structural elements of the molecule.

The vibrational energy of the molecule can be represented as[48]

$$U_v = \mathrm{tr}\,\hat{\Sigma}\hat{F} \tag{13}$$

where $\hat{F}$ is the force constant matrix, and $\hat{\Sigma}$ the matrix of the mean-square amplitudes of the vibrations.

According to the Binet–Cauchy theorem,[49] the trace of the product of two matrices A and B is equal to the sum of the paired products of the corresponding elements

$$\sum_{i,j} a_{ij}b_{ij} \ .$$

Thus

$$U_v = \mathrm{tr}\,\hat{\Sigma}\hat{F} = \sum_{i,j}\sigma_{ij}F_{ij}, \tag{14}$$

where σ_{ij} represents the elements of the matrix of the mean-square amplitudes in natural coordinates, and F_{ij} the force constants.

The relationship (14) can be represented in the following clear form.[47] We write the matrix $\hat{A}_{U_v}$, whose elements are the products of the corresponding elements of the matrices $\hat{\Sigma}$ and $\hat{F}$:

$$\hat{A}_{U_v} = \begin{pmatrix} \sigma_{11}F_{11} & \sigma_{12}F_{12} & \ldots\ldots & \sigma_{1N}F_{1N} \\ \sigma_{12}F_{12} & \sigma_{22}F_{22} & \ldots\ldots & \sigma_{2N}F_{2N} \\ \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots\ldots \\ \sigma_{1N}F_{1N} & \sigma_{2N}F_{2N} & \ldots\ldots & \sigma_{NN}F_{NN} \end{pmatrix} \tag{15}$$

This matrix is obviously symmetrical. According to Eqns. (14), the sum of all the elements of the matrix (15) is equal to the vibrational energy U_v of the molecule. The term at the intersection of the ith column and the jth row of matrix (15) represents the contribution made to the vibrational energy by the interaction of the ith and jth vibrational coordinates. In particular, the terms on the diagonal of matrix (15) represent the contributions due to the interaction of each vibrational coordinate with itself.

The matrix (15) readily gives the representation of the isotopic difference in the energies as the sum of the contributions with respect to the coordinates. Thus

$$\Delta U = \Delta\,\mathrm{tr}\,\hat{\Sigma}\hat{F} = \mathrm{tr}(\Delta\hat{\Sigma})\,\hat{F},$$

since the matrix $\hat{F}$ remains unchanged on isotopic replacement (here, $\Delta\hat{\Sigma}$ is the matrix $\hat{\Sigma}^* - \hat{\Sigma}$).

Thus we can write the matrix

$$\hat{A}_{\Delta U} = \hat{A}^*_{U_v} - \hat{A}_{U_v}, \tag{16}$$

made up of the elements $\Delta\sigma_{ij}F_{ij}$, where the term at the intersection of the ith column and the jth row represents the contribution made to the isotopic difference in the energies by the interaction of the ith and jth vibrational coordinates. The sum of all the elements of matrix (16) is equal to ΔU.

To obtain the corresponding expansion with respect to vibrational coordinates for the difference in the heat capcities ΔC_V, we have to differentiate the matrix (16) with respect to temperature. This can easily be done by representing the matrix $\hat{\Sigma}$ as $\hat{\Sigma} = \hat{L}\hat{\Delta}\tilde{\hat{L}}$, where $\hat{L}$ is the matrix of the modes of the vibrations, the tilde above the letter denotes transposition of the matrix, and $\hat{\Delta}$ is the diagonal matrix with the elements[48]

$$\delta_{ii} = [h/8\pi^2 c\nu_i]\,\mathrm{cth}[hc\nu_i/2kT] \ .$$

From this we have[47]

$$\Delta C_v = C_v^* - C_v = \left(\frac{\partial\,\Delta U}{\partial T}\right)_v = \mathrm{tr}\left(\frac{\partial\hat{\Sigma}^*}{\partial T} - \frac{\partial\hat{\Sigma}}{\partial T}\right)\hat{F}. \tag{17}$$

Here,

$$\partial\hat{\Sigma}^*/\partial T = \hat{L}^*(\partial\hat{\Delta}^*/\partial T)\hat{\tilde{L}}^*;\ \partial\hat{\Sigma}/\partial T = \hat{L}\,(\partial\hat{\Delta}/\partial T)\,\hat{\tilde{L}},$$

where $\partial\hat{\Delta}/\partial T$ is the diagonal matrix with the elements

$$\frac{\partial\delta_{ii}}{\partial T} = h^2/\{16\pi^2T^2k\,\mathrm{sh}^2[hc\nu_i/2kT]\} \ .$$

Using the Binet–Cauchy theorem, we can represent the trace of the product of the two matrices in Eqns. (17) as the matrix

$$\hat{A}_{\Delta C_V} = \hat{A}^*_{C_{V_v}} - \hat{A}_{C_{V_v}},$$

whose (i,j)th element is the product of the (i,j)th element of the matrix $(\partial\hat{\Sigma}^*/\partial T - \partial\hat{\Sigma}/\partial T)$ and the (i,j)th element of the matrix $\hat{F}$. The matrices

$$\hat{A}_{C_{V_v}} \text{ and } \hat{A}^{\Delta}_{C_V}$$

are respectively the representations of the vibrational heat capacity and the isotopic difference in the total heat capacities as contributions with respect to the coordinates.

For the isotopic difference in the entropies we have

$$\Delta S = (S_0^* - S_0) + \int_0^T \frac{(C_V^* - C_V)}{T}\,dT = (S_0^* - S_0) + \\ + \mathrm{tr}\left[\int_0^T\left(\frac{\partial\hat{\Sigma}^*}{\partial T}\right)\frac{dT}{T} - \int_0^T\left(\frac{\partial\hat{\Sigma}}{\partial T}\right)\frac{dT}{T}\right]\hat{F} \\ \int_0^T\left(\frac{\partial\hat{\Sigma}}{\partial T}\right)\frac{dT}{T} = \hat{L}\left\{\int_0^T\left(\frac{\partial\hat{\Delta}}{\partial T}\right)\frac{dT}{T}\right\}\hat{\tilde{L}} \ . \tag{18}$$

Here,

$$\int_0^T\left(\frac{\partial\hat{\Delta}}{\partial T}\right)\frac{dT}{T} - \ ,$$

is the diagonal matrix with elements on the diagonal

$$\frac{hc\nu_i}{2T}\,\mathrm{cth}\,\frac{hc\nu_i}{2kT} - k\ln\mathrm{sh}\,\frac{hc\nu_i}{2kT} \ .$$

The corresponding matrix $\hat{A}_{\Delta S_v}$ is easily obtained from the second term in Eqn. (18) in the same was the matrices $\hat{A}_{\Delta U}$ and $\hat{A}_{\Delta C_v}$ were constructed.

We introduce the matrix

$$\hat{A}_{\ln\beta_v} = -\frac{\hat{A}_{\Delta F_v}}{kT} = -\frac{\hat{A}_{\Delta U} - T\hat{A}_{\Delta S_v}}{kT} \quad . \tag{19}$$

The matrix obtained is symmetrical, and the term at the intersection of its ith row and jth column represents the contribution of the interaction of the ith and jth vibrational coordinates to $\ln\beta$. The sum of all the elements of the matrix $\hat{A}_{\ln\beta_v}$ is equal to $\ln\beta_v$, that is

$$\ln\beta = \ln\beta_t + \ln\beta_r - \frac{3}{2}\ln\frac{m^*}{n} + \sum_{i,j} a_{ij}, \tag{20}$$

where a_{ij} denotes the (i,j)th element of the matrix $\hat{A}_{\ln\beta_v}$.

The use of the representation (20) makes it possible to analyse $\ln\beta$, and hence the isotope effect, in terms of the vibrational coordinates, and not the vibrational frequencies. The representation (20) is exact. An example for the case of the molecule of formaldehyde H_2CO (H_2CO/HDCO replacement) is given in Fig. 1.

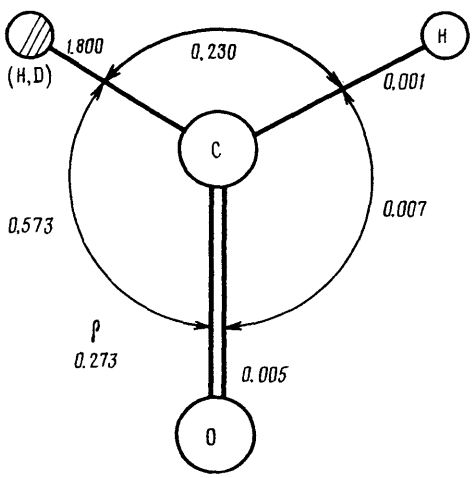


Figure 1. Representation of the vibrational component of $\ln\beta_{D/H}$ for the formaldehyde molecule (H_2CO/HDCO replacement) as the sum of the contributions of the structural elements; $\ln\beta_{dis}$ is the contribution of coordinates at a distance from the replacement centre; $\ln\beta_{n-d}$ is the contribution of the non-diagonal interactions.

$$\ln\beta_{dis} = 0.013 \quad ,$$
$$\ln\beta_{n-d} = 0.006 \quad ,$$
$$\ln\beta = 2.200 \quad ,$$

The natural vibrational coordinates used (see Fig. 1) are the changes in all the valence bonds and angles, and also the coordinate of the out-of-plane vibration ρ (the displacement of a bond from the plane). One of the coordinates (a valence angle) is redundant, and the calculation gives one frequency equal to zero.

4. Matrix representation of the translational–rotational contribution and the total value of $\ln\beta$

The representation examined in the previous paragraph makes it possible to write $\ln\beta$ as the sum of the elements of the matrix $\hat{A}_{\ln\beta_v}$ and the contribution Ω (the Teller–Redlich term), determined by the translational and rotational degrees of freedom of the molecule:

$$\ln\beta = \sum_{ij}{}' a_{ij} + \Omega, \tag{21}$$

where

$$\Omega = \Delta S_t/k + \Delta S_r/k - \frac{3}{2}\ln\frac{m'}{m} = \frac{1}{2}\ln\frac{\det\hat{G}'}{\det\hat{G}} \quad , \tag{22}$$

(m is the mass of the atom being replaced).

The Teller–Redlich term Ω is determined by the geometry and the distribution of the masses in the molecule as a whole. In particular, this contribution cannot be transferred in homologous series.

Nevertheless, there is no difficulty in constructing an accurate representation of the Teller–Redlich term and the total value of $\ln\beta$ as the matrix of the contributions of the interactions of the structural elements of the molecule, analogous to the matrix (19) for $\ln\beta_v$. To construct the required representation,[46,47] it is sufficient to note that the value of $\ln\beta \to 0$ as $T \to \infty$. The Teller–Redlich term is independent of temperature, so that Eqn. (21) gives

$$\lim_{T\to\infty} \ln\beta_v = -\Omega \quad , \tag{23}$$

which leads to the required matrix representation for the term (22) (the matrix $\hat{A}_\Omega$):

$$\hat{A}_\Omega = -\lim_{T\to\infty}\hat{A}_{\ln\beta_v} = \begin{pmatrix} \lim\limits_{T\to\infty} a_{11} & \cdots & \lim\limits_{T\to\infty} a_{1N} \\ \cdots & \cdots & \cdots \\ \lim\limits_{T\to\infty} a_{1N} & \cdots & \lim\limits_{T\to\infty} a_{NN} \end{pmatrix}. \tag{24}$$

Eqns. (24) and (21) readily give the matrix representation for the total value of $\ln\beta$:

$$\hat{A}_{\ln\beta} = \hat{A}_{\ln\beta_v} + \hat{A}_\Omega, \tag{25}$$

where each element of the matrix $\hat{A}_{\ln\beta}$ is the sum of the corresponding elements of the matrices $\hat{A}_{\ln\beta_v}$ and $\hat{A}_\Omega$.

The matrices $\hat{A}_\Omega$ and $\hat{A}_{\ln\beta}$ for the formaldehyde molecule (H_2CO/HDCO replacement) have been published.[46] The principal contributions to the value of $\ln\beta$ are made by the following coordinates: the bond CH* (contribution 1.484), the valence angle H*CO (0.377), the out-of-plane vibration ρ (0.168), and the valence angle H*CH (0.160). The contributions of the other coordinates and of the interactions between the coordinates are small.

Thus in the works cited[46,47] a complete and accurate representation of the logarithm of the β-factor as the sum of the contributions of the structural elements of the molecule was constructed for the first time.

5. The use of the representations of ln β to analyse isotope effects. The analysis of the rule of the geometric mean

If a molecule contains a group of l equivalent atoms, the following rule applies approximately when they are successively replaced by the atoms of an isotope[50–52]

$$\ln\beta=\frac{1}{x}\ln f_{(AD_xH_{l-x}/AH_l)}=\frac{1}{l}\ln f_{(AD_l/AH_l)}, \qquad (26)$$

where f is the ratio of the partition functions with respect to the states of the isotopic forms indicated in brackets.

It can be seen from Eqn. (26) that the rule of the geometric mean states that $\ln f$ is linearly dependent on the number of atoms x being replaced or, which is the same thing, that the value of $\ln\beta$ is independent of x.

We can take as a measure of the deviation from the rule (26) the difference between the actual value of $\ln\beta_{AD_xH_{l-x}/AH_l}$, calculated using Eqn. (5), and the estimate of this quantity obtained from the value for the completely substituted form using the rule of the geometric mean:

$$\delta=\frac{1}{x}\ln f_{(AD_xH_{l-x}/AH_l)}-\frac{1}{l}\ln f_{(AD_l/AH_l)}. \qquad (27)$$

We define the relative deviation as $\delta_{rel}=\delta/\ln\beta_{(AD_l/AH_l)}$. We can consider a molecule of the type H_2A, where A represents an arbitrary molecular group. Eqn. (9) has been used[53] to obtain the following equation for δ:

$$\delta=\frac{1}{2}\sum_{k=1}^{\infty}\ln\left[1+\frac{(\varkappa/k)^4(p_2-q_2)+\ldots+(\varkappa/k)^{4N}(p_{2N}-q_{2N})}{1+(\varkappa/k)^2p_1+\ldots+(\varkappa/k)^{4N}p_{2N}}\right], \qquad (28)$$

where

$$q_1=\sigma_1^{AH_2}+\sigma_1^{AD_2},\quad q_2=\sigma_2^{AH_2}+\sigma_1^{AH_2}\sigma_1^{AD_2}+\sigma_2^{AD_2},\ \ldots,\ q_{2N}=\sigma_N^{AH_2}\sigma_N^{AD_2}$$

$$p_1=2\sigma_1^{AHD},\quad p_2=2\sigma_2^{AHD}+(\sigma_1^{AHD})^2,\ \ldots,\quad p_{2N}=(\sigma_N^{AHD})^2.$$

In Eqn. (28), account is taken of the fact that in the harmonic approximation we always have $p_1=q_1$. Since at temperatures which are not too low the series (28) converges rapidly and since it is usually necessary only to estimate the value of δ, we can restrict ourselves, at $T=300$ K, to the first term of the expansion.

Eqn. (28) shows that the deviation from the rule of the geometric mean is related to the difference in the values of p_i and q_i for $i\geqslant 2$. In other words, in terms of the force field and the geometry of the molecule, fulfilment of the rule of the geometric mean is due to similarity in the values of p_i and q_i.

It should be noted that p_i-q_i for $i\geqslant 2$ depends only on higher powers of the difference in the reciprocal masses $(\Delta\mu)^i$, $i\geqslant 2$. Thus the inaccuracy of the geometric-mean rule is essentially a non-linear effect.

From the form of the expressions for p_i and q_i it is clear that the relative magnitude of the numerator of the terms in the series (28) relative to the denominator is greater, the greater the number of frequencies in the molecule undergoing an appreciable shift on isotopic replacement. This is due to the fact that the numerator of the terms in Eqn. (28) depends on the differences p_i-q_i, which are determined by the isotopic shifts of the frequencies, whereas the denominator contains the quantities p_i, which depend only on the absolute magnitude and number of the frequenices. Thus with increase in the number of frequencies in the molecule remaining unchanged or changing only slightly on isotopic replacement, the denominator of the terms of the series (28) will increase much more rapidly than the numerator, with a corresponding decrease in the values of δ and δ_{rel}.

Thus the greatest deviations from the geometric-mean rule should be expected for the H_2 molecule and small molecules of the type H_3B, in which the hydrogen atoms being replaced are joined to one central atom B, so that all the vibrations are vibrational modes of hydrogen and undergo a marked shift on isotopic replacement. The molecules of this type include molecules (H_2O, H_2S, NH_3) of practical interest for chemical exchange.[54] For organic molecules (except CH_4), it is clear that the deviations from Eqn. (26) should be negligible.

6. Localisation of the isotope effect of hydrogen

In the examination of the dependence of ln β on the remoteness of the substituents it should be borne in mind that isotopic replacement is equivalent to a perturbation which can be regarded as small in all cases except the case of the replacement of hydrogen atoms. This perturbation influences the whole molecule, but the influence is different for its different parts, decreasing with increase in the distance between the vibrational coordinates and the atom being replaced. It is possible, however, to have strong interaction between vibrational coordinates separated from one another, as a result of the fact that the frequencies of the vibrations to which these coordinates contribute are similar (resonance interaction).

This raises the question of the accuracy with which the fragmentary model reproduces the value of the β-factor of the whole molecule. The importance of this question follows from the fact that fragmentary models (see Fig. 2) are used to calculate isotope effects, particularly for complex molecules, and frequently this approach is the only one possible. It is therefore necessary to know the magnitude of the errors introduced by this approximation. In particular, it is important to know whether the value of the β-factor is influenced significantly by accidental resonance of the vibrations of the atom being replaced with the vibrations of coordinates at a distance.

This question has been studied in relation to the kinetic isotope effect. For example, a calculation[55] for a number of systems involving comparison with "truncated" models showed that the "removal" of an atom separated by more than two bonds from the atom being replaced introduces practically no error in the calculation of the kinetic isotope effect. No theoretical analysis of the problem has been published, however, and the case of resonance has not been studied.

The representation (9) has been used[56] to analyse the question of the "extent" of the isotope effect. To study this problem, the model four-atom molecule represented in Fig. 2 was examined. The following natural coordinates were introduced: the changes in the bond lengths r_1, r_2, and R, the changes in the valence angles φ_1 and φ_2, and the out-of-plane twisting coordinate χ. The calculation was carried out using force constants and geometric parameters characteristic of saturated hydrocarbons. To obtain the fragmentary model from the original molecule, the matrix of kinematic coefficients $\hat{G}$ was left unchanged, but the rows and columns of the force constant matrix of the original molecule were multiplied by a weighting factor x if these columns and rows corresponded to a natural coordinate including the atom removed.

The calculation was carried out for two cases: in the first case, an atom separated by three bonds ("third neighbour") from the atom being replaced was "removed" (x was taken as zero); in the second case, in addition, an atom separated by two bonds ("second neighbour") from the atom being replaced was also removed.

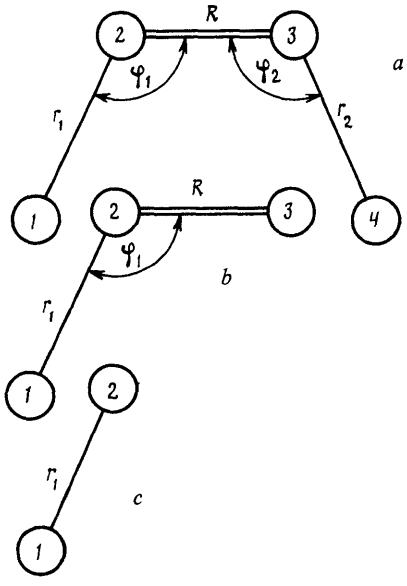


Figure 2. Fragmentary models.

The influences of the removal of the second and third neighbours differ significantly in scale. The removal of an atom separated by three bonds from the atom being replaced introduces a small error. The influence of an atom separated by two bonds from the atom being replaced cannot be neglected, however.

In the multiplication, described above, of the force constants for the coordinates removed by the factor x, the quantities ∂_i in Eqn. (9) can be represented as

$$\sigma_i=\sigma_i^{(0)}+\sigma_i^{(1)}x+\sigma_i^{(2)}x^2+\ldots+\sigma^{(N-m)}x^{N-m}, \qquad (29)$$

where $\sigma_i^{(0)}$ includes only the force constants and geometric parameters relating to the coordinates closest to the atom beign replaced. After substituting Eqn. (29) in Eqn. (9) and reducing similar terms in the numerator and denominator, Eqn. (9) takes the form

$$\ln\beta=\ln\beta_0+\delta(x), \qquad (30)$$

where $\delta(x)$ is a correction. Here, the term $\ln\beta_0$ in the right-hand side includes only the force constants and geometry of the remaining part of the molecule and is therefore the principal component of $\ln\beta$ (the contribution of the immediate environment of the atom being replaced). The second term in the right-hand side of Eqn. (30) depends on x, and for $x = 1$ it is a correction reflecting the contribution of molecular fragments at a distance.

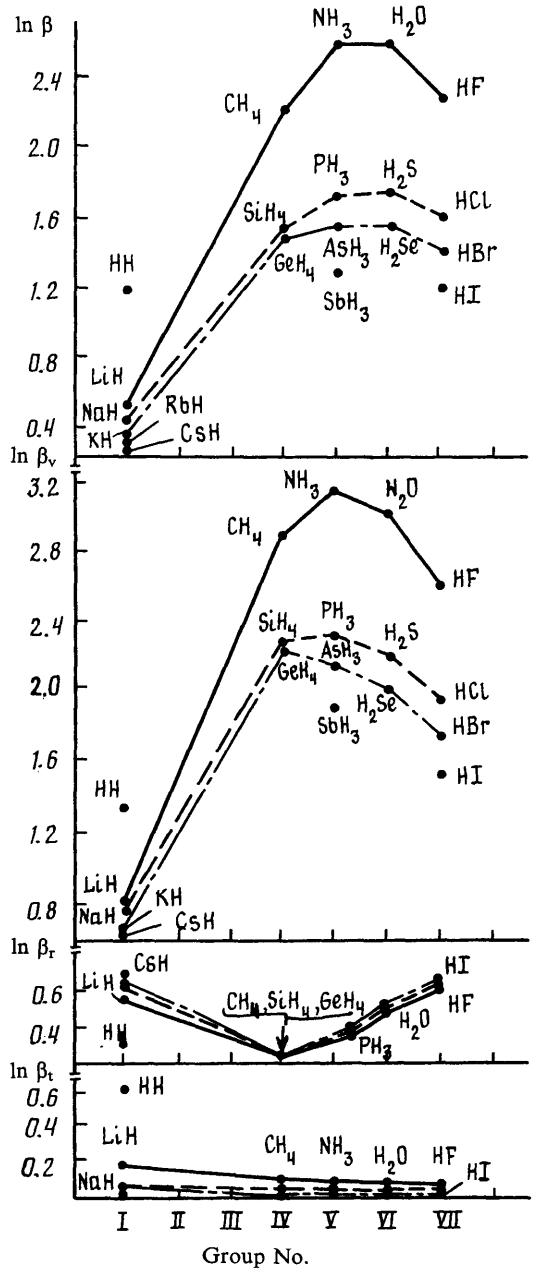


Figure 3. Components of $\ln\beta$ for normal hydrides.

Eqn. (30) has also been analysed.[56] At room temperature the isotope effect is localised at the replacement centre, as shown by the small size of the correction in Eqn. (30). The correction increases with decrease in temperature, however, and at 30 K its value is comparable with that of $\ln\beta_0$. This reflects the increasing delocalisation of the isotope effect with decrease in temperature, revealed by the fact that remote coordinates begin to make a significant contribution to $\ln\beta$.

The representation of Eqns. (29) and (30) also makes it possible to solve the problem of expressing $\ln\beta$ as the sums of the contributions of the first, second, and higher environments of the atom being replaced.[56]

IV. Analysis of quantitative data on the β-factors of hydrogen compounds

1. Dependence of $\ln\beta_{D/H}$ on the nature of the atom directly joined to the hydrogen atom being replaced. Analysis of $\ln\beta_{D/H}$ for normal hydrides

It is known empirically that the values of the ratio of the reduced partition functions (the $\beta_{D/H}$-factor) of the isotopic forms of molecules is determined primarily by the nature of the atom directly joined to the hydrogen atom being replaced. To study this relationship it is natural to consider the large number of so-called normal molecular hydrides of the *s*- and *p*-elements (that is the molecular hydrides of a given element with the general formula EH_n). The normal hydrides can serve as a model for examining more complex compounds, and therefore represent a key group in the chemistry of the isotopes of hydrogen.

Attempts have been made to obtain a phenomenological description of $\ln\beta$ for normal hydrides,[2] and also to interpret $\ln\beta_{D/H}$ in terms of the force field using the approximate methods of interpretation and correlations described above.[57–59]

The values of $\ln\beta_{D/H}$ for normal hydrides were recently re-examined by Bigeleisen.[58] It was concluded that the contribution of each ith vibrational coordinate to $\ln\beta$ is proportional to $(f_{ii}\Delta g_{ii})^{1/2}$, where f_{ii} is a diagonal element of the force constant matrix, nd $\Delta g_{ii} = g_{ii} - g^*_{ii}$ the difference in the diagonal elements of the matrices of the kinematic coefficients for the H- and D-forms of the molecule. It should be noted, however, that although the contribution made to $\ln\beta$ by the valence bond coordinates is in fact approximately linearly dependent on $(f_{ii}\Delta g_{ii})^{1/2}$, this correlation is not completely satisfactory for the valence angle coordinates, particularly for the normal hydrides of groups IV and V.

The representation (20) described above has been used to analyse the behaviour of $\ln\beta_{D/H}$ for normal hydrides.[59] Figs. 3 and 4 give the force constants and the contributions of different coordinates to $\ln\beta$. In the analysis of these data it should first be noted that the Teller–Redlich term $\ln\beta_t + \ln\beta_r + (^3/_2)\ln(m_D/m_H)$, which depends on the geometry and the masses, changes little and does not determine the behaviour of $\ln\beta$ for normal hydrides. The decisive factor is the variability of the vibrational contribution $\ln\beta_v$. For all normal hydrides, a predominant part is played by the contribution made to $\ln\beta_v$ by the H–E valence bond coordinate, and this contribution increases regularly in each period together with the force constant F_{HE} on going from group I to group VII, and decreases regularly in each group with increase in the atomic number of the element.

The contribution made by the angular coordinates depends both on the magnitude of the contribution of an individual valence angle and on the total number of valence angles. This number is equal to 3 for the hydrides of the group IV elements, 2 for group V, and 1 for group VI. On going from group VI to group IV, the contribution made by one angle (see Fig. 4) decreases, whereas the total contribution from the angular coordinates increases, since the total number of angles increases. The part played by the number of angles is extremely significant, and the total contribution made to $\ln\beta_v$ by the angular coordinates is greatest for the normal hydrides of the elements of group IV. This contribution does not exist for diatomic molecules, and it is for this reason that $\ln\beta$ for the hydrogen halides is smaller than that for the hydrides of the elements of groups V and VI, despite the larger force constant and the corresponding larger contribution of the H–E bond to $\ln\beta$.

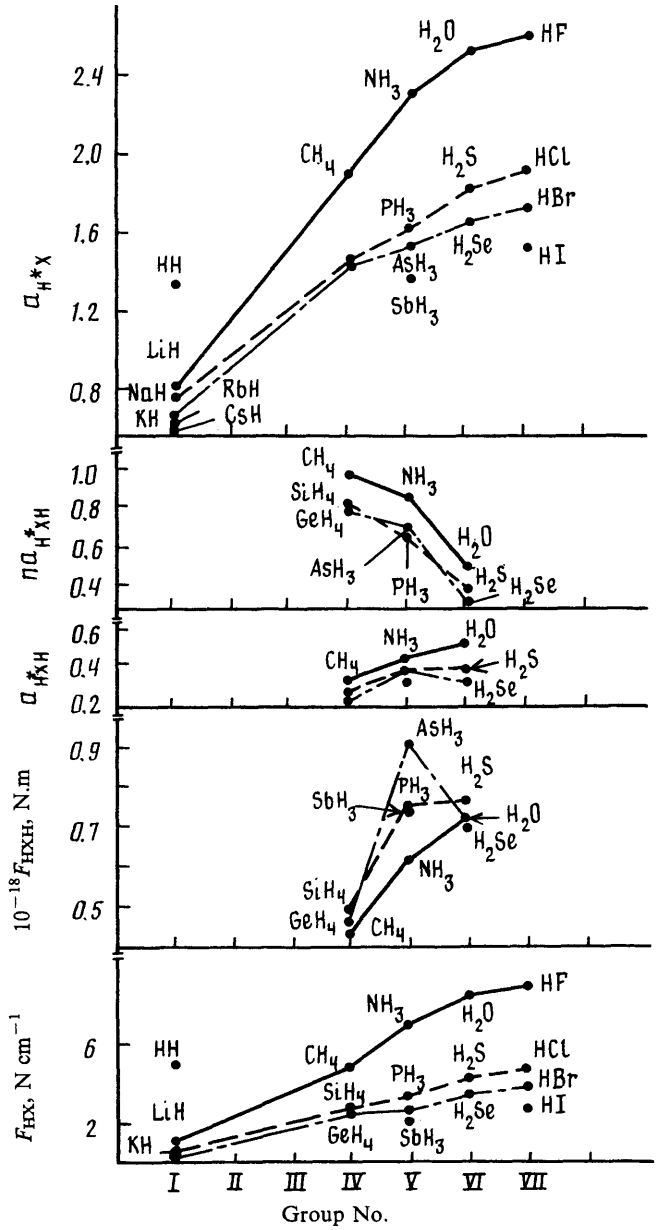


Figure 4. Contributions of different structural elements to $\ln\beta$ for normal hydrides: a_{H^*-X} is the contribution of the H*–X bond, a_{H^*XH} the contribution of the valence angle H*XH, and na_{H^*XH} the contribution of the valence angles with allowance for their multiplicity; F_{HX} and F_{HXH} are the bond and valence angle force constants respectively.

The magnitude of the contribution of the angular coordinates to $\ln\beta$ is not related in simple fashion to the magnitude of the angle force constant F_{HEH}. Here, a significant feature is that the numerical values of F_{HEH} for normal hydrides are comparable with one another. For the hydrides AsH_3 and SbH_3, the values of F_{HEH} and hence the contributions of the angles to $\ln\beta$ are anomalously large, and for AsH_3 this feature is observed when the calculation is carried out using force fields obtained by different authors.[59] Moreover, for these molecules, the values of the non-diagonal elements $F_{(HE,HEH)}$ in the force constant matrix are appreciable. The contribution of the non-diagonal interactions to $\ln\beta_v$ is correspondingly large. In this case the coordinates HE (bond) and HEH (angle) are strongly coupled, and therefore cannot be considered independently. The contributions of coordinates at a distance (bonds and angles not involving the atom being replaced) are small (< 0.06) for the normal hydrides.[59,60]

Thus for the normal hydrides as a class of compound, $\ln\beta_{D/H}$ shows approximately the same dependence on the H—E bond force constant, the contribution of a single angular coordinate, and the number of angular coordinates contributing to $\ln\beta$. As a consequence of the localisation of the isotopic effect, these conclusions apply not only to the normal hydrides themselves, but also to their derivatives.

2. Dependence of $\ln\beta_{D/H}$ on the number, type, and remoteness of the substituents. Compounds of hydrogen with carbon with sp^3-hybridisation

The value of $\ln\beta_{D/H}$ is determined not only by the nature of the hydride-forming element but also by the nature and number of the substituents on the atom joined directly to the hydrogen atom being replaced. The dependence of $\ln\beta_{D/H}$ on the nature and number of the substituents is also large-scale, and comparable with the dependence of $\ln\beta$ on the nature of the hydride-forming atom. For example, for carbon, even without a change in the hybridisation in the compounds CH_3X, the value of $\ln\beta_{D/H}$ may vary from 2.49 (X = $OCOCH_3$) to 2.26 (X = H), which is almost equal to the range of variation of $\ln\beta$ for the normal hydrides from group IV to group VII in period II. The number of substituents has an equally marked influence (see Table 2).

Comparison of the values of $\ln\beta_{D/H}$ for molecules of the type CH_2XY with the values of $\ln\beta$ for CH_2X_2 and CH_2Y_2 molecules shows that for replacement on several different substituents, additivity of $\ln\beta_{D/H}$ may in general not be observed.

The representation (20) has been used[60] to calculate the contributions of vibrational coordinates of different types to $\ln\beta_{D/H}$ for molecules of the form $CH_{4-n-m}Y_nX_m$, where X, Y = F, Cl, Br, I. This set of values of the contributions is sufficiently representative for an analaysis of the relationship being considered. In fact, the range of change in $\ln\beta_{D/H}$ for the methyl group is almost completely covered by the above set. Moreover, this set of molecules can also be regarded as a model set in the general case of isotopic replacement with respect to hydrogen, since the hydrogen effect is localised at ordinary temperatures.

To be definite, and for simplicity, we shall consider the case of the replacement of only one hydrogen atom. Some of the published results[60] are given in Table 2. It can be seen from this Table that the principal contribution to $\ln\beta$ is made by the C—H* bond, and that this contribution remains approximately constant, changing by not more than 5% in the whole set of molecules studied (here and subsequently, the asterisk indicates the atom replaced by the isotope). This range of change is much smaller than the variation in the actual value of $\ln\beta_{D/H}$, but larger than the variation of the force constant F_{CH} in the given set. The explanation is that the vibrational coordinate corresponding to change in the C—H* bond length, subsequently denoted in the text as CH*, shows, particularly for fluorine-containing molecules, considerable dynamic coupling with the coordinates CX and with the valence angle coordinates, so that the magnitude of its contribution to $\ln\beta_{D/H}$ cannot be determined entirely by the force constant of one given coordinate.

Table 2. Values of $\ln\beta_{D/H}$ for halogenomethanes and $CH_2(CN)_2$ (T = 300 K).

Molecule	$\ln\beta_{D/H}$	Translational–rotational contribution	Σ	C—H* bond contribution	Contributions of the angles H*CX
CHF_3			2.67±0.03 (E)		
$CHClF_2$	2.70	0.05	0.07	1.97	2·0.57 (HCF) 0.51 (HCCl)
$CHBrF_2$	2.65	0.05	−0.25	1.93	2·0.67 (HCF) 0.63 (HCBr)
CH_2F_2	2.64	0.15	−0.39	1.94	2·0.79 (HCF) 0.40 (HCH)
$CHCl_2F$	2.64	0.04	−0.03	1.98	0.63 (HCF) 2·0.50 (HCCl)
CH_2Cl_2			2.52±0.02 (E)		
$CHBr_2F$	2.62	0.03	−0.08	1.94	0.76 (HCF) 2·0.50 (HCBr)
CH_2FCl	2.62	0.12	−0.20	1.95	0.74 (HCF) 0.67 (HCCl) 0.38 (HCH)
$CHBrClF$	2.61	0.04	0.03	1.95	0.58 (HCCl) 0.56 (HCF) 0.50 (HCBr)
$CHCl_3$			2.54±0.02 (E)		
CH_2BrF	2.58	0.11	−0.18	1.95	0.80 (HCF) 0.55 (HCBr) 0.38 (HCH)
$CHBrCl_2$	2.56	0.02	−0.03	1.94	2·0.57 (HCCl) 0.52 (HCBr)
$CHBr_2Cl$	2.51	0.02	−0.10	1.93	0.68 (HCCl) 2·0.51 (HCBr)
CH_2BrCl			2.57±0.06 (E) calculated value:		
	2.51	0.10	−0.07	1.95	0.67 (HCCl) 0.55 (HCBr) 0.38 (HCH)
$CHBr_3$			2.55±0.03		
CH_2Br_2			2.47±0.05 (E)		
CH_2ICl	2.48	0.10	−0.07	1.94	0.60 (HCl) 0.60 (HCCl) 0.36 (HCH)
CH_3Br			2.33±0.04 (E)		
CH_2IBr	2.44	0.09	−0.10	1.95	0.62 (HCBr) 0.57 (HCl) 0.35 (HCH)
$CH_2(C{\equiv}N)_2$	2.43 (E)				

Note. The letter "E" denotes a value obtained from the experimental frequencies; the contributions of the vibrational coordinates are given only for those molecules for which the most reliable data on the force constants in natural coordinates are available; Σ is the sum of the contribution of the interaction of coordinates of different kinds and the contribution of bonds and angles not including the atom being replaced.

Alcohols and ethers

Compound	$CH_3^*-O-C(=O)-CH_3$	$CH_3^*-O-C(=O)-H$	$CH_3^*-O-CH_2CH_3$	$CH_3^*-OCH_3$	CH_3^*OH
$\ln\beta_{D/H}$	2.49±0.13	2.48±0.09	2.45	2.44±0.05	2.40±0.05

Nitrogen-containing compounds

Compound	$CH_3^*NH_3^+$	$CH_3^*-N=N-CH_3^*$	$CH_3^*NH_2$	$CH_3^*-N=NH$	CH_3^*-NC
$\ln\beta_{D/H}$	2.42	2.41±0.04	2.39	2.36	2.35±0.02

Compounds with halogens and other elements

Compound	CH_3^*F	CH_3^*Cl	CH_3^*Br	CH_3^*I	CH_3^*-H	$CH_3^*SCH_2CH_3$	$CH_3^*-GeH_3$	$CH_3^*-SnH_3$
$\ln\beta_{D/H}$	2.46±0.05	2.36±0.04	2.33±0.04	2.32±0.05	2.26±0.02	2.35	2.29	2.21±0.03

Compounds with carbon

Compound	$CH_3^*-CH_2CH_3$	$CH_3^*CH_2I$	$CH_3^*-CH_2OCH_3$	$CH_3^*CH_2F$	$CH_3^*CH_3$	$CH_3^*-C\equiv CH$	$CH^*-C\equiv N$	
$\ln\beta_{D/H}$	2.45±0.06	2.40	2.38	2.37	2.36±0.07	2.41±0.05	2.36±0.02	
Compound	$CH_3^*-C(=O)-OH$	$CH_3^*-C(=O)-OCH_3$	$CH_3^*-C(=O)-Cl$	$CH_3^*-C(=O)-NH_2$	$CH_3^*-C(=O)-CH_3$	$CH_3^*-C(=O)-D$	$CH_3^*-C(=O)-F$	$CH_3^*-C(=O)-H$
$\ln\beta_{D/H}$	2.39	2.38±0.13	2.38	2.37	2.36±0.08	2.31±0.03	2.31±0.04	2.30

In general, and in contrast to the normal hydrides, for substituted methanes the interactions of the vibrational coordinates make a significant contribution to $\ln\beta$. This feature means that in this case the coordinates cannot be considered independently, as confirmed by an analysis of the force constant matrices.

The fairly marked scatter and the non-characteristic nature of the contributions of the valence angles to $\ln\beta_{D/H}$ are obvious. For a given molecule, the scatter in these contributions obtained by calculation from the force fields given by different authors, often exceeds even the scatter in the actual values of $\ln\beta$. This is not surprising, since the numerical value of $\ln\beta$ is determined only by the frequencies, which are obtained unambiguously from the force field, while the values of the contributions of specific coordinates are determined by the force field, which is found unambiguously from the experimental frequencies. In other words, slight scatter in the frequencies or in even individual frequencies may correspond to a large scatter in the values of the force constants. The difference in the force fields is also responsible for the scatter in the values of the contributions.

At the same time it is obvious that the physically correct solution for the force field is unique, and, moreover, that from its physical significance the scale of the variation in the contributions in a set of molecules should not exceed the scale of the variation of $\ln\beta$. It is therefore appropriate to solve the inverse problem, that is to find the values of the contributions of the coordinates by solving the over-determined system of linear equations by the least-squares method for a sufficiently representative set of molecules, using the known values of $\ln\beta_v$. The values of the contributions of the vibrational coordinates obtained in this way may serve as a criterion of the physical correctness of the force fields.

Since the solution of the system of linear equations in this case (the replacement of one hydrogen atom) is in principle unique, it is necessary to fix one of the contributions. The contribution of the CH* bond was chosen as this contribution. The accuracy of the additive scheme indicated corresponds to that of the calculation of $\ln\beta$ from the experimental vibrational frequencies.[60]

For the calculation of the β-factor for carbon replacement, Galimov[61] proposed an empirical additive scheme which has been widely applied, chiefly in the study of geochemical effects. In this scheme, the β-factor itself (and not its logarithm) is calculated, as the sum of the increments in the chemical bonds without allowance for the angles; this is quite permissible for carbon. From what has been said above it is clear that the additive representation is also possible and useful for hydrogen effects, but in this case it is more natural to expand the logarithm of the β-factor with necessary allowance for the valence angles.

Moreover, the dependence of $\ln\beta_{D/H}$ on the number and type of substituents for a given hydride-forming element is obviously determined primarily by the contribution of the valence angles H*EX and by the contribution of $\ln\beta_t + \ln\beta_r$. The electronic influences of the substituents on the force constant and hence on the contribution of the E–H* bond play a secondary role. Even if it is assumed that the contributions of the angles and bonds of each type to $\ln\beta_v$ are unchanged and depend only on the number of substituents, it cannot be expected that $\ln\beta$ will vary linearly with respect to the number of substituents, since the linearity breaks down when account is taken of the rotational contribution (it can readily be seen that the rotational contribution changes non-linearly with change in the number of substituents). There is even less reason to expect linearity when account is taken of the contributions of the interactions between the coordinates.

sp$_3$-Hybridisation

Compound	$CH_3^*CH_3$	$CH_3O^*CH_3$	$CH_3^*-CH_2CH_3$	$H^*-C(CH_3)_3$	$CH_3^*CH_3$	CH_3^*-H	CH_3^*F	CH_3^*OH	$CH_3^*NH_2$
$\ln\beta_{D/H}$	2.57±0.09	2.51	2.45±0.06	2.42	2.36±0.07	2.26±0.02	2.46±0.05	2.40±0.05	2.39

sp$_2$-Hybridisation

Carbonyl compounds

Compound	$H^*-C(=O)OCH_2Cl$	$H^*-C(=O)OH$	$H^*-C(=O)OCH_3$	$H^*-C(=O)NH_2$	$H^*-C(=O)F$	$H^*-C(=O)CH_3$	$H^*-C(=O)C(=O)H$	$H^*(H)C=O$
$\ln\beta_{D/H}$	2.42	2.39	2.38±0.16	2.35	2.31	2.30±0.07	2.16±0.07	2.13±0.04

Unsaturated hydrocarbons

Compound	$H^*(F)C=C(H)F$	$H^*(H)C=CCl_2$	$F(H^*)C=C(H)F$	$H^*(H)C=CH_2$	$H^*(Cl)C=C(H)Cl$	$H^*(Cl)C=C(Cl)H$	$CH_2^*=C=CH_2^*$	$H^*(H)C=N=N$	$H^*(H)C=CH-CH=CH_2$
$\ln\beta_{D/H}$	2.43±0.08	2.34±0.07	2.33±0.05	2.33	2.31±0.04	2.28±0.05	2.21	2.16	2.09

sp-Hybridisation

Compound	$H^*-C\equiv CF$	$H^*-C\equiv C-CF_3$	$H^*-C\equiv CH$	$H^*-C\equiv CBr$	$H^*-C\equiv N$	$H^*-C\equiv CCl$	$H^*-C\equiv C-CH_3$	$H^*-C\equiv C-C\equiv N$
$\ln\beta_{D/H}$	2.11	2.06±0.02	2.06±0.02	2.04	2.035±0.005	2.03	1.97±0.11	1.88

Cyclic compounds

Compound	CH_2-CH_2 (O)	Cyclohexane	Cyclo-butane-D_6	Benzene-D_6	Cyclo-propane D_6	HCH^* (CH=CH)	Cubane-D_1	$CH^*=CH$ (CH_2)
$\ln\beta_{D/H}$	2.44	2.42	2.40	2.38±0.06	2.39±0.04	2.32	2.22	2.10

The new coordinates which appear when substituents are introduced, particularly the coordinates of adjoining angles, make a contribution to $\ln\beta$ which may be either larger than or smaller than the contribution of the coordinates which disappear. Moreover, replacement brings about a change in the contribution of $\ln\beta_t + \ln\beta_r$. Thus with increase in the number of substituents of the same type, the value of $\ln\beta$ may either increase or decrease. The dependence of $\ln\beta_{D/H}$ for the methyl group on the nature of the substituents in compounds of the type CH_3^*R is shown by the data given below (T = 300 K).[57,60,62]

In the analysis of these data it should be borne in mind that they were calculated for the replacement of the three hydrogen atoms in the methyl group, whereas in the calculation for the $CHX_nY_mZ_l$ molecules only one hydrogen atom was replaced. Thus the values of $\ln\beta_{D/H}$ for the compounds CH_3R are 0.5–1% too high, as a result of the inaccuracy of the geometric-mean rule. The variation in $\ln\beta$ for the methyl group for a given substituent X is determined primarily by the rotational contribution and by the value of the force constant of the HCX angle, and to a much smaller extent by the influence of the substituent on the force constants of the C–H and C–X bonds. These factors may act in opposite directions. Thus on going from CH_3F to CH_3I the angle force constant (F_{HCX}/r^2_{CH}) changes from 0.900 N cm^{-1} to 0.651 N cm^{-1}. This also determines the change in $\ln\beta$, which goes from 2.457 to 2.320. On going from F to I, the force constant of the C–X bond also decreases, from 5.535 N cm^{-1} to 2.338 N cm^{-1}, but this factor has less influence on $\ln\beta$. The constant F_{CH}, however, generally changes in the opposite direction in this series, although the change is slight (from 4.878 N cm^{-1} for CH_3F to 5.002 N cm^{-1} for CH_3I).

3. Compounds of carbon with hydrogen with *sp*^{2}- and *sp*-hybridisation. Dependence of $\ln\beta$ on the geometry of the molecule

We can compare the logarithms of the $\beta_{D/H}$-factors of compounds with *sp*^{3}-, *sp*^{2}-, and *sp*-hybridisation of the hydride-forming carbon atom. First of all, the general decrease in the value of $\ln\beta_{D/H}$ for *sp*^{2}- and *sp*-hybridisation compared with *sp*^{3}-hybridisation should be noted. At the same time, the bond force constants F_{CH} and the corresponding contributions of the bonds to $\ln\beta$ are greatest for *sp*-hybridised and smallest for *sp*^{3}-hybridised molecules. The factor responsible for the decrease in $\ln\beta$ on going from *sp*^{3}-hybridisation to *sp*^{2}- and *sp*-hybridisation can therefore only be the decrease in the number of vibrational coordinates contributing to $\ln\beta$. To confirm this, we can consider the contributions of the vibrational coordinates to $\ln\beta$ for monosubstituted derivatives of ethane, ethylene, and acetylene (see Fig. 5).[63]

Fig. 5 shows that the number of coordinates closest to the atom being replaced decreases in the order ethane–ethylene–acetylene, leading to a decrease in $\ln\beta$, despite the increase in the force constants and hence in the contributions made to $\ln\beta_{D/H}$ by each individual vibrational coordinate.

The values of $\ln\beta_{D/H}$ for substituted ethylenes $HR^1C=CR^2R^3$ are given below [the dependence of $\ln\beta_{D/H}$ (on the carbon atom) on the type of hybridisation of the atom directly joined to the atom being replaced (T = 300 K)].[57,60,62]

It should be borne in mind that for replacement in ethylene the substituents R^2 and R^3 are separated by three bonds from the hydrogen being replaced. The influence of the substituents R^2 and

R^3 is therefore weaker than that of the substituent R^1, but stronger than the corresponding influence for the methyl group.

Fig. 5 shows that for ethylene, an appreciable contribution to $\ln\beta$ is made by the out-of-plane coordinates. In substituted ethylenes, the out-of-plane vibrations depend markedly on the substituent.[5]

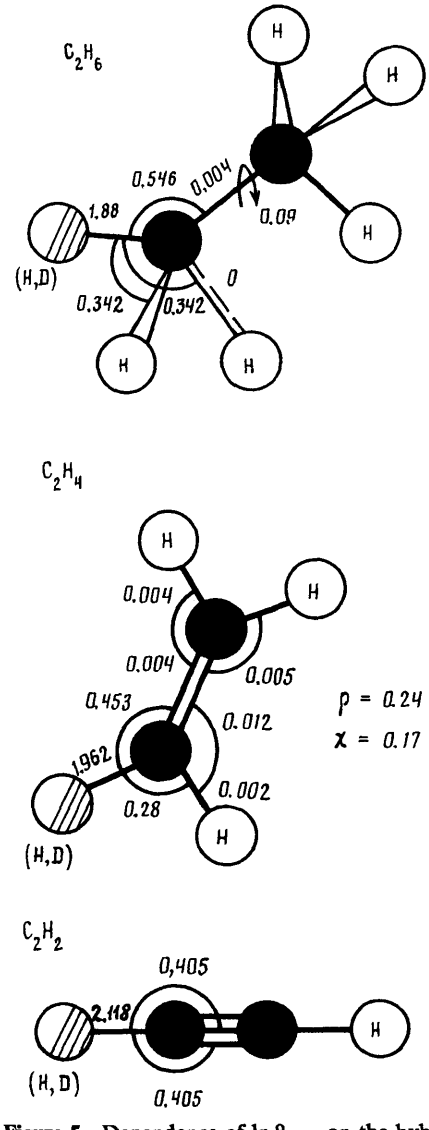
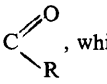


Figure 5. Dependence of $\ln\beta_{D/H}$ on the hybridisation; the change in the contributions of the vibrational coordinates in the series ethane–ethylene–acetylene; only the non-zero contributions are given; the values of $\ln\beta_{D/H}$ are 2.372 (ethane), 2.334 (ethylene), and 2.105 (acetylene); the vibrational components of $\ln\beta_{D/H}$ are 3.222, 3.124, and 2.889 respectively.

The influence of the substituents R^2 and R^3 on $\ln\beta$ is therefore also much stronger than for the methyl group. In fact, the atoms R^2 and R^3 are included in the twisting coordinate χ (rotation of the planes CHR^1 and CR^2R^3 about the C=C bond in different directions) and cannot in this case be regarded as separated neighbours. This must be taken into account in all cases of substitution at a double bond.

Another group of carbon compounds with sp^2-hybridisation consists of compounds of the type  , which can be regarded as substituted formaldehydes. All that has been said about the β-factors of ethylenic compounds applies in this case also, except that in the substituted formaldehydes there is no vibrational coordinate χ. The value of $\ln\beta$ for the formaldehyde is therefore low. In carbonyl compounds, an important part is played by the electronic influences of the substituents. The introduction of electron-acceptor groups such as –OH and –F increases the strength of the H–C bond, leading to an increase in its contribution and hence to an increase in $\ln\beta$.

The relative random error in the value of $\ln\beta_{D/H}$ for compounds with a double bond, particularly carbonyl compounds, is extremely large. This makes it impossible to analyse fine effects. This large error is related to the difficulty of obtaining accurate data on the vibrational spectra of these substances, due to the difficulty of purifying the substances, the indeterminacy (in a number of cases) in the number of conformers, and other factors. These factors make it difficult to interpret the spectrum to obtain an unambiguous assignment of the bands to fundamental vibrations even for simple compounds. Thus in the above case of formaldehyde-D_1 the published set of fundamental frequencies for HDCO is clearly erroneous. The case of this molecule also shows that the calculation of $\ln\beta$ can provide an additional criterion for the correctness of the interpretation of an experimental spectrum.

The error in $\ln\beta$ for complex molecules is generally greater than that for simple molecules. This is also related to the inaccuracy of the spectroscopic data for large molecules. At the same time, because of the localisation of the hydrogen effect, the molecular fragments at a distance do not influence the β-factor significantly. The use of small molecules as models therefore acquires particular further importance because of the higher accuracy of their β-factors.

For compounds of the acetylene series, the $\ln\beta$ values change very little with change in the nature of the substituents, due to the remoteness of the latter. At the same time, when heavy substituents are present, $\ln\beta$ for these molecules is smaller as a result of the decrease in the contribution of the angular coordinates.

In view of the fruitfulness and general character of the approach used, the study can be extended by examining different versions of the C–H bond. $\ln\beta_{D/H}$ has its highest values for sp^3-hybridised molecules, and $\ln\beta$ for methylene groups is higher than that for methyl groups. The value of $\ln\beta_{D/H}$ for isobutane-D_1 is apparently too low, because of the incorrect published[5] assignment of the frequencies of the isotopic forms.

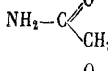
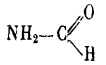
The high values of $\ln\beta$ for benzene is related to the rigidity of its structure and to the significant contribution from the large number of out-of-plane coordinates. Many vibrations of the benzene ring cannot be assigned to one definite bond or angle.[5] Thus as in the case of the halogen-substituted methanes considered above, it is appropriate to examine the benzene ring as a whole, without distinguishing "distant" and "nearest" fragments within it.

On the other hand, alicyclic molecules have lower $\ln\beta$ values compared with open-chain molecules, and $\ln\beta$ decreases with increase in the strain in the ring. This is related to the increase in the H*–C–C angles compared with the tetrahedral angle, which leads to a decrease in their strength and a decrease in their contribution to $\ln\beta$.

4. The values of $\ln \beta_{D/H}$ for compounds of hydrogen with nitrogen and oxygen

In the approach being used, the regularities of the change in the $\ln \beta_{D/H}$ values for compounds of nitrogen and oxygen are the same as for carbon compounds. All that has been said above about the dependence of $\ln \beta_{D/H}$ on the type of hybridisation and the number, nature, and remoteness of the substituents is also applicable to these molecules. The number of compounds of nitrogen and oxygen for which experimental spectroscopic data are available, however, is much smaller than that for carbon compounds. The $\ln \beta_{D/H}$ values for some of these compounds are given in Table 3. The $\ln \beta_{D/H}$ values for the corresponding normal hydrides show that the behaviour of $\ln \beta_{D/H}$ for nitrogen compounds with sp^3-hybridisation is similar to the case of the methyl group, but the $\ln \beta$ values for nitrogen compounds are on the average 0.2 unit greater than for the methyl group with identical substituents. For nitrogen compounds with sp^2-hybridsation, the $\ln \beta_{D/H}$ values are lower, as they should be (thus for NH_3, $_{D/H}$ = 2.21).

Table 3. Values of $\ln \beta_{D/H}$ (T = 300 K) for compounds containing NH and OH bonds.[57,60,62]

N–H bond	$\ln \beta_{D/H}$	O–H bond	$\ln \beta_{D/H}$
$NH(CH_3)_2$	2.71	$HO-NO_2$	2.59±0.02
NH_2-NH_2	2.59	$HO-NH_2$	2.59
NH_2-CH_3	2.58±0.03	HO–F	2.54
		$HO-CH_3$	2.51±0.04
	2.56		
			2.50±0.05
	2.49	HO–Cl	2.44±0.02
NH_2-OH	2.45		
NH_3	2.42		2.42
HN=NH*(cis)	2.40		
HN_3	2.29±0.2	HO–H	2.38±0.02

The $\ln \beta_{D/H}$ values for the O–H bond in oxygen compounds are close to the values for N–H bonds.

Practically all compounds containing NH and OH groups are capable to some extent of forming hydrogen bonds; this leads to a change in the immediate environment of the hydrogen atom being replaced and to a change in the force constants, and also influences $\ln \beta$ (the $\ln \beta$ values given in Table 3 were calculated for the monomers). At the same time, it is known that hydrogen bond formation has only a weak influence on the value of $\ln \beta$. This follows from the low values of the isotope effects of vapour pressure at 300 K. When a hydrogen bond is formed, compensation of the contributions made to $\ln \beta$ by the newly produced degrees of freedom takes place, and this explains the weak influence of association on the β-factor.[64]

In addition to hydrogen bond formation, another specific process is possible for the amino-group, namely protonation, which takes place in practice in aqueous solutions of aminoacids. On protonation of the amino-group, as a result of the increase in the number of vibrational degrees of freedom, $\ln \beta_{D/H}$ increases (2.68 for the ammonium ion, compared with 2.42 for ammonia). It should be emphasised, however, that protonation cannot be regarded simply as the mechanical addition of new structural elements to the molecule, since it is accompanied by a radical rearrangement of the force field. This may change in $\ln \beta$ in either direction. Thus protonation of oxygen and fluorine leads to a considerable decrease in $\ln \beta_{D/H}$. The published[65,66] separation coefficients for the H_3O^+/H_2O system show that $\ln \beta_{D/H}$ for the hydroxonium ion is ~0.3 unit lower thn $\ln \beta_{D/H}$ for H_2O. This is related to the difference in the electronic structures of the O and N atoms, as a result of which the protonation of the water molecule or the removal of an electron from it lead to a decrease in the strength of the bond, a sharp decrease in the force constants, and hence a decrease in $\ln \beta$. These marked changes in $\ln \beta_{D/H}$ on protonation may be significant in isotopic fractionation processes in biological systems.

References

1. *Synthesis and Applications of Isotopically Labeled Compounds* (Edited by R R Muccino), Elsevier, Amsterdam, etc., 1986
2. Ya M Varshavskii, S E Vaisberg *Usp. Khim.*, 1957, **26** 1434
3. J Bigeleisen, M G Mayer *J. Chem. Phys.*, 1947, **15** 261
4. E M Gailimov *Zh. Fiz. Khim.*, 1971, **45**(5) 1187 [English translation in *Russ. J. Phys. Chem.*, 1971(5)]
5. L M Sverdlov, M A Kovner, E P Krainov *Kolebatel'nye Spektry Mnogoatomnykh Molekul* (The Vibrational Spectra of Polyatomic Molecules), Nauka, Moscow, 1970
6. O Redlich *Z. Phys. Chem. (Liepzig), B*, 1935, **28** 371
7. L I Kleinman, M Wolfsberg *J. Chem. Phys.*, 1973, **59** 2043
8. L I Kleinman, M Wolfsberg *J. Chem. Phys.*, 1974, **60** 4740
9. L I Kleinman, M Wolfsberg *J. Chem. Phys.*, 1974, **60** 4749
10. M Wolfsberg, L I Kleinman *ACS Symp. Ser.*, 1975, (11) 64
11. J M Postma, L F Silvester, P A Rock *J. Phys. Chem.*, 1988, **92** 1308
12. J Bron, C Chang, M Wolfsberg *Z. Naturforsch, B*, 1973, **28** 129
13. A Farkas *Orthohydrogen, Parahydrogen, and Heavy Hydrogen* (Translated into Russian), ONTI, Moscow, 1936
14. D Z Goodson, S K Sarpal, P Bopp, M Wolfsberg *J. Phys. Chem.*, 1982, **86** 659
15. C L Chen, P Bopp, M Wolfsberg *J. Chem. Phys.*, 1982, **77** 579
16. J Bigeleisen *J. Chem. Phys.*, 1961, **34**(5) 1485
17. I B Rabinovich *Vliyanie Izotopii na Fiziko-khimicheskie Svoistva Zhidkostei* (The Influence of Isotopy on the Physicochemical Properties of Liquids), Nauka, Moscow, 1968
18. B M Andreev, Ya D Zel'venskii, S G Katal'nikov *Tyazhelye Izotopy Vodoroda v Yadernoi Tekhnike* (Heavy Isotopes of Hydrogen in Nuclear Technology), Energoatomizdat, Moscow, 1987
19. B M Andreev, G H Sicking *Ber. Bunsenges. Phys. Chem.*, 1987, **91** 177
20. T Shimanouchi *Tables of Molecular Vibrational Frequencies, Consolidated*, Vol. 1, Washington: NSRDS-NBS, 1972
21. T Shimanouchi *J. Phys. Chem. Ref. Data*, 1977, **6** 993
22. K S Krasnov, N V Filippenko, V A Bobkova, et al. *Molekulyarnye Postoyannye Neorganicheskikh Soedinenii: Spravochnik* (Molecular Constants of Inorganic Compounds: A Reference Book), Khimiya, Leningrad, 1979

23. A A Ivlev *Zh. Fiz. Khim.*, 1972, **46**(11) 2733 [English translation in *Russ. J. Phys. Chem.*, 1972(11)]
24. A A Ivlev, M Ya Koroleva, V A Dement'ev *Zh. Fiz. Khim.*, 1974, **48**(10) 2424 [English translation in *Russ. J. Phys. Chem.*, 1974(10)]
25. R E Weston *Z. Naturforsch, A*, 1973, **28** 177
26. C G Swain, E C Stivers, J R Reuwer, L J Schaad *J. Am. Chem. Soc.*, 1958, **80** 5885
27. J Bigeleisen *Tritium in the Physical and Biological Sciences*, Vol. 1, Vienna: IAEC, 1962, p. 161
28. D A Knyazev, N F Myasoedov, S V Demin, A V Bochkarev *Zh. Fiz. Khim.*, 1984, **58**(9) 2265 [English translation in *Russ. J. Phys. Chem.*, 1984(9)]
29. D A Knyazev, N F Myasoedov, A V Bochkarev, S K Myrzalieva *Zh. Fiz. Khim.*, 1984, **58**(9) 2260 [English translation in *Russ. J. Phys. Chem.*, 1984(9)]
30. J Bigeleisen, M Wolfsberg *Adv. Chem. Phys.*, 1958, **1** 15
31. J Bigeleisen, T Ishida *J. Chem. Phys.*, 1968, **48** 1311
32. T Ishida, J Bigeleisen *J. Chem. Phys.*, 1976, **64** 4775
33. J Bigeleisen, R C Hom, T Ishida *J. Chem. Phys.*, 1976, **64** 3303
34. J Bigeleisen, T Ishida, M W Lee *J. Chem. Phys.*, 1981, **74** 1799
35. G Nemeth, B Gellai, G Jancso *J. Chem. Phys.*, 1971, **54** 1701
36. D A Knyazev, T L Blank, A A Ivlev, A D Blank *Dokl. Akad. Nauk SSSR*, 1977, **233** 126
37. D A Knyazev, T L Blank, A A Ivlev, A D Blank *Zh. Fiz. Khim.*, 1979, **53**(7) 1682 [English translation in *Russ. J. Phys. Chem.*, 1979(7)]
38. T Oi, A M Popowicz, T Ishida *J. Phys. Chem.*, 1986, **90** 3080
39. J Bigeleisen, T Ishida *J. Chem. Phys.*, 1975, **62** 80
40. G Singh, M Wolfsberg *J. Chem. Phys.*, 1975, **62** 4165
41. S A Skaron, M Wolfsberg *J. Am. Chem. Soc.*, 1977, **99** 5253
42. D A Knyazev, I V Shimanogova, A V Bochkarev *Osobye Tochki Chastotnoi Funktsii Molekuly i Nevozmozhnost' Postroeniya Universal'nogo Algebraicheskogo Razlozheniya β-Faktora* (Unique Points of the Frequency Function of a Molecule and the Impossibility of Constructing a Universal Algebraic Expansion of the β-Factor), Moscow, 1988, Dep. in VINITI, 13th January 1988, No. 212-V88
43. L V Gladun, D A Knyazev, A V Bochkarev *Izv. Timiryazev. Sel'sk.-Khoz. Akad.*, 1985, (1) 179
44. D A Knyazev, N F Myasoedov, A V Bochkarev, A D Blank *Dokl. Akad. Nauk SSSR*, 1986, **287** 1415
45. D A Knyazev, N F Myasoedov, L V Gladun, A V Bochkarev *Tr. Mosk. Khim.-Tekhnol. Inst. im. D I Mendeleeva*, 1984, (130) 98
46. D A Knyazev, N F Myasoedov, A V Bochkarev *Zh. Fiz. Khim.*, 1988, **62**(12) 3131 [English translation in *Russ. J. Phys. Chem.*, 1988(12)]
47. D A Knyazev, N F Myasoedov, A V Bochkarev, N M Zhavoronkov *Teor. Osn. Khim. Tekhnol.*, 1987, **21**(4) 472
48. S J Cyvin *Molecular Vibrations and Mean Square Amplitudes* (Translated into Russian), Mir, Moscow, 1971
49. F R Gantmakher *Teoriya Matrits* (The Theory of Matrices), Nauka, Moscow, 1988
50. N M Zhavoronkov, D A Knyazev, A A Ivlev, G D Klinskii *Usp. Khim.*, 1980, **49**(3) 385 [English translation in *Russ. Chem. Rev.*, 1980]
51. J Bigeleisen *J. Chem. Phys.*, 1955, **23** 2264
52. J Bigeleisen *J. Chem. Phys.*, 1958, **28** 694
53. D A Knyazev, N F Myasoedov, A V Bochkarev *Zh. Fiz. Khim.*, 1986, **60** (9) 2293 [English translation in *Russ. J. Phys. Chem.*, 1986(9)]
54. P Sharlin *Acta Chem. Scand., Ser. A*, 1986, **40** 441
55. M Wolfsberg, M J Stern *Pure Appl. Chem.*, 1964, **8** 225
56. D A Knyazev, N F Myasoedov, A V Bochkarev, L V Gladun, A D Blank *Zh. Fiz. Khim.*, 1986, **60**(12) 2943 [English translation in *Russ. J. Phys. Chem.*, 1986(12)]
57. D A Knyazev, A N Bantysh, A A Ivlev *Kernenergie*, 1969, **12** 9
58. J Bigeleisen *Proc. Nat. Acad. Sci. USA. Phys. Sci.*, 1981, **78** 5271
59. D A Knyazev, N F Myasoedov, A V Bochkarev *Zh. Fiz. Khim.*, 1988, **62**(12) 3186 [English translation in *Russ. J. Phys. Chem.*, 1988(12)]
60. D A Knyazev, A V Bochkarev, M A Sytdykova *Zavisimost' β-Faktora ot Chisla i Tipa Zamestitelei* (The Dependence of the β-Factor on the Number and Type of Substituents), Moscow, 1990, 21 pp. Dep. in VINITI
61. E M Galimov *Priroda Biologicheskogo Fraktsionirovaniya Izotopov* (The Biological Fractionation of Isotopes), Nauka, Moscow, 1981
62. D A Knyazev, G D Klinskii *Isotopenpraxis*, 1978, **14**(2) 41
63. D A Knyazev, N F Myasoedov, A V Bochkarev, I V Shimanogova *Vsesoyuznyi Simpozium po Stabil'nym Izotopam v Geokhimii. Tezisy Dokladov* (Summary of Papers Presented at the All Union Symposium on Stable Isotopes in Geochemistry), Izd. GOEKhI Akad. Nauk SSSR, Moscow, 1989, p. 380
64. D A Knyazev, N F Myasoedov, I V Shimanogova, A V Bochkarev *Izv. Timiryazev. Sel'sk.-Khoz. Akad.*, 1989, (5) 168
65. J W Larson, T B McMahon *J. Am. Chem. Soc.*, 1986, **108** 1719
66. J L Kurz, M T Myers, K M Ratcliff *J. Am. Chem. Soc.*, 1984, **106** 5631

Translated from *Uspekhi Khimii* **61** 415–455 (1992) U.D.C. 547.1'118:541.49:546.185.546.33:546.34:546.386.546.562.562:547.233

Cyclopendant ligands

F I Bel'skii, Yu M Polikarpov, M I Kabachnik
A N Nesmeyanov Institute of Heteroorganic Compounds, Russian Academy of Sciences

ABSTRACT. The numerous cyclopendant ligands are described in the review. These contain a cyclic fragment, with donor atoms, with groups added which are capable of coordinating cations. An attempt has been made to systematise the literature data on the methods of synthesis and the properties of cyclopendant ligands. Fundamental results of authors on the application of a quantitative method of assessing the efficiency and selectivity of action of ligands (criteria *A* and *S*) are given.

It has been shown that the use of cyclopendant ligands enables the efficiency and selectivity of complex formation to be increased.

The bibliography contains 182 references.

Contents

I.	Introduction	221
II.	The first synthetic cyclopendants	222
III.	Cyclopendants: derivatives of oxygen macrocycles (crown-ethers)	223
IV.	Cyclopendants based on crown-polyaza-polyethers	224
V.	Cyclopendants: derivatives of nitrogen macrocycles	226
VI.	Acid dissociation of cyclopendant complexones: derivatives of polyazamacrocycles	236
VII.	Cyclopendants with a large cyclic fragment	237
VIII.	Effect of the nature of pendant groups and the structure of the cyclic fragment of cyclopendants on the efficiency and selectivity of complex-formation	239

I. Introduction

Polydentate reagents capable of binding cations with various coordination polyhedra have acquired considerable importance in coordination chemistry in recent years. By this means not only is the binding energy of the donor centres of the ligand added together but a chelate effect is also displayed (mainly entropic in origin). A polydentate ligand makes it possible to close several chelate rings, increasing in this way the binding equilibrium constant, i.e. the free energy of formation of the complex.

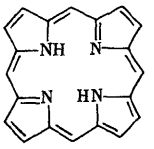
Polydentate reagents are widely used in analytical chemistry, in the technology of separating non-ferrous and rare metals, in processes of flotation and extraction, in the textile industry (mordent dyeing) and in many other areas of science and technology.

Polydentate reagents have acquired great importance mainly because of two properties, viz. the efficiency of binding cations (displayed in the stability if the resulting complexes) and the selectivity of complex-formation. This applies equally both to neutral reagents and to molecules containing both acidic and basic functional groups. The majority of complexones are characterised by a polydentate nature and chain flexibility, which bind donor complex-forming centres. The stability of the resulting complexes is high but the selectivity is comparatively low.

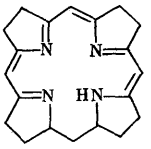
A higher selectivity among cyclic polydentate ligands is possessed by the neutral crown polyethers, basic polynitrogenous macrocycles, cryptands and certain other compounds. The cyclopendant ligands are of interest in this connection and are ligands containing a cyclic (usually macrocyclic) nucleus, frequently including donor centres, to which are added side groups, viz. pendant or lariat groups which also carry donor centres capable of coordination with metal cations.[1,2] Hence the name cyclopendants.†

The simultaneous binding of metal cations with the donor centres of the ring and the pendants frequently achieves high binding stability and selectivity for the cyclopendant ligands. The ligand shape arising in this way may not accommodate every cation.

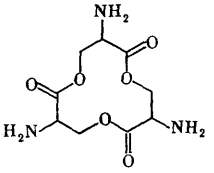
The nature cyclopendant ligands have high binding selectivity. Examples are derivatives of porphin, corrin and polyglycidic ethers, carrying various pendant groups. The variety of cyclopendants, i.e. vitamins, antibiotics, cytochromes, siderophores, etc., is explained by the variety of pendant groups and the central metal ion.



Porphin



Corrin

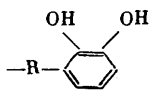


Serine trilactide

The addition of further pendant groups to the plane-coordinated metal complexes porphin and corrin occurs by a form of extra coordination. The pendant substituents occupy an apical position on the *z* axis perpendicular to the plane of the macrocycle.[3] Similar coordination proves to be a most important feature of such compounds as chlorophyll, blood haem, vitamin B-12, etc. With extra coordination the cations of various metals are bound selectively by the donor atoms of the pendant groups. Blood haem coordinates Fe^{3+} ions with the formation of haemin or haematin, chlorophyll acids (*a* and *b*) selectively bind the Mg^{2+} ion with the formation of chlorophyll. In the vitamin B-12 molecule the Co^{2+} ion is coordinated by the four nitrogen atoms of the corrin ring, the CN^- group and the nitrogen atom of a benzimidazole act as extra

† Originates from the Latin pendere (to hang) and the English pendant (a pendant). Occasionally ligands are also known as 'lariatnye' from the English lariat (lasso or rope). It seems to us that the term 'lariat' in relation to the whole ligand precludes the occurrence of donor centres in the ring which are frequently encountered and are reflected in the name cyclopendant. The actual 'pendant' is now widespread in the English language literature.

ligands (see Figures[1,4]). Cytochromes have the same ferroporphin fragment in the molecule. The differences in their properties are caused by the difference in pendant substituents. The phenolic hydroxyls of the pendant groups in the complex enterobactin



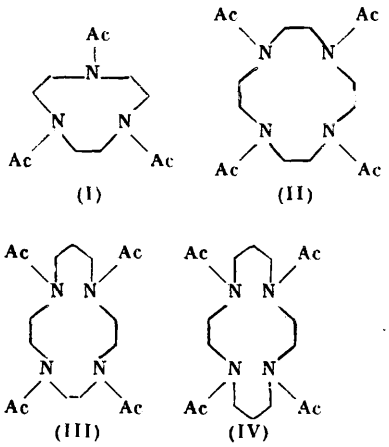
occupy the six coordination positions of the Fe^{3+} cation and form a stable complex.[5] All the natural cyclopendants possess high efficiency of action in addition to high selectivity of complex-formation, forming stable complexes with metal cations. The high stability of such complexes is caused not only by the high binding energy but also by the complete complementarity (spatial fit) of their ligand shape (in the presence of extra coordination) to the coordination polyhedraon of the cation in question.[3]

It is necessary to bear in mind the general principles of complex-formation. The equilibrium of this process is determined by the free energy of complex-formation $A = RT \lg K_{st}$ [sic], where K_{st} is the stability constant.‡ The energy of the coordination bond [sic] ΔH depends on the free energy and on the entropy. Frequently $\lg K_{st}$ is taken as a measure of the strength of the binding of the ligand and the cation in the complex. The strength naturally depends on the nature of the cation and the character of the ligand. This problem has been well studied in the chemistry of coordination compounds and is not examined in the present paper.

However there are other aspects to complex-formation linked mainly with the entropy factor. In the case of a polydentate ligand with several binding centres (donor centres) in one molecule, the problem of the complementarity of a ligand and the coordination polyhedron of the cation becomes important. If the polydentate ligand possesses a flexible chain of atoms than it can take up a conformation, without a large consumption of energy, corresponding to such complementarity. The strength of the resulting complex will be determined by the binding energy of the cation with the donor centres. With inadequate chain flexibility or with a structure such that the population of the complex-forming conformation (for the given cation) is low, the stability of the complex depends not only on the binding energy but also on the complementarity of the complex-forming conformation i.e. its energy of formation. If two polydentate ligands with the same set of donor centres are compared then the energy of complementarity becomes determining. It is clear that reagents with flexible chains of molecules may not be highly selective. Other conditions being equal (parity of the number and character of donor centres), the introduction of more rigid links into the chain of a polydentate ligand increases selectivity.

II. The first synthetic cyclopendants

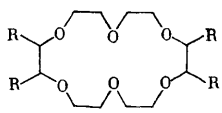
These ligands recall the natural ligands since they contain a cyclic fragment with added pendant groupings possibly acting as extra ligands. In 1975 Hama and Takamoto[6] synthesised and studied the complex-formation of the ligand (I) with transition metals (TM) and also with Cd^{2+} and Pb^{2+}. In 1976 Stetter and Frank obtained and investigated the complex-forming ability of complexones (II)–(IV) in relation to the alkaline earth metals (AEM) and the TM.[7]



Here and subsequently Ac = CH_2COOH.§

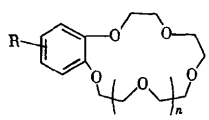
In the same year Behr and collaborators synthesised and investigated ligands (V) with ions of NH_4^+, K^+, $MeNH_3^+$ and $PhCH_2CH_2NH_3^+$ (25 °C, water).[8] The complex-formation of ligands (VI) with Na^+ and K^+ ions at 25 °C in acetone has been studied.[9]

The extraction[10] and complex-forming[11] properties of ligands of formula (VII) in relation to NH_4^+ and the alkali metals have been investigated.



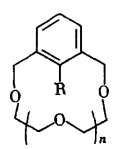
(V)

R = 1. C(O)NMe$_2$
2. COOH etc.



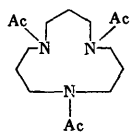
(VI)

n = 1,2, R = NH_2, COOH, COOMe etc.



(VII)

n = 1 to 4, R = COOH, OH, CH_2OH etc.



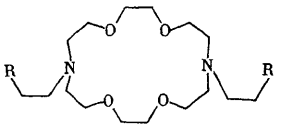
(VIII)

Takahashi and Takamoto in 1977 obtained and investigated (spectroscopically) the complexes $[ML]^0$ of Fe^{3+}, Cr^{3+}, and Co^{3+} cations with ligands (I) and (VIII).[12] In the same year Chang obtained ligands (IX)[13] and in 1978 Takagi and co-workers synthesised and studied the complex-formation of ligand (IX) (R = COOH) with ions of the AEM and TM.[14] Finally, in 1979 ligands (X) and (XI) were synthesised and complexes of (X) with

‡ The values of stability constants of complexes with the various cations used in this study were taken as a rule from reference literature, in which they had been critically assessed.

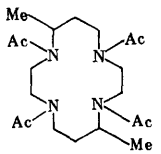
§ Note that the symbol Ac in the literature usually denotes the acetyl residue CH_3CO-. Here Ac = $-CH_2COOH$.

TM were isolated.[15] Ligand (XI), an analogue of enterobactin, binds Fe^{3+} ions effectively.[16]

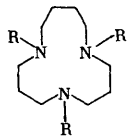


(IX)

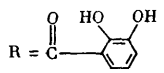
R = CN, CH_2NH_2 [13]
R = COOH [14]



(X)



(XI)

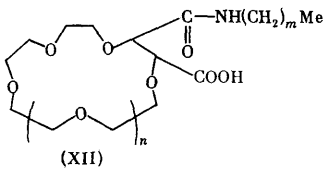


The reagents indicated were the first representatives of the synthetic cyclopendants. A great number of ligands with various groups were obtained later. The polyalkylenepolyamines, crown-ethers and crown-polyaza-polyethers with several modifications and various pendant groups form part of practically all new (synthesised up to 1988) cyclopendant reagents.

III. Cyclopendants: derivatives of oxygen macrocycles (crown-ethers)

Values of $\lg K_{st}$ have been determined for complexes of ligand (V, 2) with NH_4^+, K^+, $MeNH_3^+$ and $PhCH_2CH_2NH_3^+$ cations in water at 25 °C and are 3.51, 5.48, 2.88 and 2.41 respectively.[8] Pendant COOH groups evidently participate in the coordination since the ligand without these groups, 18-crown-6, forms complexes with NH_4^+ and K^+ ions with $\lg K_{st}$ = 1.1 and 2.06.[17]

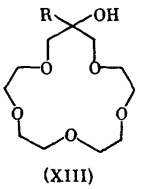
The complex-formation of ligands of formula (XII) with n = 1, m = 7 and 17; n = 1 and 2, m = 3, 7 and 13 with ions of Na^+, K^+ and Rb^+ has been investigated.[18]



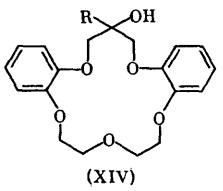
(XII)

The length of the hydrocarbon chain (variation of m) has no effect on the stability of the complexes. An increase in the size of the ring (transition from n = 1 to n = 2) leads to an increase of all the stability constants and a shift in the maximum efficiency of complex-formation towards cations of larger ionic radius.

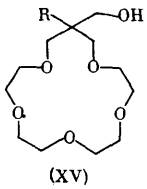
The ligands (XIII)–(XV) have been synthesised[19] and extraction and association constants with Na^+ and K^+ picrates were found. The substituents R showed an electronic and a steric effect on the extraction process.



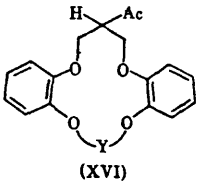
(XIII)



(XIV)



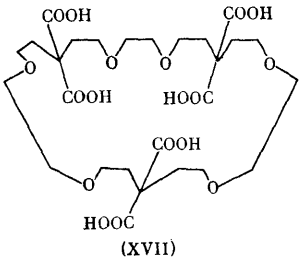
(XV)



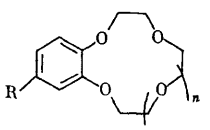
(XVI)

R = H, Me, Ph, n-$C_{10}H_{21}$ etc.
1. Y = CH_2CH_2; 2. Y = $(CH_2)_3$; 3. Y = CH_2OCH_2;
4. Y = $CH_2OCH_2OCH_2$.

The ligands (XVI) are efficient extractants for Na^+, K^+, Rb^+ and Cs^+.[20] The stability constants for (XVI, 3) with Ca^{2+}, Na^+ and K^+ ions have been determined.[21]



(XVII)

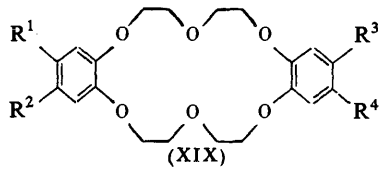


(XVIII)

1. n = 1 to 4, R = PPh_2 [Ref. 23]; 2. n = 2 to 3, R = = $CH(OH)CH_2NHMe$ [Ref. 24]; 3. n = 2, R = COOH, CH_2OH etc. [Ref. 25]; 4. n = 2, R = OH [Ref. 26].

The acid (XVII) was synthesised as a reagent for the UO_2^{2+} ion.[22] Ligands (XVIII) contain various numbers of donor oxygen atoms and various pendant groups R. Equilibrium constants were determined for compounds (XVIII, 1) (with various ring sizes) for the extraction of Li, Na^+, K^+ and Cs^+ picrates. The equilibrium constant for the ion of large ionic radius, K^+ and Cs^+, was increased for these compounds as n was increased. The pendant groups of ligands (XVIII, 1 and 2) seemingly do not participate in coordination with these cations since the corresponding compounds without the pendant groups in the molecule possess practically the same extraction and complex-forming properties.[23,24] Ten ligands (XVIII, 3) with various pendant groups have been synthesised.[25] Their extraction properties in relation to the picrates of Li^+, Na^+ and K^+ have been studied. Complexes of Li^+, Na^+, K^+, Rb^+, Mg^{2+}, Ca^{2+} and Ba^{2+} with ligand (XVIII, 4) of composition ML, ML_2, and M_2L have been obtained.[26] X-Ray structural analysis (XSA) of the complex $[KCNS(L)_2]$ showed that the K^+ ion in it was coordinated with ten donor atoms of the ligand. The pendant group and the CNS^- anion did not participate in coordination.

Cyclopendants based on dibenzo-18-crown-6 of formula (XIX) have been synthesised and investigated.



(XIX)

1. $R^1=R^2=R^3=R^4=H$ [Ref. 27]; 2. $R^1=R^4=H$, $R^2=R^3=NH_2$ [Ref. 28]

3. $R^1=R^4=H$, $R^2=R^3=N=CH-$ [Ref. 28];

4. $R^1=R^2=R^3=R^4CH_2PPh_2$ [Ref. 27];

5. $R^1=R^3=H$, $R^2=R^4=\overset{O}{\overset{\|}{C}}NHP(OH)^2$ [Ref. 29]

6. $R^1=R^3=H$, $R^2=R^4=NHP\begin{matrix}A\\ \|\\ O\quad B\end{matrix}$ (A, B = OEt, OBu, OPh) [Ref. 30];

7. $R^1=R^3=H$, $R^2=R^4=NHP(Me)(Ph)$ [Ref. 30].

The complex-formation of ligands (XIX, 2 and 3) with the ions Cu^{2+}, Co^{2+} and K^+ has been studied.[28] It was established that both pendant NH_2 groups of ligand (XIX, 2) participate in coordination with Co^{2+} and Cu^{2+}. The ring oxygen atoms do not participate in the coordination with these cations. The complex [(L)KI], in which K^+ is in the plane of the macrocycle, forms a chelate with the Co^{2+} ion of the same spectral type (infra-red: IR) as does free (XIX, 3). Stability constants for complexes of the alkali metals with ligand (XIX, 4) and dibenzo-18-crown-6 (XIX, 1) have been compared.[27] The pendant groups $CH_2P(O)Ph_2$ hinder the coordination of the cations investigated with the ring oxygen atoms (Table 1).

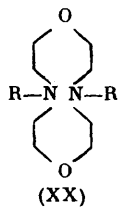
Table 1. Values of $\lg K_{st}$ for complexes $[ML]^+$ of ligands (XIX, 1 and 4) (solvent, ethanol : chloroform 1 : 1, T = 25 °C).[27]

Cation	(XIX.1)	(XIX.4)
Li^+	3,48	3,09
Na^+	3,97	3,86
K^+	4,51	3,95
Cs^+	3,49	3,47

The complex-forming properties of ligands (XIX, 5–7) have not been investigated.[29,30] In the complex $[(CoCl_2)_2KCl(L)]$ the K^+ ion is in the plane of the macrocycle but the Co^{2+} ions are bound only with the oxygen atoms of the pendant groups [L = (XIX, 4)].[27] As an extractant, ligand (XIX, 4) is better in separation factor for the U/Am pair than the best of a large series of reagents.[31]

IV. Cyclopendants based on crown-polyaza-polyethers

These compounds contain a cyclic polyaza-polyether fragment, the pendant groups being added at the nitrogen atoms. Ligands (XX) have been synthesised.[32]

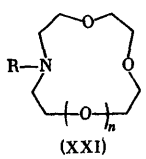


(XX)

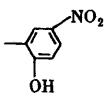
1. $R = CH_2CH_2\overset{O}{\overset{\|}{C}}NMe_2$
2. $R = (CH_2)_3\overset{O}{\overset{\|}{C}}NMe_2$
3. $R = CH_2CH_2OH$
4. $R = CH_2COOH$

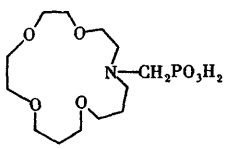
X-Ray structural analysis of the free ligand (XX, 2) showed that its donor atoms (N and O) are disposed at the vertices of an octahedron. The thermodynamic parameters ($\lg K_{st}$, $\Delta H°$ and $\Delta S°$) have been determined for ligands (XX, 1–3) with ions of the alkali and alkaline earth elements and Ag^+.[32] Evidently the pendant groups participate in the coordination with cations since the stability of the resulting complexes depends strongly on the nature of these groups. Thus ligand (XX, 1) forms far more stable complexes with a given cation than (XX, 2 and 3). Compound (XX, 4) has been mentioned[33] without citing its synthesis and properties.

Complex-formation of ligand (XXI, 1) with ions of the alkaline earth metals has been studied.[34]



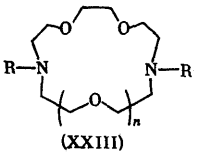
(XXI)

1. R = CH_2CH_2OH, n = 1;
2. R = CH_2  , n = 2, 3;
3. R = $CH_2PO_3H_2$, n = 2.



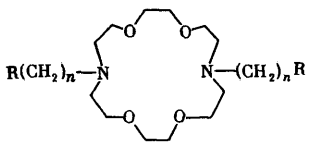
(XXII)

Moving from n = 2 to n = 3 leads to a change in the selectivity of extraction of alkaline earth metals by ligands (XXI, 2).[35] The complex-forming ability of ligands (XXI, 3), (XXII) and (XXIII, 4) with $CH_2PO_3H_2$ as pendant group was investigated in water in relation to the Na^+ ion.[36]



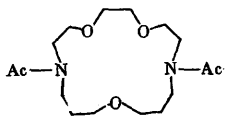
(XXIII)

1. $n=2$, R=$CH_2PO_3H_2$ [36];
2. $n=1$, R=Ac [38];
3. $n=2$, R=Ac [37, 39];
4. $n=2$, R=CH_2Ac [14];
5. $n=2$, R = [43]; etc. [40–42].

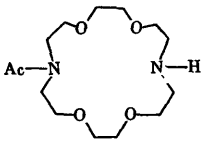


(XXIV)

$n=1-3$, R=PO_3H_2, COOH, NH_2 etc.



(XXV)



(XXVI)

The synthesis of ligands (XXIV) has been described, their ability to dissolve $BaSO_4$ was recorded in the same paper.[37]

The complex-formation of ligands (XXIII, 2–4) has been studied in relation to a large number of cations. The stability constants of complexes of (XXIII, 2–4), (XXV) and (XXVI) are given in Table 2. The stability of complexes of other ligands of formula (XXIII) has not been determined.[40–42]

Table 2. Values of $\lg K_{st}$ for complexes [ML] of ligands (XXIII, 2–4), (XXV) and (XXVI).

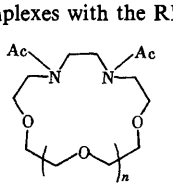
Cation	(XXIII,2)	(XXIII,3)	(XXIII,4)	(XXV)	(XXVI)
K^+	1.7	3.9	–	–	–
Mg^{2+}	7.4	–	<2	<2	–
Ca^{2+}	8.7	8.4	4.0	7.7	–
Sr^{2+}	7.9	8.3	4.4	7.7	–
Ba^{2-}	7.3	7.6	3.8	7.7	–
Co^{2-}	13.7	–	see*	7.0	–
Ni^{2+}	12.2	7.4		7.5	5.4
Cu^{2+}	16.0	14.5	~6–7	>14	10.5
Zn^{2-}	14.1	8.4	see*	8.0	5.4
Cd^{2+}	13.0	11.1	–	–	7.8
Pb^{2+}	12.9	13.6	8.1	–	10.4
La^{3+}	10.1	12.2	–	–	6.6
REE	10.3–11.9	10.8–12.2	–	–	6.0–7.4

Note. The numbers given are rounded up to tenths. Experimental conditions: T = 25 °C, μ = 0.1 (Me_4NCl), solvent was water.
*Complex-formation was so weak that at $a > 1$ the ions of Co^{2+}, Ni^{2+} and Zn^{2+} precipitated as hydroxides (a is the number of equivalents of alkali per mole ligand).

The increase of the cyclic fragment on going from ligand (XXIII, 2) to ligand (XV) is accompanied by a reduction in the stability constant of the complexes of all cations apart from Ba^{2+}, the most bulky of the cations being compared. A reduction in the stability constant of the complexes also occurs on increasing the length of the pendant group on going from (XXIII, 3) to (XXIII, 4). The removal of one pendant group in ligand (XXVI) compared with (XXIII, 3) leads to an appreciable reduction in the stability of the complexes. This means that carboxyl pendant groups participate in the coordination.[44] An increase in the cyclic fragment with the simultaneous inclusion of one more donor oxygen atom in it involves a reduction in the stability of complexes of ligand (XXIII, 3) with cations of small ionic radius and an increase in the stability of complexes with cations of larger ionic radius compared with ligand (XXIII, 2). For cations of ionic radius > 1.1 Å and rare earth elements (REE) the complexes of ligand (XXIII, 3) are more stable, for all the remainder the complexes of (XXIII, 2) with a smaller cyclic fragment are the more stable. The stability constants of complexes of REE with ligand (XXIII, 3) fall continuously from Ce^{3+} and Lu^{3+} with the reduction in ionic radius of these cations.[39] In contrast, the complex-formation of REE ions with ligand (XXIII, 2) is maximal at the Eu^{2+} ion.[45] The rare earth elements of larger and smaller ionic radii form less stable complexes with this ligand.

The cyclopendant ligands based on crown-polyazapolyethers display interesting complex-forming properties. Usually the complexes with the classical complexones of Sr^{2+} are less stable than the complexes of Ca^{2+}. Ligands (XXIII, 3) and (XXV) form complexes of practically identical stability with Ca^{2+} and Sr^{2+}, but ligand (XXIII, 4) chelates Sr^{2+} more efficiently than Ca^{2+}. Ligand (XXV) shows a very high difference in stability constants for the complexes of the small Mg^{2+} ion and the bulky Ca^{2+} ion. It is interesting that Co^{2+} and Ni^{2+} form complexes of lower stability than the ions of the alkaline earth metals with the ligands (XXIII, 3), (XXV) and (XXIII, 4) (see Table 2), which is also unusual for complexones of linear structure. This may be caused by the fact that the ions of the transition metals have a lower ionic radius than the ions of the alkaline earth metals. The stability constants of the complexes of Ca^{2+}, Sr^{2+}, and Ba^{2+} with ligand (XXV) do not depend on the ionic radius of the cation.

Chang and collaborators investigated the kinetics of the dissociation of complexes of lanthanides with ligands (XXIII, 2 and 3).[46,47] The complex-formation of REE ions with ligands (XXVII) with different sizes of cyclic fragment has been investigated.[48] The value of $\lg K_{st}$ for complexes of (XXVII, 1) increased continuously with the reduction in ionic radius from La^{3+} to Lu^{3+}. An increase in the ring size led to an increase in the stability of the complexes of REE with ligands (XXVII, 1–3) but transfering from ligand (XXVII, 3) to (XXVII, 4) did not cause a further increase in K_{st} for the complexes with the REE.



(XXVII)

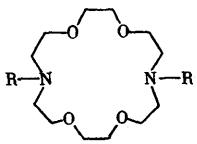
1. n = 0
2. n = 1
3. n = 2
4. n = 3

The complex of the Cu^{2+} ion with ligand (XXIII, 3) has been investigated by XSA.[49] It was found that Cu^{2+} is in a square plane formed from two nitrogen atoms of the ring and two oxygen atoms of the carboxyl groups.

The selectivity factor of a ligand in relation to Zn^{2+} and Ca^{2+} ions is important in medicine when checking the elimination of Pb^{2+} ions from animals.[50]

$$\lg K_{st\ Pb^{2+}} / \lg K_{st\ Zn^{2+}} = \varphi_1 \text{ and } \lg K_{st\ Pb^{2+}} / \lg K_{st\ Ca^{2+}} = \varphi_2.$$

For example, the size of φ_1 is 1.6 for ethylenediaminetetraacetate (EDTA). With the aim of obtaining a reagent with a high selectivity factor the ligand (XXIII, 5) mentioned above, containing a crown-diaza-polyether ring and pendant α-pyridylmethyl groups, was synthesised.[43] Values of the stability constants are given in Table 3 for ligands (XXVIII) with five different pendant groups.



(XXVIII)

1. R = H; 2. R = CH_2CHMe (OH); 3. R = CH_2COOH;
4. R = CH_2–(N-heterocycle); 5. R = CH_2CH_2SH

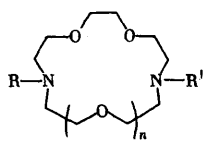
A characteristic feature of these ligands is their ability to chelate efficiently cations of large ionic radius. This leads to very high values for φ_1 and φ_2 [particularly with pendant (4)]. The stability constants for complexes of the small Zn^{2+} ion and the bulky Cd^{2+} and Pb^{2+} differed sharply.

Table 3. Values of $\lg K_{st}$ for complexes [ML] of ligands (XXVIII) with various pendant groups (T = 25 °C).

Cation	1	2	3	4	5*
Ca^{2+}	1.74	3.59	8.39	3.63	7.0
Sr^{2+}	2.60	4.05	8.29	4.87	–
Ba^{2+}	2.97	4.65	7.63	4.99	–
Ni^{2+}	–	–	7.39	8.80	–
Cu^{2+}	6.10	5.97	14.49	13.55	–
Zn^{2+}	3.10	3.00	8.42	6.96	16.3
Cd^{2+}	5.25	7.64	11.07	10.96	22.9
Pb^{2+}	6.80	8.57	13.55	11.67	26.1
La^{3+}	3.00	3.24	12.21	3.58	–

* Predicted values for ligand (XXVIII, 5).[43]

The preferential complex-formation of ligands (XXVIII, 1–5) with cations of large ionic radius leads to the result that ions of Sr^{2+} and Ba^{2+} are chelated more efficiently than Ca^{2+} ions by groups 1, 2 and 4 which is unusual for the classic complexones and is important in medical investigations.



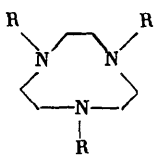
(XXIX)

1. R=R′=CH_2COOH, n=2
2. R=R′=CH(Me)COOH, n=2
3. R=R′=CH_2COOH, n=1
4. R=H, R′=CH_2COOH, n=2

The kinetics of the reaction of Cu^{2+} ion with ligands (XXIX, 1–4) have been studied.[52]

V. Cyclopendants: derivatives of nitrogenous macrocycles

1. Cyclopendants based on 1,4,7-triazacyclononane



(XXX)

1. R = H [73]
2. R = $CH_2PO_3H_2$ [55,·56]
3. R = $(CH_2)_2PO_3H_2$ [57]
4. R = CH_2COOH [6, 12]
5. R = $(CH_2)_2OH$ [58]
6. R = $(CH_2)_2NH_2$ [59, 60]
7. R = $(CH_2)_3NH_2$ [61]
8. R = CH_2CHOH (Me) [62]
9. R = $(CH_2)_2SO_3H$ [63]
10. R = $CH_2P(O)Ph_2$ [64–66]
11. R = CH_2–(N-heterocycle) [90, 91]

The stability constants of the complexes of a large number of cations with (XXX, 2) and (XXX, 3) have been determined, consequently it is possible to compare quantitatively the efficiency and selectivity of their complex-formation.

2. Means of assessing the efficiency and selectivity of ligands

A quantitative assessment of the complex-forming ability of ligands has been given.[67–69] The efficiency is the mean value of the sizes of $\lg K_{st}$ for complexes of composition ML.

$$A = \left(\sum_{i}^{n} \lg K_i\right) / n.$$

As a measure of the selectivity of action of a ligand the mean difference of $\lg K_{st}$ of complexes ML for all the cations taken in pairs.

$$S = \left[\sum_{i=1}^{n}\sum_{i=j}^{n} (|\lg K_j - \lg K_i|)\right] / n(n-1),$$

where n is the number of cations compared. The simplest algorithm for the calculation is the following.[68]

$$\Delta = \begin{vmatrix} \lg K_1 - \lg K_2 & & & \\ \lg K_1 - \lg K_3 & \lg K_2 - \lg K_3 & & \\ \lg K_1 - \lg K_4 & \lg K_2 - \lg K_4 & \lg K_3 - \lg K_4 & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ \lg K_1 - \lg K_n & \lg K_2 - \lg K_n & \lg K_3 - \lg K_n & \ldots \lg K_{n-1} - \ln K_n \end{vmatrix}$$

The sum of the absolute values of all the differences in brackets is

$$\Delta = \frac{1}{2}\sum_{i=1}^{n}\sum_{i=j}^{n} |\lg K_i - \lg K_j|, \quad S = 2\Delta / n(n-1).$$

Other means of assessing selectivity are given in the literature. Occasionally a selectivity factor is used in studies on cryptates and crown-ethers which is the ratio of the stability constants for complexes of two cations, i.e. K_1/K_2.[70–72] In this of course only two cations are compared, the choice of them is arbitrary. The selectivity of action of ligands is assessed as the ratio of the stability constants of the complexes with ions of NH_4^+ and K^+.[72] On examining only two cations with stability constants K_1 and K_2 the previous formula is transformed into

$$S = \lg (K_1/K_2).$$

Certainly the values of A and S depend appreciably on the set of cations being compared, consequently to use them as a characteristic of the complex-forming ability of a ligand is only possible for the same set of cations. It is necessary to consider this when assessing the data calculated in the manual for efficiency and selectivity.[73]

3. Efficiency and selectivity of complexones of triazacyclononane derivatives

Values of $\lg K_{st}$ for complexes and A and S for complex-formation are given in Table 4 for ligands (XXX, 2), (XXX, 3) and (I). The values of the stability constants for the complexes of the remaining ligands (XXX) with the given cations in water were not determined.

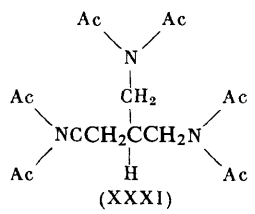
The selectivity of action of complexones (I), (XXX, 2) and (XXX, 3) is explained with the aid of a model of the spatial fit of the ligand shape (in an energetically favourable conformation) with the stereochemical requirements of the cation.[1,57] On coordination the metal cation falls into the cavity formed by the ligand as into a basket, the bottom of which is the nitrogen heterocycle and the walls are the pendant groups. Only a cation of suitable ionic radius may be placed in the basket cavity. This also determines the selectivity of complex-formation of the given ligands. The existence of a basket structure was confirmed by X-ray data on the complex of (XXX, 2) with the Fe^{3+} ion which has a very high stability ($\lg K_{st}$ = 29.6 [56]). The Fe^{3+} (ionic radius r = 0.64 Å) in a complex of composition $[FeH_3L]^0$ is in fact in the cavity of this ligand as in a basket.[74]

The complexone (XXX, 2) is selective, other conditions being equal, for cations of small ionic radius¶ such as Mg^{2+}, Zn^{2+} and Fe^{3+} with which it forms stable complexes. On turning to a cation with larger ionic radius, such as Ca^{2+}, Cd^{2+} or La^{3+}, the stability of the complexes is reduced by many orders of magnitude.[56] A large difference is shown in the values of K_{st} for complexes of Mg^{2+} and Ca^{2+}. Usually complexes of Ca^{2+} are more stable than complexes of Mg^{2+} with a small difference in the values of their stability constants. It is rare to encounter cases when the complexonate with Mg^{2+} is more stable than the complexonate with Ca^{2+} and their stability constants differ by one to two orders of magnitude. Only the *N*-oxide of nitrilotris(methylphosphonic acid) chelates the Mg^{2+} ion more effectively, the difference in K_{st} values being 2.6 log. units.[76] The difference of about 5 orders of magnitude observed for (XXX, 2) is unprecedented. It also shows the highest difference of all the complexones in the stability constants for the complexes of Zn^{2+} and Cd^{2+}.[73]

Cations of large ionic radius form fairly stable complexonates with the acid (XXX, 2). Calculations by molecular mechanics showed that just one low energy conformation is possible for this ligand, a 'ladle' in which two pendant groups continue as though forming the internal cavity of the ligand but one is tilted away like the handle of a ladle. The cavity of the ladle is larger and may take up huge cations occupying five of their coordination positions. When octahedral coordination is characteristic of the cation, the sixth place is occupied by the remaining monodentate ligand.

The Cu^{2+} ion also has a small radius but it is inclined to be pentacoordinate and forms a complex in the form of a ladle with (XXX, 2) (XSA data).

The size of the cavity of a complexone basket, into which the metal cation is placed, may vary either with a change in the size of the cyclic fragment or with a change in the length of the pendant groups. The complexone (XXX, 3) with phosphonoethyl pendant groups was synthesised to study this effect. The nitrogen atoms and the phosphorus are separated by ethylene bridges. The efficiency of complex-formation of this complexone is lower than that of (XXX, 2). Evidently this is linked with the lower stability of the six-membered chelate rings formed by it with the pendant groups compared with the five-membered formed by the phosphonomethyl pendant groups of complexone (XXX, 2). However the stability constants of both complexes are equal for the copper cation which requires a ligand shape of a tetragonal pyramid (see Table 4). The selectivity of action of the new cyclopendant in relation to the second group of cations is greater than for acid (XXX, 2). Complexones (XXX, 2) and (XXX, 3) have the same set of donor centres consequently the difference in complex-formation with various TM is impossible to explain by the non-uniformity of the covalent binding energy. This means that the spatial factor has a leading role. There is a very large difference in stability for the complexes of Co^{2+} and Ni^{2+} with (XXX, 3). Usually the complexes of Ni^{2+} are somewhat more stable than the complexes of Co^{2+} and have a small difference in stability constant.[73] Complexone (XXXI) shows the maximum difference in size of K_{st} for these cations, $\lg K_{st}$ [CoL] = 13.8 and $\lg K_{st}$ [NiL] = 18.0.[77] Complexone (XXX, 3) gives the same difference in stability constants but in this case the Co^{2+} complex is more stable than the Ni^{2+} complex.



(XXXI)

Table 4. Values of $\lg K_{st}$ for complexes [ML] and values of A and S.

Cation	(XXX.2)	(XXX.3)	(I)	Cation A, S	(XXX.2)	(XXX.3)	(I)
Be^{2+}	11.5	13.4	–	Zn^{2+}	24.9	17.00	18.3
Mg^{2+}	11.01	6.10	9.69	Cd^{2+}	19.7	15.83	16.0
Ca^{2+}	6.38	<2	8.92	Hg^{2+}	23.0	–	–
Sr^{2+}	5.34	<1	6.83	Pb^{2+}	22.1	sce *	16.6
Ba^{2+}	4.37	<1	5.10	Fe^{3+}	29.6	–	–
Mn^{2+}	16.6	12.77	14.3	La^{3+}	14.3	–	–
Co^{2+}	19.7	13.38	17.5	A **	6.8	–	7.6
Ni^{2+}	19.4	9.20	–	S **	3.5	–	2.6
Cu^{2+}	21.3	21.3	19.8	A ***	20.4	16.1	17.2
				S ***	3.6	4.1	2.7

* Complex insoluble in water.

** For the set of cations Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}.

*** For the set of cations Mg^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}.

¶ Values of the ionic radii have been reported.[75]

Lengthening the small chain linking the nitrogen atom and phosphorus in (XXX, 3) increases the size of the basket, corresponding to the selectivity of complex-formation, when compared with complexone (XXX, 2). The larger octahedron characteristic of Co^{2+} requires a larger volume for the cavity than the tetrahedron characteristic of Ni^{2+} (at almost the same ionic radius). As a result, complexone (XXX, 3) fits better with the Co^{2+} ion than with the Ni^{2+} ion and this difference leads to the observed selectivity of action. Complexone (XXX, 3) forms a much less stable chelate than (XXX, 2) with the Mg^{2+} ion, which is too small for the cavity of ligand (XXX, 3). On the other hand, evidently the Ca^{2+} ion is too large for the basket of this ligand without even considering the more voluminous ions of Sr^{2+} and Ba^{2+} (the binding here is undoubtedly ionic). The stability constants of the complexes of (XXX, 2) with Co^{2+} and Cd^{2+} were no different, but for the new complexone the complex with the more bulky Cd^{2+} ion was significantly more stable than the complex with Co^{2+} (see Table 4). The difference in stability constants for (XXX, 2) with the small Zn^{2+} ion and the larger Cd^{2+} ion was very great but for (XXX, 5) it was far less. The bulky Mn^{2+} ion forms a more stable complex than Ni^{2+}. This leads to a breaking of the Irving–Williams series[78] which is characteristic of the traditional complexones. It is therefore seen that the size of the basket for complexone (XXX, 3) is somewhat larger than that for (XXX, 2).

When investigating the complex-formation of ligands (XXX, 1) and (XXX, 3) with Cu^{2+} and Zn^{2+} ions in water it was shown[58] that hydroxyethyl substituents, although playing no part in coordination, reduced the complex-forming ability of the amines as a result of electronic and steric effects. Since complexes are formed in the case of ligand (XXX, 5) which are more stable than the complexes of the free amine (XXX, 1), it must be deduced that the problem of the participation of the hydroxyethyl pendant groups in coordination with cations remains open.

The thermodynamics of complex-forming of complexone (I) with Mg^{2+}, the AEM and Cu^{2+} ions, have been investigated (Table 5).[81]

Table 5. Thermodynamic parameters for complex-formation of complexone (I) with certain cations (T = 25 °C).

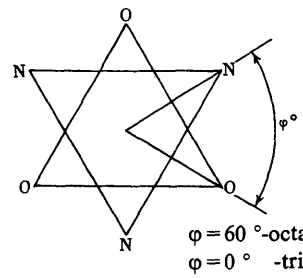
Cation	$\lg K_{st}$	$\Delta H°$, kcal mole^{-1}	$\Delta S°$, kcal mole^{-1} K^{-1}
Mg^{2+}	9.69	+0.4	45
Ca^{2+}	8.92	−5.9	21
Sr^{2+}	6.83	−2.1	24
Ba^{2+}	5.10	−1.38	18.6
Cu^{2+}	21.63	−13.4	54

The greater stability of the complex of (I) with Mg^{2+} compared with Ca^{2+} is caused purely by the entropy factor. It might be supposed that for complexone (XXX, 2) also, the greater stability of the Mg^{2+} complex compared with that of Ca^{2+} is caused by the entropy factor, when the conformation of the free ligand is ideal for the approach of the small Mg^{2+} ion.

According to XSA data the complexes of ligand (I) have the conformation of a basket for which 1,4,7-triazacyclononane serves as the base and the pendant carboxyl groups the walls.

In 1982 Wieghardt and collaborators obtained a large series of complexes of composition $[M^{III}L]$ and $Na[M^{II}L]$, where L = (I), M^{III} = Al^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+} and Co^{3+} and M^{II} = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}.[84] The authors examined the complexes $[Cr^{3+}L]$, $[Fe^{3+}L]$, $Na[Cu^{2+}L]2NaBr.8H_2O$ by XSA in this study. It was shown that only in the complex with VO^{2+} was ligand (I) pentadentate (one carboxyl group did not participate in coordination). In all the remaining complexes all the donor atoms of the ligand participated in coordination (Scheme 1).

Scheme 1



φ = 60 °-octahedron
φ = 0 ° -trigonal prism

Later, XSA was carried out on complexes of (I) with Ni^{2+} and Ni^{3+} ions.[86] The reaction of (I) with Ni^{2+} occurs even in dilute HNO_3. The complex $[NiL].H_3O$ (crystalline) was isolated from this solution the XSA of which showed that all the nitrogen atoms and the oxygen atoms of the carboxyl groups coordinated with the Ni^{2+} ion and the hydroxonium ion is separate from the complex anion. In dilute HNO_3 the blue $[Ni^{2+}L]H_3O$ complex is converted into the rose $[Ni^{3+}L]$ complex of trivalent nickel (Table 6).

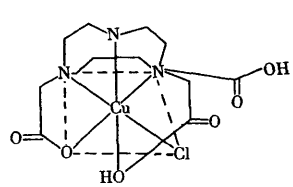
Table 6. Crystal lattice parameters for complexes of ligand (I) with certain cations from XSA data.[84,86]

Cation	φ (Scheme 1), deg	Mean bond length, Å	
		M–N	M–O
Ni^{3+}	53.1	1.93	1.91
Ni^{2+}	48.0	2.04	2.08
Cr^{3+}	49.0	2.06	1.96
Cu^{2+}	26.6	2.12	2.07
Fe^{3+}	25.0	2.18	1.96

The geometries of the complexes of Ni^{3+} and Cr^{3+} with (I) are close to tetrahedral and the geometries of the complexes of ligand (I) with Cu^{2+} and Fe^{3+} ions are close to a trigonal prism. The protonated complex $[CuClLH_2]$ has a ladle conformation.[87]

One of the protonated groups of ligand (I) turns away to the side. Two nitrogen atoms, one chlorine atom and one oxygen atom of the deprotonated carboxyl group are coordinated to the Cu^{2+} ion in the equatorial plane (Scheme 2).

Scheme 2



One nitrogen atom of the ring and an oxygen atom of one of the protonated carboxyl groups are in the axial positions with longer bonds. Such a structure for the complex of Cu^{2+} with complexone (I) may be caused by steric hindrance arising in the coordination of the 1,4,7-triazanonane fragment with the Cu^{2+} ion. It was established by XSA [88,89] that in the complexes of (XXX) with $CuCl_2$ and $CuBr_2$ two nitrogen atoms and two halogen atoms are located in the equatorial plane and the third nitrogen atom occupies the fifth apical position with a longer coordinate bond length. According to XSA of the complex $[CoL](ClO_4)_3$ with ligand (XXX, 6) the Co^{3+} ion is in the plane of the ligand as in a basket with the three-nitrogen ring serving as the base and the pendant ethylamino groups as the walls.[59] The complexes of Co^{3+} and Ni^{2+} of composition $[CoL]Br_3$ and $[NiL]Br_2.H_2O$ with ligand (XXX, 7) containing pendant propylamino groups in the molecule have the structure of a regular octahedron (according to XSA data).[61]

Wieghardt and collaborators have synthesised a large number of complexes of ligand (XXX, 11) with the TM, Cr^{3+}, Fe^{3+}, Pd^{2+}, Ru^{2+} and Ru^{3+}.[90] X-Ray structural analysis was carried out on complexes of $[NiL](ClO_4)_2$, $[MnL](ClO_4)_2$, $[PdL](PF_6)_2$ and $[FeL](ClO_4)_2$ with this ligand.[90,91] The complexes of Mn^{2+}, and Fe^{2+} and Ni^{2+} ions with (XXX, 11) were coordinated with three ring nitrogen atoms and three nitrogen atoms of the α-pyridylmethyl pendant groups. The Pd^{2+} ion was pentacoordinated, one pendant group did not participate in chelation.

Table 7. Values of $\lg K_{st}$ for complexes [ML] of cyclopendant complexones and EDTA, *A* and *S*.

Cation *A*, *S*	(XXXII.2)	(XXXII.3)	(II)	EDTA
Be^{2+}	–	15.9	13.6	9.2
Mg^{2+}	7.3	<2	11.0	8.8
Ca^{2+}	10.3	<2	15.9	10.6
Sr^{2+}	9.8	<1	12.8	8.7
Ba^{2+}	8.8	<1	11.3	7.8
Mn^{2+}	16.9	12.4	17.8	13.8
Co^{2+}	20.8	14.8	18.4	16.3
Ni^{2+}	19.0	12.0	17.3	18.5
Cu^{2+}	25.4	27.1	19.0	18.7
Zn^{2+}	24.8	24.6	18.9	16.4
Cd^{2+}	22.9	20.8	19.0	16.4
Hg^{2+}	25.1	29.6	–	21.5
Pb^{2+}	23.3	16.3	19.9	17.9
A *	9.0	–	12.8	9.0
S *	1.7	–	2.7	1.6
A **	21.9	18.3	18.6	17.0
S **	3.8	7.0	1.0	2.0

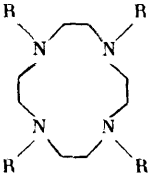
* For the set of cations Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}.
** For the set of cations Mn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}.

The Ni^{2+} ion in the complex of composition $Na[NiL.H_2O].5H_2O$ (L = XXX, 9) has a distorted octahedral structure. Three ring nitrogen atoms and an oxygen atom of the $CH_2CH_2SO_3^-$ group were in a square plane. The apical positions were occupied by a second $CH_2CH_2SO_3^-$ group and a water molecule. One pendant group was not coordinated to Ni^{2+}. The complex of copper ion of composition $Na[CuL].3H_2O$ is a distorted pyramid, two ring nitrogen atoms and two oxygen atoms of $CH_2CH_2SO_3^-$ groups form the base and at the vertex of the pyramid is a third nitrogen atom bound to a pendant group uncoordinated to Cu^{2+}.[63] The protonated complex of (XXX, 2) of composition $[CuH_4L].H_2O$ has the same structure according to XSA data[92] as does the complex of Cu^{2+} with ligand (XXX, 9). Two nitrogen atoms and two oxygen atoms of $CH_2PO_3H^-$ groups are at the base of the square pyramid and the third ring nitrogen atom, bound to a protonated pendant group, occupies the apical position. As is seen, a ladle conformation is characteristic for the protonated complexes of ligands (I) and (XXX, 2) and the complex of (XXX, 9) with the Cu^{2+} ion. In this conformation one pendant group of these complexones is turned away to the side and does not participate in chelation.

The coordination of 1,4,7-triazacyclononane with the Cu^{2+} ion occurs, as a rule, in the same manner. Two nitrogen atoms of the cyclic fragment are located in the equatorial plane and the third nitrogen atom occupies the apical position. The coordination of all three ring nitrogen atoms in one plane seemingly encounters difficulties and does not take place.

4. Cyclopendants based on cyclene

The following cyclopendant complexones are known which contain a 1,4,7,10-tetra-azacyclododecane (cyclene) fragment.



(XXXII)

1. R = H [73];
2. R = $CH_2PO_3H_2$ [67];
3. R = $CH_2CH_2PO_3H_2$ [93];
4. R = CH_2COOH [94, 95];
5. R = CH_2CH_2OH [96, 97];
6. R = $CH_2CH_2P(O)Ph_2$ [149].

The formation of more stable complexes with cations of small ionic radius was observed for complexone (XXX, 2) with a nine-membered ring. In (XXXII, 2) the size of the cyclic fragment is larger, consequently a shift of the maximum efficiency of complex-formation in the direction of cations with a large ionic radius might be expected. In reality the overall tendency towards complex-forming ability for this complexone is the formation of stable chelates with cations of relatively large size. In contrast to (XXX, 2) compound (XXXII, 2) gives a more stable complex with Ca^{2+} than with Mg^{2+}. For cations with an ionic radius less than 0.7 Å the complexes of ligand (XXX, 2) are the more stable. Ions with an ionic radius 0.7–0.8 Å form complexes of approximately the same stability but cations of larger size form more stable complexes with (XXXII, 2) (Table 7). The exception is the Cu^{2+} ion (small size) which gives an extremely stable complex with this complexone.

All the cyclopendant organophosphorus complexones, containing a tetra-aza-amine fragment, such as cyclene and 1,5,8,12-tetra-azacyclotetradecane (cyclam), form especially stable complexes with the Cu^{2+} ion, possibly with four ring nitrogen atoms in square coordination. The simultaneous presence in these complexones of a cyclic tetra-amine fragment and pendant alkylphosphonyl groups evidently leads to the high value for the stability constant of the complexes with Cu^{2+}. The carboxyl-containing analogues, ligands (II) and (IV), give complexes with $\lg K_{st}$ 19.0 and 18.6 respectively with the Cu^{2+} ions.[94] The unsubstituted cyclene and cyclam form

complexes with $\lg K_{st}$ equal to 23.3 and 26.5 respectively with the Cu^{2+} ion,[96], i.e. the pendant Ac^- behave as if interfering with coordination. The complex of (XXXII, 2) with the bulky La^{3+} ion is far more stable than the complex of this ion with complexone (XXX, 2). It is possible that this enables a coordination number of eight, natural for La^{3+}, to be put into effect. Seemingly, ligand (XXXII, 2) has a large plane size which leads to an increase in the metal–nitrogen distance on arranging the cation above the plane of the nitrogen atoms (the cations are not located within the plane). Hence its ability to form highly stable complexes with such cations as Cd^{2+}, Hg^{2+}, Pb^{2+} and La^{3+}.

The stability constants for the complexes of Zn^{2+}, Cd^{2+} and Hg^{2+} with complexone (XXXII, 3) with ethylphosphonic acid pendant groups differ significantly from the stability constants of Mn^{2+}, Co^{2+} and Ni^{2+} with the same complexone. None of the known complexones give such a large difference.[73] This ligand forms the most stable complex with the Cu^{2+} ion among all the cyclopendant organophosphorus complexones. It does not form complexes with Mg^{2+} and the alkaline earth elements although organophosphorus complexones of linear structure with four or more phosphonic acid groups in the molecule form fairly stable complexes with Mg^{2+} and Ca^{2+}.[98] Complexone (XXXII, 3) gives the most stable of the known complexes with the Hg^{2+} ion. It exceeds significantly all previously known complexones in selectivity of complex-formation (see Table 7).

Comparison of the complex-forming ability of the ligands (XXX, 2), (XXX, 3) (XXXII, 2 and 3) etc. shows that steric factors operate in a fairly complicated manner in the chelation of various cations. They cannot be reduced solely to the effect of the ionic radius of the cation and are developed on a background of electronic factors. Thus ligand (XXX, 3) shows a very high difference in the stability constants of complexes of Cu^{2+} and Ni^{2+} ions, which are close to one another in size[75] but differ in the stability of the polyhedra formed by them (octahedron, tetrahedron, square plane). Complexone (XXXII, 3) forms a highly stable complex with Zn^{2+}, which is more stable than the complexes with Co^{2+} and Ni^{2+}, but all three possess ionic radii which are close to one another. With the large cations Hg^{2+} and Pb^{2+}, clearly larger than Zn^{2+}, ligand (XXXII, 3) [like (XXXII, 2)] gives highly stable complexes, particularly with the Hg^{2+} ion ($\lg K_{st}$ = 29.6).

When coordinating with complexones (XXX, 3) and (XXXII, 3) the energy of the covalent bonding of a metal cation with the donor centres of the ligand has a fundamental importance and in the end is strongly dependent on the nature of the cation. Furthermore the structure of the coordination polyhedron of the cation also exerts a strong effect. Ligands with phosphonoethyl pendant groups may seemingly be reshaped under the stereochemical requirements of particular cations and this also makes a contribution to the observed high selectivity of these complexones. Evidently the bonding energy also provides the very high difference in stability constants of the complexes of ligands (XXX, 3) and (XXXII, 3) with the Cu^{2+} ion compared with other transition metals having similar ionic radii.

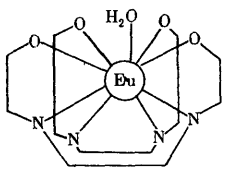
The carboxyl-containing cyclopendant complexone (II) surpasses the organophosphorus complexones in efficiency and selectivity of reaction with the ions of Mg^{2+} and the alkaline earth elements, but is itself significantly surpassed in selectivity of complex-formation with the TM, Cd^{2+} and Pb^{2+} not only by the organophosphorus complexones but also by EDTA, a complexone of linear structure (see Table 7). In contrast to the organophosphorus cyclopendant complexones which are cyclene derivatives, acid (II) forms highly stable water-soluble complexes with the REE. Stability constants are given in Table 8 for complexes of (II), EDTA and diethylene-triaminepenta-acetic acid (DTPA) with REE ions.[99,100]

The complex of (II) with the Eu^{3+} ion of composition $Na[Eu^{3+}L.H_2O].4H_2O$ has been investigated by XSA and ^1H NMR.[101] In this, Eu^{3+} is nine-coordinate with four coordinate bonds from nitrogen atoms lying at the base of prism of mean length 2.71 Å, four from oxygen atoms of the carboxyl groups of mean length 2.34 Å and one bond with a water molecule of length 2.48 Å.

Table 8. Values of $\lg K_{st}$ for complexes [ML] (T = 20 °C, μ = 1.0, NaCl).

Cation	(II)	EDTA	DTPA
Eu^{3+}	28.2	17.3	22.4
Tb^{3+}	28.6	17.9	22.7
Lu^{3+}	29.2	19.8	22.4

The Eu^{3+} ion is in a basket of eight donor atoms of ligand (II). The bond lengths are greater than in complexes of other ligands with the TM.



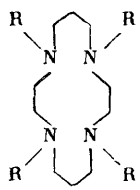
The authors called such a coordination polyhedron a distorted square antiprism.[101] Complexes of the following composition have been investigated by IR and visible spectroscopy: $[Cu(H_2L)]$, $[Ni(H_2L)]$, $[Zn(H_2L)]$, M[Cu(L)] and M[Ni(L)] (M = Ca^{2+}, Sr^{2+}, Ba^{2+}).[102] X-Ray structural analysis was carried out on the first two complexes in the same study. It was shown that they have an octahedral structure. Two nitrogen atoms and two oxygen atoms of carboxyl groups are at the corners of a square plane. On the axis perpendicular to the square plane are two ring nitrogen atoms. Two protonated CH_2COOH groups do not participate in the coordination. X-Ray structural analysis was carried out on the complex $[Cu_2(L)].5H_2O$.[103] The two Cu^{2+} ions in this complex have different coordination spheres. One of them is coordinated in the same way as in the mononuclear complex $[Cu(H_2L)]$. There are two nitrogen atoms and two oxygen atoms at the corners of a square plane. Two nitrogen atoms of ligand (II) are on the axis perpendicular to the square plane. The second Cu^{2+} ion has a square-pyramidal environment. Four oxygen atoms from CH_2COO^- groups lie at the base of the pyramid and a water molecule is found at its apex.

Complexone (II) is the best shift reagent among the ligands (I), (IV), etc. used for the quantitative determination of Eu^{3+} by NMR in water.[104,105] The kinetics of the reaction of (II) with Mg^{2+}, AEM, Ni^{2+}, Cu^{2+} and Zn^{2+} have been studied in water over a wide pH range.[106]

X-Ray structural analysis has been carried out on the complexes $[2Li(L)].Cl_2.2H_2O$, $[Na(L)].CNS$, $[K(L)].SCN$ and $[(L)H_2O]$ with ligand (XXXII, 5).[107] Four cyclene nitrogen atoms and the pendant hydroxyethyl groups participate in the coordination with these cations. For Li^+ one hydroxyethyl participates, for Na^+ three and for K^+ all four. In the monohydrate of this ligand a water molecule is bound to two ring nitrogen atoms and two oxygen atoms of the pendant groups.

5. Cyclopendants based on cyclam

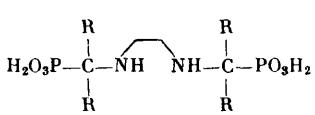
The following ligands containing a 1,5,8,12-tetraazacyclotetradecane (cyclam) fragment are known



(XXXIII)

1. R = H [73]; 2. R = $CH_2PO_3H_2$ [69]; 3. R = CH_2COOH [94]; 4. R = = CH_2CH_2OH [108]; 5. R = $CH_2CH_2NH_2$ [109—114]; 6. R = $(CH_2)_3NH_2$ [112]; 7. R = CH_2CH_2CN [113], 8. R=CH_2— [114, 115]; 9. R = = $CH_2P(O)Ph_2$ [116]; 10. R = $CH_2CH_2P(O)Ph_2$ [116].

Complexone (XXXIII, 2) based on cyclam is significantly lower in complex-forming efficiency than with analogous complexone (XXXII, 2) based on cyclene. With all cations (except Cu^{2+}) a sharp reduction is observed in the stability constants of complexes. A similar reduction in the stability of complexes is also observed for carboxyl-containing complexones on changing from complexone (II) to (IV).[94] Seemingly the reason for the reduction in the stability constants of the complexones in both cases is linked with the size and conformation of the tetra-azacyclic compounds. It might be thought that the cyclic fragment of complexones (XXXIII, 2) and (IV) (cyclam) are conformationally more flexible than the cyclene fragment. If the stability constants of ML complexes of complexone (XXXIII, 2) and ethylenediamine-*N,N'*-bis(methylphosphonic acid) (EDMP),[117] which is an acyclic fragment of complexone (XXXIII, 2), are compared (Table 9) then it is not difficult to understand the parallel change of these values (with the exception of K_{st} for the complexes of Cu^{2+}). EDMP is a complexone of high flexibility.



R = H (EDMP), R = Me (EDIP)

where EDIP is ethylenediamine-*N,N'*-bis(isopropylphosphonic acid).

The observed reduction in the size of the stability constants of the complexes is evidently entropic in origin.

The complexone (XXXIII, 2) forms complexes, which are close to one another in stability (Table 10), with all the cations investigated. Seemingly the size of the cyclic fragment of this ligand is sufficiently large and the ring sufficiently flexible to satisfy the steric requirements of any cations and this also determines its lack of selectivity of action.

Table 9. Values of $\lg K_{st}$ for complexes [ML] of certain cations.

Cation	(XXXIII.2)	EDMP
Mn^{2+}	10.8	7.55
Co^{2+}	15.3	10.8
Ni^{2+}	15.6	12.0
Zn^{2+}	17.6	12.0
Cd^{2+}	16.7	10.9
Cu^{2+}	26.6	18.6
Cations of the alkaline earth metals	<2	<2

Table 10. Values of $\lg K_{st}$ for complexes [ML] of compounds (XXX, 2), (IV) and (XXXIII, 4).

Cation *A, S*	(XXXIII.2)	(IV)	(XXXII.4)
Mg^{2+}	<2	3.0	1.86
Ca^{2+}	<2	9.5	–
Sr^{2+}	<2	6.2	–
Ba^{2+}	<2	4.3	–
Mn^{2+}	10.8	11.2	–
Co^{2+}	15.3	15.0	6.10
Ni^{2+}	15.6	15.3	7.31
Cu^{2+}	26.6	18.6	15.69
Zn^{2+}	17.6	15.8	6.43
Cd^{2+}	16.7	15.5	9.38
Hg^{2+}	–	–	17.94
Pb^{2+}	15.5	14.7	6.28
A *	16.9	14.7	–
S *	5.1	2.4	–
A **	17.9	15.8	8.53
S **	4.3	1.5	3.88

* For the set of cations Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}.

** For the set of cations Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}.

Table 11. Values of $\lg K_{st}$ and $\Delta \lg K_{st}$ for complexes [ML] of Cu^{2+} and Ni^{2+}.

Cation, $\Delta \log K_{st}$	(XXX.2)	(XXXII.2)	(XXXIII.2)	(XXXII.3)	(XXX.3)	(XXXIII.4)	EDIP
Cu^{2+}	21.3	25.4	26.6	27.1	21.3	15.69	20.35
Ni^{2+}	19.4	19.0	15.6	12.0	9.2	7.31	11.13
$\Delta \log K_{st}$	1.9	6.4	11.0	15.1	12.1	8.38	9.22

The selectivity of complex-formation in relation to the copper ion (Cu^{2+}) may be assessed by the difference:

$$\Delta \lg K_{st} = \lg K_{st}(Cu^{2+}) - \lg K_{st}(Ni^{2+}).$$

These values are given in Table 11 for the cyclopendant organophosphorus complexones and for the best of the other cyclopendants in this respect (XXXIII, 4),[108] and also for the linear complexone EDIP.[117]

It follows from the data shown that the ligands (XXXIII, 2) and especially (XXX, 3) and (XXXII, 3) surpass significantly the others in efficiency (A) and selectivity (S) of binding the Cu^{2+} ion.

The complexes of ligand (IV) of composition $[MH_2L]$ ($M = Ni^{2+}$, Cu^{2+} and Zn^{2+}) have been investigated.[102] X-Ray structural analysis of the binuclear complex $[Cu_2(L)].6H_2O$ shows that both Cu^{2+} ions have a square-pyramidal conformation. Two nitrogen atoms and two oxygen atoms of a COO^- group form the base of the pyramid. A water molecule is located at the vertex of the pyramid for one Cu^{2+} ion and a COO^- group for the other. The carboxyl-containing cyclopendants (II) and (IV), in contrast to their phosphorus analogues, form water-soluble complexes with the REE. The values of K_{st} for these complexes increase from 14.5 (Nd^{3+}) to 16.6 (Yb^{3+}).[99] It was established that complexes $[ML]^-$, where $M = Tb^{3+}$, Yb^{3+}, Pr^{3+} and Lu^{3+}, and L = (IV) are conformationally very rigid.[119]

Hay and coworkers[108] investigated the complex-formation of ligand (XXXIII, 4) (Table 10) with Cu^{2+}, Ni^{2+} and Pb^{2+} ions. The values of $\lg K_{st}$ for the complexes were in good agreement with those found previously.[118] X-Ray structural analysis of the complex of this ligand with the Ni^{2+} ion shows that the environment of the Ni^{2+} ion is almost a regular octahedron. Four ring nitrogen atoms are set at the corners of the square and oxygen atoms from CH_2CH_2OH groups are in the perpendicular positions. One pendant group in the complex with Ni^{2+} is deprotonated.

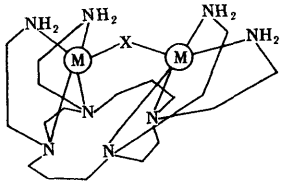
The ligand (XXXIII, 5) has eight donor positions in the molecule and as a rule forms binuclear complexes $[M_2L]$. Protonation constants for this ligand and stability constants were found for complexes with the Cu^{2+} ion of composition $[CuH_2L]^{4+}$ and $[Cu_2L]^{4+}$ (T = 25 °C, μ = 0.5, 0.5 M $NaNO_3$).[120]

X-Ray structural analysis of the complex of composition $[Cu_2L(ClO_4)_2].(ClO_4)_2$ has been carried out.[110] The environment of both Cu^{2+} ions is square-pyramidal. Four nitrogen atoms lie at the base of the pyramid and an oxygen atom of a ClO_4^- group is in the apical position with a much longer bond. A complex of the same structure is also formed with ligand (XXXIII, 5) by the Ni^{2+} ion, viz. $[Ni_2L(ClO_4)_2].(ClO_4)_2$.[111] The complex $[Cu_2L].Br(ClO_4)_3$ has a chain like structure and the bromine atom serves as a bridge between the Cu^{2+} ions, which have a square-pyramidal structure as a result of coordination with two cyclam nitrogen atoms and two nitrogen atoms of the pendant aminoethyl groups. The halogen atom at the vertex is able to complete the building of the square-pyramid in the Cu^{2+} complexes of chain-like structure. The addition constants for halide ion to the $[Cu_2L]$ complex have been found[112,120]

$$[Cu_2L]^{4+} + X^- = [Cu_2LX]^{3+},\ K_{st} = [Cu_2LX]^{3+}/[Cu_2L]^{4+}[X^-],$$

and are 2.6–5.1 for the ions F^-, Cl^-, Br^-, N_3^-, CN^-, OH^- and I^-.

Scheme 3



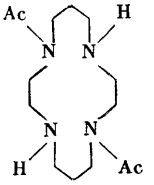
$[M_2L(X)]^{3+}$;
$M = Co^{2+}$, Cu^{2+};
$X = OH^-$ (for Co^{2+}),
$X = F^-$, I^-, NO_3^-,
N_3^-, NCO^- (for Cu^{2+}).

According to XSA data the complexes of Cu^{2+} [121] and Co^{2+} [122] with the ligand (XXXIII, 3) of composition $[M_2L(X)].(ClO_4)_3$ are of a similar structure in which each metal ion has a square-pyramidal environment (Scheme 3). Two ring nitrogen atoms and two pendant aminoethyl group nitrogen atoms are at the base of each pyramid. The X^- anion is at the vertex of the pyramid, common to both metal atoms.

X-Ray structural analysis has been carried out on the complex $[Ni_2LCl].Cl_3.H_2O$.[109] The Ni^{2+} atoms in this complex are not equivalent. One has square-planar coordination with two nitrogen atoms from the cyclam and two from the pendant aminoethyl groups. The second Ni^{2+} ion in the complex has a square-pyramidal environment with a Cl^- ion in the apical position.

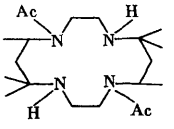
Lengthening the pendant groups leads to a change in complex-formation. The complex of (XXXIII, 6) with Ni^{2+} has a square-pyramidal structure. Four ring nitrogen atoms lie at the base of the pyramid and an amino group from a pendant aminopropyl group is in the apical position.[112]

Hay and Bembi[113] synthesised and investigated the complex of the Cu^{2+} ion with ligand (XXXIII, 7). In the [CuL(NCS)].(NCS) complex the Cu^{2+} ion has a square-pyramidal environment. The four cyclam nitrogen atoms are at the base of the pyramid and the NCS group is in the apical position. The pendant cyanoethyl groups do not participate in the coordination. Complexes of composition $[Cu_2LBr_2].(ClO_4)_2$ [123] and $[Ru(HL).(ClO_4)_3.H_2O$ [124] have been obtained for ligand (XXXIII, 8) and investigated by XSA. In the first complex the Cu^{2+} ion is coordinated with two nitrogen atoms of the pendant α-pyridylmethyl groups and with a bromine atom located on the axis perpendicular to the plane of the square in the corners of which lie nitrogen atoms. In the second complex the Ru^{2+} ion has a distorted octahedral environment with three ring nitrogen atoms and three nitrogen atoms of the α-pyridylmethyl groups. One pendant group in this complex is protonated and does not participate in coordination.

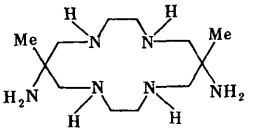


(XXXIV)

Ligand (XXXIV) has not been isolated in the free form since it is slowly converted into the corresponding lactam. However a crystalline complex of composition $[Cu^{2+}(L)]$ has been successfully obtained, XSA of which shows that it has an octahedral structure.[125] Four ring nitrogen atoms are located in the square plane and two oxygen atoms of the pendant groups are in the perpendicular positions.



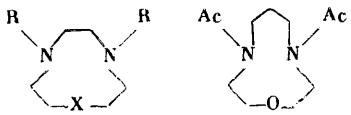
(XXXV)



(XXXVI)

The Ni^{2+} ion in the complex of composition $[Ni(L)].HBr.H_2O$ is coordinated (regular octahedron) with six donor atoms of the ligand (XXXV) (XSA data).[126] The complex-formation of ligand (XXXVI) with Co^{3+}, Ni^{2+} and Cu^{2+} ions has been investigated. According to XSA data the pendant NH_2 groups do not participate in coordination in the complex with Cu^{2+}.[148] The complex of Co^{3+} with this ligand is almost a regular octahedron with very short coordinate bond lengths at 1.94 to 1.95 Å due to chelation of the nitrogen atoms of the ring and pendant groups. The complex of the Ni^{2+} ion is also octahedral but with a large tetragonal distortion. On protonation, the pendant NH_2 groups add on protons and stop participating in coordination. The octahedral complexes of Co^{3+} and Ni^{2+} are converted by this into square-planar or into a *trans*-diaqua cation.

6. Unsymmetrical polyazamacrocyclic cyclopendants



(XXXVII) (XXXVIII)

1. R = CH_2COOH, X = NH; 2. R = CH_2COOH, X = O;
3. R = $CH_2CH_2NH_2$, X = NH; 4. R = $CH_2CH_2NH_2$, X = S;
5. R = $CH_2CH_2NEt_2$, X = O; 6. R = $CH_2CH_2CH_2NEt_2$, X = O.

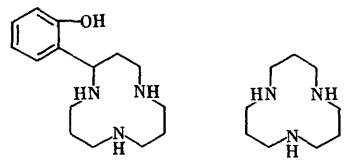
The thermodynamic parameters for complex-formation have been determined for ligand (XXXVII, 2) and (XXXVIII).[85] The increase in size of the cyclic fragment on transfering from (XXXVII, 2) to (XXXVIII) leads to a reduction in the stability of the complexes of the cations investigated, viz. Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}.

For the potentially pentadentate ligands (XXXVII, 1 and 2) complexes $[VO(L)].H_2O$, where L = 1 and $[VO(L)]$ where L = 2 have been obtained in which vanadium is tetravalent. A third complex was obtained by the oxidation of the first complex and in this $[VO_2(L)H].2H_2O$ vanadium is pentavalent.[128] It was shown by XSA that the first and third complexes have a distorted octahedral structure.

The environment of the VO^{2+} ion is square-pyramidal. At the apex of the pyramid is a nitrogen atom with coordinate bond length 2.31 Å. Two nitrogen and two oxygen atoms lie at the base of the pyramid. In the third complex one protonated pendant CH_2CH_2COOH group does not participate in coordination with the VO_2^+ ion. The short lengths for V=O bonds (1.61 Å in the first, 1.63 and 1.64 in the third complex) are characteristic of the double bond in vanadyl ions.

Complexes of composition $[Co^{3+}LCl].(ClO_4)_2$ were obtained by oxidation of the corresponding complexes of Co^{2+} with ligands (XXXVII, 3 and 4). It was shown that the complexes of Co^{3+} with these ligands exist as two isomers in which the chlorine atom occupies either an equatorial or an apical position.[129] On coordination of ligands (XXXVII, 3 and 4) with VO^{2+} and Co^{3+} ions one ring nitrogen atom occupies the apical position, i.e. the disposition of all three ring nitrogen atoms in one plane seemingly encounters steric difficulties, which is also observed for complexes of Cu^{2+} with ligands (XXX, 2), (I) and (XXX, 9) based on 1,4,7-triazacyclononane. The VO^{2+} ion has a coordination number of five since on coordination with ligand(I) one dentate position of this complexone proved to be unused. Ligands (XXXVII, 5 and 6) show a physiological effect on the central nervous system of mice.[130] The complex-forming properties of these compounds have not been studied.

The stability constants of the complexes of compounds (XXXIX) and (XL) with the TM have been determined (Table 12).



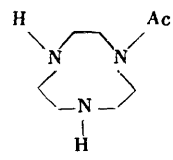
(XXXIX) (XL)

Protonation of complexes of ligand (XXXIX), when the oxygen atom of the pendant hydroxyphenyl group ceases to participate in coordination, shows that this group participates actively in the binding of cations. Ligand (XXXIX) forms far more stable complexes than the free amine. According to XSA data, the complex of this ligand with the Zn^{2+} ion has a trigonal-bipyramidal structure.[82] Two ring nitrogen atoms and the oxygen atom of the phenolic hydroxyl are located in the equatorial plane (triangle) with very short coordinate bond lengths (which shows the strong bonding). A ring nitrogen atom and a molecule of water are located in the apical positions with large bond lengths.

Table 12. Values of $\lg K_{st}$ complexes [ML] (T = 25 °C, μ = 0.1).

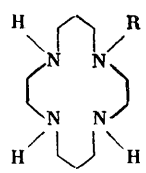
Cation	(XXXIX) [79]	(XL) [80]
Co^{2+}	11.4	–
Ni^{2+}	14.0	10.93
Cu^{2+}	18.4	12.63
Zn^{2+}	12.6	8.75

The ligand (XLI) has been synthesised.[131] Its complex-forming properties were not studied.

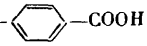


(XLI)

The complexes of Ni^{2+} and Cu^{2+} with the following ligands have been investigated.

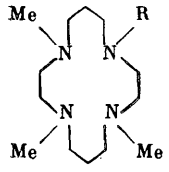


(XLII)

1. R = H; 2. R = CH_2COOH; 3. R = CH_2CH_2COOH;
4. R = $(CH_2)_3COOH$; 5. R = CH_2– ;
6. R = CH_2–  –COOH [131].

The pendant carboxyl groups of ligands (XLII, 2 and 5) participate in coordination. The pendant groups of ligands (XLII, 3, 4 and 6) do not participate in coordination. On reducing the pH the carboxylate groups COO^- are protonated and cease participation in complex-formation with M^{2+}.

Complexes of Ni^{2+} and Cu^{2+} with ligands (XLIII, 1–8) have been synthesised.[133]



(XLIII)

1. R = H; 2. R = CH_2CN; 3. R = $CH_2CH_2NH_2$; 4. R = CH_2CH_2CN;
5. R = $(CH_2)_3NH_2$; 6. R = $CH_2CH_2\overset{\overset{O}{\|}}{C}NH_2$; 7. R = $CH_2CH_2\overset{\overset{O}{\|}}{C}Me$;
8. R = CH_2CH_2COOH; 9. R = Me; 10. R = CH_2COOMe;
11. R = CH_2COOEt; 12. R = CH_2CH_2COOEt; 13. R = $CH_2C(O)NMe_2$;
14. R = $CH_2CH_2P(O)(OEt)_2$; 15. R = $CH_2CH_2P(O)(OEt)(OH)$;
16. R = CH_2COOH; 17. R = $CH_2C(O)NH_2$; 18. R = CH_2CH_2SH;
19. R = $CH_2CH_2NMe_2$.

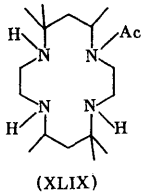
In the complexes of Ni^{2+} and Cu^{2+} ions with ligands (XLIII, 1–8) of composition $[ML].(ClO_4)_2$ the pendant group participates in coordination since, according to spectral data, these cations are pentacoordinated. The cyanoethyl pendant group and the protonated ethyl- and propylamino groups do not participate in complex-formation with Ni^{2+} and Cu^{2+}.

Finally, ligands with the same general formula but with other pendant substituents (XLIII, 9–19) have been obtained and investigated.[134]

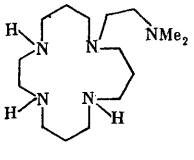
It was established spectroscopically that the pendant groups of ligands (XLIII, 10–18) coordinate the Cu^{2+} ion in the axial position (at the apex of a square pyramid).

X-Ray structural analysis of complexes of composition $[HL.H_2O].2Br$, $[NiL(H_2O)].Br$ and $[NiL(NCS)].H_2O$ showed that the Ni^{2+} ion in these complexes is coordinated (octahedral environment) with five donor atoms of ligand (XLIX) and one water molecule or NCS group.[135]

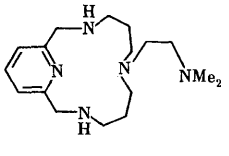
The complexes of Ni^{2+} and Cu^{2+} with ligands (L) and (LI), also containing one pendant group, were obtained by Alcock and collaborators.[136]



(XLIX)



(L)



(LI)

The complexes of ligands (L) and (LI) with Ni^{2+} and Cu^{2+} ions have a trigonal-bipyramidal structure in neutral media which is transformed into square-planar at low pH. The pendant group is protonated by this and stops participating in coordination. The XSA of complex $[Ni(L)].(ClO_4)_2$ showed that it has a trigonal-bipyramidal structure.[136]

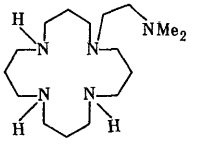
Complexes of Ni^{2+} of composition $[Ni(L)(NCS)].(ClO_4)$ and $[Ni(LH)(NCS)_2].(ClO_4)$ have been obtained and investigated.[137]

One or two (when the pendant group is protonated and does not participate in coordination) NCS^- groups occupy apical positions in hexacoordinated complexes of Ni^{2+}. The thermodynamic parameters have been calculated for the protonation of the complex of Cu^{2+} with ligand (L).

$$[Cu(L)]^{2+}+H^+ \rightleftharpoons [Cu(HL)]^{3+} \quad (L=(L)).$$

Complexes of ligands (L) and (LI) with the Zn^{2+} ion of composition $[Zn(L)].(NO_3)_2$ have also been synthesised. It was shown that the pendant dimethylaminoethyl group participates in coordination in the complexes of ligands with Zn^{2+}.

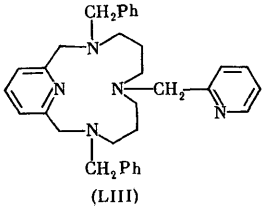
Alcock and collaborators[138] have synthesised and studied the complex-forming properties of ligand (LII) in relation to Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+}.



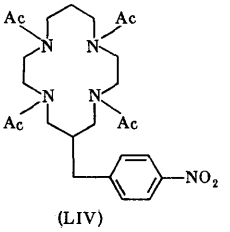
(LII)

It was established that the ions of Ni^{2+}, Co^{2+} and Cu^{2+} were pentacoordinated, i.e. the pendant group participates in coordination. The problem of the participation of the pendant group of ligand (LII) in coordination with Zn^{2+} and Cd^{2+} ions remains unresolved. On acidification, the complex $[Ni(L)].(ClO_4)_2$ is decomposed completely. The square-pyramidal complex $[Cu(L)].(ClO_4)_2$ is transformed on acidification with $HClO_4$ into the square-planar $[Cu(HL)].(ClO_4)_3$ in which the protonated pendant group has ceased participating in coordination [L = (LII)].

The same authors have synthesised and investigated ligand (LIII) having a pendant α-pyridylmethyl group.[139] It was discovered that the pendant group participates in coordination in the complexes $[M(L)].(ClO_4)_2$ (M = Ni^{2+} and Zn^{2+}). Acidification of the blue pentacoordinated complex of (LIII) with Ni^{2+} leads to the yellow $[NiHL].(ClO_4)_3$ complex in which the protonated pendant group does not participate in coordination.



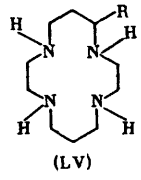
(LIII)



(LIV)

The complex of Cu^{2+} with ligand (LIV) has been studied by XSA.[140] In this complex the Cu^{2+} ion has an octahedral environment due to the ring nitrogen atoms and the two pendant carboxyl groups. The ring nitrogen atoms do not lie in one plane as was observed previously for the complex $[Cu(H_2L)]$ with ligand (II).[102]

Kimura and collaborators have synthesised and investigated the complexes of ligands (LV, 1–4).



(LV)

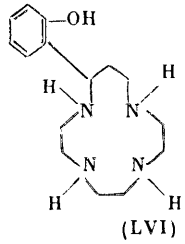
1. R = [140, 141];
2. R = [142];
3. R = [143];
4. R = CH_2OH [144].

The stability constants have been found for the complexes of Fe^{2+} and Fe^{3+} with the ligand (LV, 1).[140] The XSA of the complex with the Ni^{2+} ion shows that Ni^{2+} is in a plane of four ring nitrogen atoms.[141] The oxygen atom of the phenolic hydroxyl is at the vertex of a square pyramid and in this complex occupies an axial position with a very short coordinate bond length. At pH > 6 the phenolic oxygen atom is protonated and ceases to participate in coordination.

According to XSA data the conformation of the complex of Cu^{2+} ion with ligand (LV, 2) is square-pyramidal. Four ring nitrogen atoms are located in the plane of the pyramid and the oxygen atom of the phenolic group is at the vertex. The $K_{st}[CuL] = 1 \times 10^{32}$ M^{-1}, but for the protonated complex with the pendant group not participating in coordination $K_{st}[CuHL] = 2.5 \times 10^{29}$ M^{-1}. It is evident from this that the pendant 2-hydroxyphenyl group makes a contribution to the stability of the resulting complex.[145]

For ligand (XXXIX) based on triazacyclododecane the difference in the values of $\lg K_{st}$ of the complexes [CuL] and [CuHL] was 5.8 with the 2-hydroxyphenyl pendant group not participating in coordination.[79]

A reduction in the size of the ring in ligand (LVI) compared with (LV, 1) leads to a change in the structure of the complex formed with the Ni^{2+} ion.



(LVI)

The octahedral Ni^{2+} complex has the following structure. At the vertices of the square cross section are three ring nitrogen atoms and a water molecule. Perpendicular to this square are a ring nitrogen atom and the oxygen atom of the phenolic group. On reducing the pH the protonated pendant group ceases to participate in coordination and the blue high-spin octahedral Ni^{2+} complex is transformed into the yellow square-planar low-spin complex.[147]

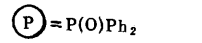
The complex of the Ni^{2+} ion with ligand (LV, 2), with a pyridine substituent, of composition $[Ni(L)H_2O].(ClO_4)_2$ has been studied. According to XSA data the high-spin complex has an octahedral structure.[142] Four cyclam nitrogen atoms are at the vertices of the square and the nitrogen atom of the pyridine ring and a water molecule are on the perpendicular axis. The XSA data on the complexes with the ligands described have been reported.[132] An XSA was carried out on the complex of the Ni^{2+} ion with ligand (LV, 3) which has an imidazole substituent in the molecule.[143] In this complex the Ni^{2+} ion has an octahedral environment. Four nitrogen atoms are found at the vertices of the square and the imidazole nitrogen and an oxygen of the ClO_4^- group are on the perpendicular axis.

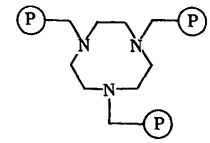
The stability constants of the [NiL] complex of ligand (LV, 2) have been determined.[147]

It was established that in the complex of ligand (LV, 4) with $NiCl_2$ four ring nitrogen atoms and the pendant hydroxymethyl group participate in coordination with the Ni^{2+} ion.[146]

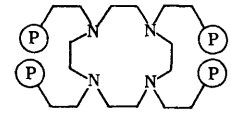
7. Polyazacyclopendants with diphenylphosphoryl pendant groups

Ligands (XXX, 10), (XXXII, 6), (XXXIII, 9) and (XXXIII, 10) contain cyclic polyalkylene-polyamine fragments considered above and pendant diphenylphosphoryl-methyl and -ethyl groups. These ligands form complexes with ions of the alkali, alkaline earth and transition metals in non-aqueous media by participation of the nitrogen atoms of the cyclic fragment and the oxygen atoms of the pendant groups in coordination.

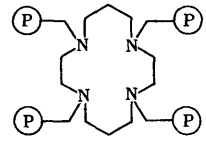




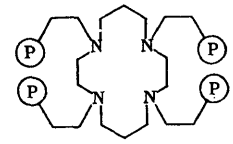
(XXX. 10) [64–66]



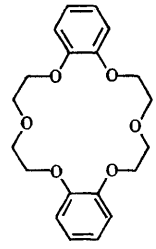
(XXXII. 6) [149]



(XXXIII. 9) [116]



(XXXIII. 10) [116]



(XIX. 1) [149]

Stability constants are given in Table 13 for complexes of these ligands and also (for comparison) for dibenzo-18-crown-6 (XIX, 1) with alkali metals. The selectivity of the ligands with diphenylphosphoryl pendant groups was reduced with the reduction in the conformational rigidity.

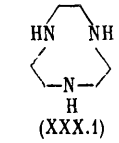
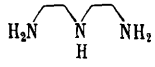
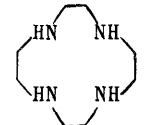
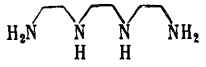
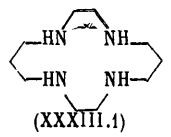
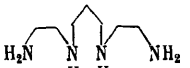
Compounds (XXX, 10), (XXXII, 6) and (XXXIII, 10) form complexes with the Li^+ ion exceeding in stability the complexes with all the ligands known until 1988.[150]

It was established that the ring nitrogen atoms and the oxygen of the pendant $P(O)Ph_2$ groups take part in the formation of complexes of the ligands represented with ions of the alkali metals, AEM and TM.[64, 65,151] In contrast to (XXX, 2) with its phosphonic acid pendant groups, the ligand (XXX, 10) is not specific complex-forming agent for the Mg^{2+} ion. It forms a more stable complex with Ca^{2+} than with Mg^{2+}.[64] In complexes of $Co(SCN)_2$ with the ligands (XXX, 10) and (XXXIII, 10) either all or only a portion of the donor atoms of these ligands, depending on the composition, participate in coordination with the Co^{2+} ion.[65,151]

Table 13. Values of $\lg K_{st}$ for complexes $[ML]^+$ (T = 25 °C, THF:$CHCl_3$ 4:1) and A and S of complex-formation for the set Li^+, Na^+, K^+ and Cs^+.[149]

Cation A, S	(XXX.10)	(XXXII.6)	(XXXIII.9)	(XXXIII.10)	(XIX.1)
Li^+	5.6	5.91	4.7	6.2	4.06
Na^+	4.5	6.29	3.8	5.9	5.60
K^+	3.2	5.04	3.0	4.9	4.66
Cs^+	2.2	3.60	2.3	4.1	3.30
A	3.9	5.21	3.5	5.3	4.41
S	1.9	1.49	1.3	1.2	1.25

Table 14. Values of pK_a of cyclic amines and their linear analogues.

Compound	pK_1	pK_2	pK_3	pK_4	Reference
 (XXX.1)	<2	6.82	10.42	-	[83]
	4.23	9.02	9.84	-	[73]
 (XXXII.1)	<1	<2	9.7	10.7	[152]
	3.25	6.56	9.08	9.74	[73]
 (XXXIII.1)	1.0	1.7	10.2	11.5	[152]
	6.02	7.28	9.50	10.25	[73]

VI. Acid dissociation of cyclopendant complexones: derivatives of polyazamacrocycles

The mechanism of the acid dissociation has been investigated for phosphonyl- and carboxyl-containing complexones in the molecules of which there are the cyclic polyalkylene-polyamine fragments of triazacyclononane, cyclene and cyclam. In contrast to linear polyamines with highly basic nitrogen atoms, the basicity of the nitrogen atoms in the cyclic fragment of cyclopendant complexones varies within very wide limits and a zwitterionic structure exists involving only some of the nitrogen atoms.

Values of pK_a of some cyclic amines and their linear analogues are shown in Table 14.

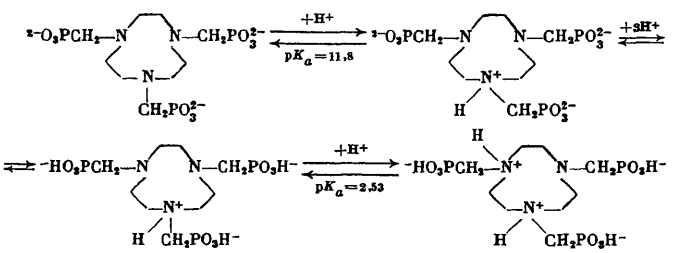
The fission of protons on acid dissociation of cyclopendant complexones with cyclic polyalkylene-polyamines in the molecule may occur both from acid (PO_3H_2 or COOH) groups or from ammonium nitrogen atoms of the cyclic fragment since they have closely similar pK_a values.

Complexones with phosphonoalkyl pendant groups have a different scheme for acid dissociation from that of compounds with carboxyl groups. The phosphonic acid group has two dissociation stages. The size of pK_1 ($PO_3H_2 \rightarrow PO_3H^- + H^+$) is less and of pK_2 ($PO_3H^- \rightarrow PO_3^{2-} + H^+$) is greater than the pK_a of a carboxyl group.[98,153] The phosphonic acid group exerts a different electronic effect on the nitrogen atoms of the cyclic fragment of complexones during the dissociation process.

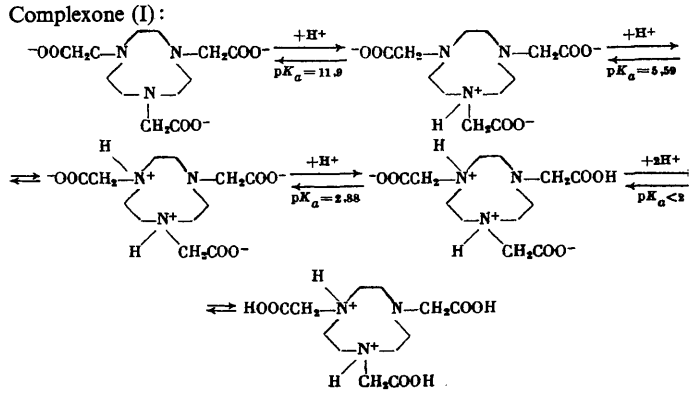
The dissociation sequence of the organophosphorus complexones (XXX, 2), (XXXII, 2) and (XXVIII, 2) has been studied by IR spectroscopy in water and in heavy water.[56,155] Complexones (XXX, 3) and (XXXII, 3) were investigated by ^{31}P NMR spectroscopy in water. ^1H NMR and IR (in D_2O) spectroscopy[154] and ^1H and ^{13}C NMR spectroscopy[156] have been used to study the protonation of the carboxyl-containing complexones (I), (II) and (IV).

The following protonation schemes are proposed.

Complexone (XXX, 2)

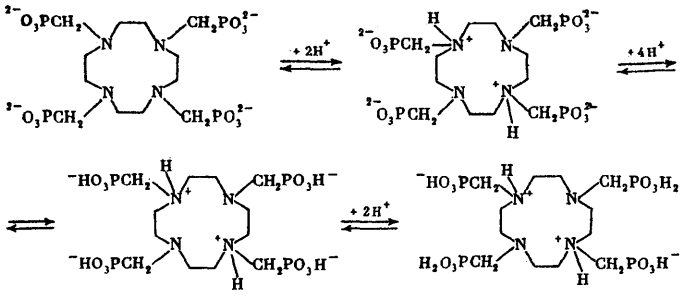


Complexone (I):



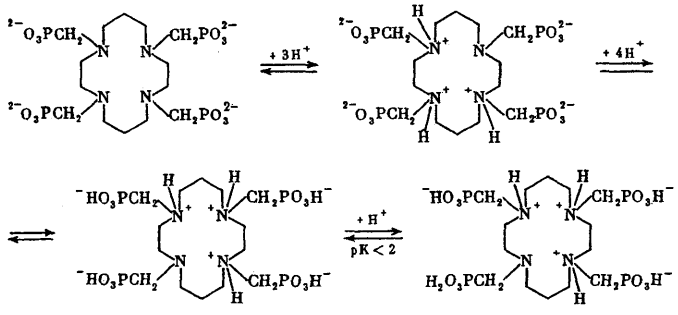
The ring nitrogen atoms of ligand (I) are protonated only at very low pH.

Complexone (XXXII, 2)

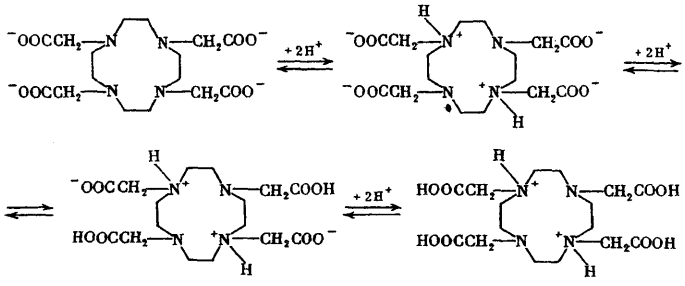


Complexone (XXXII, 2) therefore has a double zwitterion structure in solution. The nitrogen protons dissociate finally at high pH values (pK_7 and pK_8 in Table 15).

Complexone (XXXIII, 2)



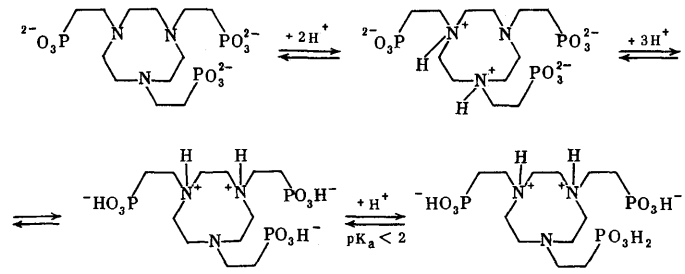
Complexone (XXXIII, 2) has a triple zwitterion structure in solution. All the nitrogen protons are finally split off in one buffer region at very high pH (pK_6, pK_7, pK_8 in Table 15). In the case of the carboxyl-containing complexones (II) and (IV) the size of the cyclic fragment has little effect on the dissociation. Complexones based on cyclene and cyclam have the same dissociation mechanism and the protonation scheme below applies to both (II) and (IV).



With increasing acidity two nitrogen atoms are protonated first and then the two carboxyl groups bound to the unprotonated nitrogen atoms. The remaining carboxyl groups are then protonated. Complexones (II) and (IV) protonate the acid groups first since the nitrogen atoms are less basic than the COOH groups in these molecules.[154]

The mechanism of the acid dissociation of complexones (XXX, 3) and (XXXII, 3) has been investigated by $^{31}P-\{^1H\}$ NMR spectroscopy in water. In the dissociation of the aminophosphonic acids the fission of protons from the PO_3H_2 group is accompanied by an insignificant reduction in the size of the chemical shift (δ) in the ^{31}P NMR spectra.[157] Dissociation of the proton from a nitrogen atom leads, on the other hand, to an increase in δ. This is explained[158] by the fundamental difference in the hybridisation of the nitrogen atoms on going from ammonium to amine and consequently by a change in the shielding of the phosphorus atom. A sharp increase in δ (shift to low field) on fission of the proton bound to the nitrogen atom is observed on dissociation of nitrilotris(methylphosphonic acid) (NTP)[159] and iminobis(methylphosphonic acid).[160]

The sequence of protonation of complexone (XXX, 3) is represented as follows.



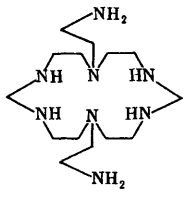
The replacement of the phosphonomethyl pendant groups by phosphonoethyl leads to a definite change in the dissociation mechanism of complexone (XXX, 3) compared with (XXX, 2). The former has the structure of a double zwitterion and the protons bound to the ring nitrogen atoms are split off last.

As is seen the acid dissociation of cyclopendant polyphosphonic complexones (like the polyphosphonic complexones with an open chain) occurs over a very wide pK region, from <1 to 13.5. The formation of complexes within wide limits of acidity of the medium is a characteristic of these compounds. Stable "hydrogen" complexes are formed in acid medium with incomplete displacement of acid group protons by the metal cation. The formation of homo- and heteronuclear complexones (when some of the protons are displaced by one cation and some by another) is also characteristic.[161–171] All these are properties specific to the polyphosphonic complexes.

The complexone (XXXII, 2) has the same order of fission of protons as (XXXII, 3).

VII. Cyclopendants with a large cyclic fragment

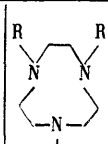
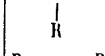
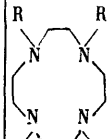
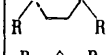
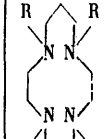
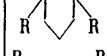
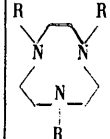
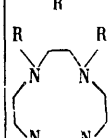
These ligands contain more than four nitrogen atoms in the cyclic fragment. The XSA of complexes (LVII) of composition $[La(L)(CF_3SO_3^-)_2]^+$ and $[Yb(L)(CF_3SO_3^-)]^+$ showed that the La^{3+} ion is decacoordinated with eight donor nitrogen atoms of the ligand and two oxygen atoms of the $CF_3SO_3^-$ group.[162]



(LVII)

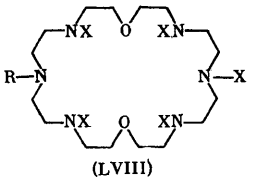
The Yb^{3+} ion complexed with this ligand is nonacoordinated. Eight sites are occupied by nitrogen atoms of the ligand and one by an oxygen atom of the $CF_3SO_3^-$ group. The mean length of the M–N-ring bonds is 2.5–2.6 Å and of the M–N-pendant groups is 2.5 Å, much greater than in cyclopendant complexes with transition metals. This was observed previously when studying the complex of Eu^{2+} with ligand (II).[101]

Table 15. Values of pK_a for the dissociation of phosphonyl- and carboxyl-containing cyclopendant complexones (T = 25 °C, μ = 1.0).[56,57,81,154,93]

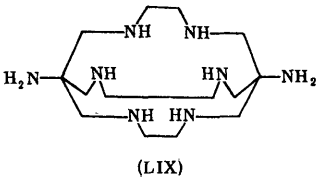
№	Complexone	R	pK_1	pK_2	pK_3	pK_4	pK_5	pK_6	pK_7	pK_8
1		$CH_2PO_3H_2$	<2	2.53	5.38	7.09	8.65	11.8	-	-
2		CH_2COOH	3.16	6.03	10.77	-	-	-	-	-
3		$CH_2PO_3H_2$	<1	<2	4.88	5.73	7.28	8.46	11.5	12.1
4		CH_2COOH	4.18	4.24	9.23	11.08	-	-	-	-
5		$CH_2PO_3H_2$	<2	4.96	6.27	7.67	9.16	11.8	12.8	13.5
6		CH_2COOH	3.38	4.05	10.18	11.56	-	-	-	-
7		$(CH_2)_2PO_3H_2$	<2	5.38	6.21	6.97	8.85	12.3	-	-
8		$(CH_2)_2PO_3H_2$	<2	2.30	6.21	6.84	7.63	8.34	11.2	12.4

Note. For complexones Nos. 2, 4 and 6 the values of pK_a found are for the addition of proton to the carboxylate group of the corresponding zwitterion.

Ligands (LVIII) have been synthesised and contain a cyclic fragment with donor atoms of nitrogen and oxygen and various pendant groups, such as CH_2CH_2CN, $(CH_2)_3NH_2$, PO_3H_2, etc. (X = H or Ts).[52,53]

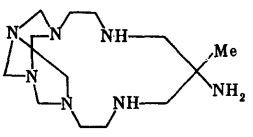


(LVIII)



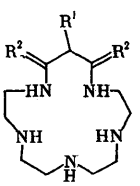
(LIX)

The pendant NH_2 groups of ligand (LIX) do not participate in coordination. The hexacoordinated complexes of Co^{3+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, etc. are formed with ring nitrogen atoms.[173] Complexes have been obtained with ligand (LX) and Ni^{2+} and Ni^{3+} ions.



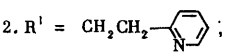
(LX)

Four ring nitrogen atoms participate in coordination and are located at the corners of a square. The fifth ring nitrogen atom and the pendant group NH_2 do not participate in coordination.[174] It was established that (LXI, 1) does not form complexes with Na^+, K^+, Mg^{2+} and Ca^{2+}.[175] The pendant group R^1 of the ligand (LXI, 2) participates in coordination with Ni^{2+}. The stability constant for the complex of Ni^{2+} with this ligand has been found.[176]

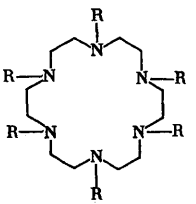


(LXI)

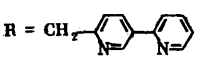
1. $R^1 = (CH_2)_4NH_2$, $R^2 = H_2$;

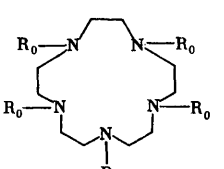
2. $R^1 =$  ; $R^2 = O$.

The complex-formation of ligands (LXII) and (LXIII), which contain bipyridinylmethyl and hydroxyethyl pendant groups in the molecule, has not been studied.[177,178] Martell and collaborators have investigated the complex-forming ability of ligands (LXIV, 1 and 2) with the Fe^{3+} ion.[172,179] The values of $\lg K_{st}$ for complexes [ML] [T = 25 °C, μ = 0.1 (KNO_3)] were 37.6 and 36.0 for (LXIV, 1) and (LXIV, 2) respectively.



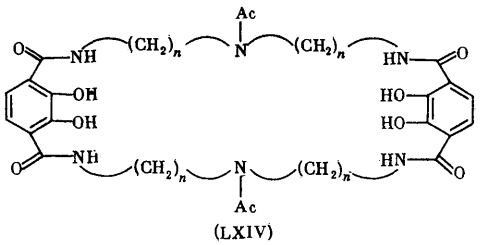
(LXII)

R = 



(LXIII)

$R_0 = CH_2CH_2OH$



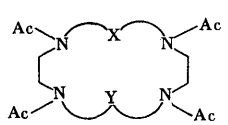
(LXIV)

1. $n = 2$
2. $n = 3$

VIII. Effect of the nature of the pendant groups and the structure of the cyclic fragment of cyclopendants on the efficiency and selectivity of complex-formation

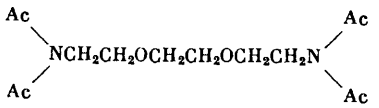
The majority of the ligands investigated contain as acids either phosphonic or carboxyl groups, consequently it is interesting to compare the efficiency and selectivity of complex-formation of the phosphoryl- and carboxyl-containing complexones having the same carbon skeleton. Such comparison were carried out previously but without using the *A* and *S* criteria.[180]

Values of *A* and *S* for complex-formation are given in Table 16 calculated from the stability constants of complexes.[67,69,105,180,181] In contrast to their carboxyl-containing analogues the organophosphorus complexones with two PO_3H_2 groups form low stability complexes with Mg^{2+} and the alkaline earth elements. For the transition metals the organophosphorus complexones exceed the carboxyl-containing in both efficiency and selectivity of complex-formation. There are few data for Mg^{2+} and the alkaline earth elements and it is difficult at present to draw conclusions on the superiority of the organophosphorus or of other complexones. On the whole the acyclic organophosphorus complexones surpass their carboxyl-containing analogues in selectivity by, on average, one order and the cyclopendants by two orders of magnitude.



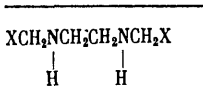
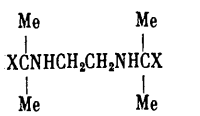
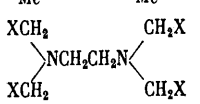
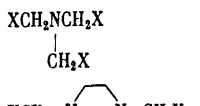
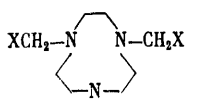
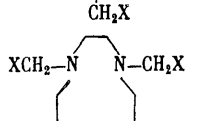
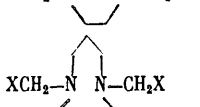
(LXV)

The effect of change of size and conformational rigidity of the cyclic fragments is shown in the efficiency and selectivity of complex-formation of the cyclopendant complexones. The complex-formation of compounds (LXV, 1–8), having the same pendant groups and various cyclic fragments, has been studied.[94] Values of *A* and *S* are given in Table 17 for two sets of cations. The change in the size of the cyclic fragment has the most striking effect on *A* and *S*. On going from ligand 1 to 2 and 3, and also from 6 to 7 the efficiency falls sharply. The selectivity may increase or decrease during this. The introduction of alkyl substituents into the bridge shows up negatively on the selectivity of action in relation to the second group of cations, the efficiency of binding is reduced to the same extent. There are no such regularities when using the TM although here also an increase in the bulk of the alkyl substituent in the bridge reduces the efficiency of complex-formation (cf. ligands 4, 5 and 6 in Table 17). Complexones (LXV, 1–8) display interesting complex-forming properties. Complexone (LXV, 1) forms the most stable complex with the Ca^{2+} ion of the known complexones ($\lg K_{st} = 15.9$). Complexone (LXV, 3) has the maximal difference in stability constant for complexes with Mg^{2+} and Ca^{2+} (values of $\lg K_{st}$ for these complexes were 3.0 and 9.5 respectively). The best linear complexone in this respect (LXVI) forms complexes with Mg^{2+} and Ca^{2+} cations with $\lg K_{st}$ 5.21 and 10.97 respectively.[182]



(LXVI)

Table 16. Values of *A* and *S* of complex-formation of organophosphorus and carboxyl-containing complexones.

Complexone	X	*A*	*S*	*A*	*S*	*A*	*S*
		Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}		Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}		Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}	
	PO_3H_2	see *	see *	12.2	4.6	–	–
	COOH	–	–	11.9	4.1	–	–
	PO_3H_2	see *	see *	12.8	5.4	–	–
	COOH	–	–	9.9	3.2	–	–
	PO_3H_2	–	–	17.6	4.7	–	–
	COOH	9.0	11.4	16.7	2.4	16.6	2.0
		6.9	0.6	14.2	3.9	–	–
	PO_3H_2	(7.1) **	(0.9) **				
	COOH	5.4	0.9	10.6	2.5	10.5	2.2
	PO_3H_2	6.8	3.5	20.4	3.7	20.7	3.4
	COOH	7.6	2.6	–	–	17.1	2.4
	PO_3H_2	9.1	1.7	21.4	4.6	22.4	3.7
	COOH	12.8	2.7	18.3	0.9	18.8	0.8
	PO_3H_2	see *	see *	17.2	6.8	17.1	5.8
	COOH	5.8	3.6	15.2	3.1	15.1	2.7

* $\lg K_{st}$ for complexes of Mg^{2+} and the alkaline earth elements < 2.
** Data.[144]

The increase in dentate number in the case of ligand 8 did not lead to an increase in the value of A but this compound forms a more stable complex with the Ba^{2+} ion than with Ca^{2+} and Sr^{2+}, which is also unusual for the classic (linear) complexones.

Table 17. Values of A and S of complex-formation of compounds (LXV, 1–8).

№ Ligand in (LXV)	X in (LXV)	Y in (LXV)	A	S	A	S
			Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}		Cu^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}	
1	CH_2CH_2	CH_2CH_2	12.8	2.7	19.0	0.6
2	CH_2CH_2	$CH_2CH_2CH_2$	8.1	2.2	15.8	1.5
3	$CH_2CH_2CH_2$	$CH_2CH_2CH_2$	5.8	3.6	15.9	1.7
4	CH_2CH_2	CH_2CHCH_2 (Me)	9.3	2.5	17.5	0.6
5	CH_2CH_2	CH_2CHCH_2 (Et)	6.8	1.2	13.8	1.8
6	CH_2CH_2	CH_2CCH_2 (Me, Me)	4.0	0.7	7.5	0.9
7	$CH_2CH_2CH_2$	CH_2CCH_2 (Me, Me)	2.8	0.4	7.5	1.8
8	$(CH_2CH_2)_2N$ (Ac)	$(CH_2CH_2)_2N$ (Ac)	7.4	1.5	15.2	0.7

References

1. M I Kabachnik *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1984, (29) 272
2. R A Schultz, D M Dishong, G W Gokel *J. Am. Chem. Soc.*, 1982, **104** 625
3. B F Berezin *Koordinatsionnye Soedineniya Porfirinov i Ftalotsianina* (Coordination Compounds of Porphyrins and Phthalocyanine), Nauka, Moscow, 1978, 465 pp
4. M N Hughes *The Inorganic Chemistry of Biological Processes* (Translated into Russian), Mir, Moscow, 1983, 493 pp
5. R D Bergeron *Chem. Rev.*, 1984, **84** 587
6. H Hama, S Takamoto *Nippon Kagaku Kaishi*, 1975, 1182
7. H Stetter, W Frank *Angew. Chem.*, 1976, **15** 686
8. J-P Behr, J-M Lehn, P Viering *J. Chem. Soc., Chem. Commun.*, 1976, 621
9. R Ungaro, B E Haj, J Smid *J. Am. Chem. Soc.*, 1975, **98** 5198
10. M Newcomb, D J Cram *J. Am. Chem. Soc.*, 1975, **97** 1257
11. M A McKervey, D L Mulholland *J. Chem. Soc., Chem. Commun.*, 1977, 438
12. M Takahashi, S Takamoto *Bull. Chem. Soc. Jpn.*, 1977, **50** 3413
13. C K Chang *J. Am. Chem. Soc.*, 1977, **99** 2819
14. M Takagi, M Tazaki, K Veno *Chem. Lett.*, 1978, 1179
15. H Häfliger, T A Kaden *Helv. Chim. Acta*, 1979, **62** 683
16. F L Weitl, K N Raymond *J. Am. Chem. Soc.*, 1979, **101** 2728
17. K B Yatsimirskii, E E Kriss, V L Gvyazdovskaya *Konstanty Ustoichivosti Kompleksov Metallov s Bioligandami* (Stability Constants of Complexes of Metals with Bioligands), Nauk. Dumka, Kiev, 1979, 284 pp
18. L A Frederick, T M Fyles, et al. *Can. J. Chem.*, 1981, **59** 1724
19. M J Pugia, B E Knudsen, et al. *J. Org. Chem.*, 1987, **52** 541
20. J Strzelbicki, R A Bartsch *Anal. Chem.*, 1981, **53** 2251
21. C A Chang, J Twu, R A Bartsch *Inorg. Chem.*, 1986, **25** 396
22. I Tabushi, Y Kobuke, et al. *J. Am. Chem. Soc.*, 1980, **102** 5947
23. T Okano, M Iwahara, et al. *J. Organomet. Chem.*, 1988, **346** 267
24. D E Fenton, D Parkin, R F Newton *J. Chem. Soc., Perkin Trans. 1*, 1981, 449
25. A H Haines, I Hodgkisson, C Smith *J. Chem. Soc., Perkin Trans. 1*, 1983, 311
26. E Weber, M Czugler *Inorg. Chim. Acta*, 1982, **61** 33
27. K B Yatsimirskii, M I Kabachnik, L V Tsymbal, et al. *Zh. Neorg. Khim.*, 1985, **30**(4) 976 [English translation in *Russ. J. Inorg. Chem.*, 1985(4)]
28. K B Yatsimirskii, E I Sinyavskaya, L V Tsymbal, et al. *Zh. Neorg. Khim.*, 1983, **28**(4) 946 [English translation in *Russ. J. Inorg. Chem.*, 1983(4)]
29. N V Lukoyanov, G I Van'kin, L V Zhuravleva, et al. *Biol. Membrany*, 1985, (2) 71
30. T N Kudrya, L M Tochilkina, V P Kazachenko, et al. *Zh. Obshch. Khim.*, 1985, **55** 2021
31. G V Bodrin, M I Kabachnik, N E Kochetkova, B F Myasoedov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 1841
32. K E Matthes, D Parker, et al. *Tetrahedron Lett.*, 1987, **28** 5573
33. R Delgado, J J R Frausto, M C Vaz, et al. *Polyhedron*, 1987, (6) 29
34. M J Calverley, J Dale *Acta Chem. Scand., Ser. B*, 1982, **36** 241
35. H Nakamura, H Sakka, et al. *Chem. Lett.*, 1981, 1305
36. M Tazaki, K Nita, M Takagi, K Ueno *Chem. Lett.*, 1982, 571
37. F Jong, A Zon, D N Reinhoudt, et al. *Recl. Trav. Chim. Pays-Bas*, 1983, **102** 164
38. C A Chang, V O Ochaya *Inorg. Chem.*, 1986, **25** 355
39. C A Chang, M E Rowland *Inorg. Chem.*, 1983, **22** 3866
40. N M Richardson, I O Sutherland *Tetrahedron Lett.*, 1985, **26** 3739
41. T Yamashita, H Nakamura, et al. *Bull. Chem. Soc. Jpn.*, 1980, **53** 1550
42. V J Thöm, M S Shaikjee, R D Hancock *Inorg. Chem.*, 1986, **25** 2992
43. K V Damu, M S Shaikjee, J P Michael, et al. *Inorg. Chem.*, 1986, **25** 3879
44. C A Chang, P H-L Chang, Manchanda, et al. *Inorg. Chem.*, 1988, **27** 3786
45. C A Chang, V O Ochaya, V C Sekhar *J. Chem. Soc., Chem. Commun.*, 1985, 1724
46. V C Sekhar, C A Chang *Inorg. Chem.*, 1986, **25** 2061
47. C A Chang, V C Sekhar *Inorg. Chem.*, 1987, **26** 1981
48. C A Chang, P A-L Chang, S-Y Qin *Inorg. Chem.*, 1988, **27** 944
49. T Uechi, I Ueda, M Tazaki, et al. *Acta. Crystallogr., Sect. B*, 1982, **38** 433
50. P M May, R A Bulman *Prog. Med. Chem.*, 1983, **20** 226
51. D Robert, R D Hancock *Pure Appl. Chem.*, 1986, **58** 1445
52. S P Kasprzyuk, R G Wilkins *Inorg. Chem.*, 1988, **27** 1834
53. M W Hosseini, J-M Lehn *J. Chem. Soc., Chem. Commun.*, 1988, 397

54. M W Hosseini, A J Blacker, J-M Lehn *J. Chem. Soc., Chem. Commun.*, 1988, 596
55. Yu M Polikarpov, B K Shcherbakov, F I Bel'skii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1669
56. M I Kabachnik, T Ya Medved', Yu M Polikarpov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 835
57. T Ya Medved', M I Kabachnik, I B Goryunova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2107
58. B A Sayer, J P Michael, R D Hancock *Inorg. Chim. Acta*, 1983, **77** 63
59. A Hammershoi, A M Sargeson *Inorg. Chim. Acta*, 1983, **22** 3554
60. S G Taylor, M R Snow, T W Hambley *Aust. J. Chem.*, 1983, **36** 2359
61. G W Bushell, D G Fortier, A McAuley *Inorg. Chem.*, 1988, **27** 2626
62. J Robb, R D Peacock *Inorg. Chem.*, 1986, **121** 15
63. K Wieghardt, Bossek, M Guttman, J Weiss *Z. Naturforsch., B*, 1983, (38) 81
64. K B Yatsimirskii, E I Sinyavskaya, L V Tsymbal, et al. *Zh. Neorg. Khim.*, 1984, **29**(4) 888 [English translation in *Russ. J. Inorg. Chem.*, 1984(4)]
65. M A Konstantinovskaya, E I Sinyavskaya, K B Yatsimirskii, et al. *Zh. Neorg. Khim.*, 1985, **30**(10) 2571 [English translation in *Russ. J. Neorg. Chem.*, 1985(10)]
66. K B Yatsimirskii, M I Kabachnik, E I Sinyavskaya, et al. *Zh. Neorg. Khim.*, 1984, **29**(4) 884 [English translation in *Russ. J. Inorg. Chem.*, 1984(4)]
67. M I Kabachnik, T Ya Medved', F I Bel'skii, S A Pisareva *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 844
68. F I Bel'skii *Izuchenie Kompleksoobrazuyushchikh Svoistv Novykh Fosfororganicheskikh Kompleksov* (Study of the Complex-forming Properties of New Organophosphorus Complexones), Dissertation for Candidate in Chemical Sciences, Moscow, 1985, p. 35
69. S A Pisareva, F I Bel'skii, T Ya Medved', M I Kabachnik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 413
70. B Dietrich, J-M Lehn, J P Sauvage *J. Chem. Soc., Chem. Commun.*, 1973, 15
71. J-M Lehn, J P Sauvage *J. Am. Chem. Soc.*, 1975, **97** 6700
72. E Graf, J-P Kintzinger, J-M Lehn, J LeMoigne *J. Am. Chem. Soc.*, 1982, **104** 1672
73. A E Martell, R M Smith *Critical Stability Constants*, Plenum Press, New York–London, 1974–1982, Vol. 15
74. M Yu Antipin, A P Baranov, M I Kabachnik, T Ya Medved', et al. *Dokl.Akad. Nauk SSSR*, 1986, **287** 130
75. R C Weast *Handbook of Chemistry and Physics. 55th Edition*, CRS Press, 1974, pp 198–199
76. R P Carter, M M Crutchfield, R R Irani *Inorg. Chem.*, 1967, **6** 943
77. Y Moriguchi, M Miyazaki, K Ueno *Bull. Chem. Soc. Jpn.*, 1968, **41** 1344
78. H Irving, R J P Williams *J. Chem. Soc.*, 1953, 3192
79. E Kimura, M Yamaoka, M Marioka, T Koike *Inorg. Chem.*, 1986, **25** 3883
80. R Yang, L J Zompa *Inorg. Chem.*, 1978, **17** 2531
81. A Bevilaequa, R I Gelb, W B Hebard, L J Zompa *Inorg. Chem.*, 1987, **26** 2699
82. E Kimura, T Koike, M Toriumi *Inorg. Chem.*, 1988, **27** 3687
83. L J Zompa *Inorg. Chem.*, 1976, **15** 1499
84. K Wieghardt, U Bossek, P Chaundhuri, et al. *Inorg. Chem.*, 1982, **21** 4308
85. G Ewin, J O Hill *J. Chem. Res. (S)*, 1985, (11) 334
86. M J Merwe, J C A Boeyens, R D Hancock *Inorg. Chem.*, 1983, **22** 3489
87. M J Merwe, J C A Boeyens, R D Hancock *Inorg. Chem.*, 1985, **24** 1208
88. R D Bereman, P Churchill, et al. *Inorg. Chem.*, 1979, **18** 3122
89. W F Schwindinger, T G Fawcett, R A Lalancette *Inorg. Chem.*, 1980, **19** 1379
90. K Wieghardt, E Schaffmann, B Nuber, J Weiss *Inorg. Chem.*, 1986, **25** 4877
91. L Christiansen, D N Hendrickson, et al. *Inorg. Chem.*, 1986, **25** 2813
92. M I Kabachnik, M Yu Antipin, B K Shcherbakov, et al. *Koord. Khim.*, 1988, **14** 536
93. Yu M Polikarpov, F I Bel'skii, S A Pisareva, M I Kabachnik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, (9) 2112
94. H Stetter, W Frank, R Mertens *Tetrahedron*, 1981, **37** 767
95. R Delgado, J J R Frausto da Silva *Talanta*, 1982, **29** 815
96. V J Thöm, G D Hosken, R D Hancock *Inorg. Chem.*, 1985, **24** 3378
97. R W Hay, D M S Clark *Inorg. Chim. Acta*, 1984, **83** 23
98. M I Kabachnik, T Ya Medved', N M Dyatlova, M V Rudomino *Usp. Khim.*, 1974, **43**(9) 1554; 1988, **57**(8) 1353 [English translatin in *Russ. Chem. Rev.*, 1974(9); 1988(8)]
99. M F Loncin, J F Desreux, E Nerciny *Inorg. Chem.*, 1986, **25** 2646
100. W P Cacheris, S K Nickle, A D Sherry *Inorg. Chem.*, 1987, **26** 958
101. M-R Spirlet, J Rebizant, J F Desreux, M-F Loncin *Inorg. Chem.*, 1984, **23** 359
102. A Reisen, M Zehnder, T A Kaden *Helv. Chim. Acta*, 1986, **69** 2067
103. A Reisen, M Zehnder, T A Kaden *Helv. Chim. Acta*, 1986, **69** 2074
104. C C Bryden, C N Reilley *Anal. Chem.*, 1982, **54** 610
105. C C Bryden, C N Reilley, J F Desreux *Anal. Chem.*, 1981, **53** 1418
106. S P Kasprzyk, R G Wilkins *Inorg. Chem.*, 1982, **21** 3349
107. S Buoen, J Dale, P Groth, J Krane *J. Chem. Soc., Chem. Commun.*, 1982, 1172
108. R W Hay, M R Pujari, W Moddie, et al. *J. Chem. Soc., Dalton Trans.*, 1987, 2605
109. M Mikuriya, S Kida, J Murase *J. Chem. Soc., Dalton Trans*, 1987, 1261
110. J Murase, M Mikuriya, H Sonoda, S Kida *J. Chem. Soc., Chem. Commun.*, 1984, 692
111. J Murase, M Mikuriya, H Sonoda, et al. *J. Chem. Soc., Dalton Trans.*, 1986, 953
112. S Kida, I Murase, C Harada, et al. *Bull. Chem. Soc. Jpn.*, 1986, **59** 2595
113. R W Hay, R Bembi *Inorg. Chim. Acta*, 1982, **65** 227
114. N W Alcock, K P Balakrishnan, P Moore *J. Chem. Soc., Dalton Trans.*, 1986, 1743
115. C-M Che, W-T Tang, T C W Mak *J. Chem. Soc., Dalton Trans.*, 1988, 2879
116. K B Yatsimirskii, M I Kabachnik, E I Sinyavskaya, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, (9) 2088
117. N M Dyatlova, M I Kabachnik, T Ya Medved', et al. *Dokl. Akad.Nauk SSSR*, 1965, **161** 607

118. C M Madeyski, J P Michael, R D Hancock *Inorg. Chem.*, 1984, **23** 1487
119. J F Desreux, M F Loncin *Inorg. Chem.*, 1986, **25** 69
120. M K Moi, M Yanuck, et al. *Inorg. Chem.*, 1987, **26** 3458
121. A Evers, R D Hancock, I Murase *Inorg. Chem.*, 1986, **25** 2160
122. M Mikuriya, S Kida, I Murase *Bull. Chem. Soc. Jpn.*, 1987, **60** 1355, 1681
123. M Mikuriya, S Kida, T Konzuma, I Murase *Bull.Chem. Soc. Jpn.*, 1988, **61** 2666
124. N W Alcock, K P Balakrishnan, P Moore *J. Chem. Soc., Dalton Trans.*, 1986, 1743
125. C-M Che, W-T Tang, T C W Mak *J. Chem. Soc., Dalton Trans.*, 1988, 2879
126. I M Helps, D Parker, J Chapman, et al. *J. Chem. Soc. Chem. Commun.*, 1988, 1094
127. J-D Xu, S-S Ni, Y-J Lin *Inorg. Chim. Acta*, 1986, **111** 61
128. A Neves, W Walz, K Wieghardt, et al. *Inorg. Chem.*, 1988, **27** 2484
129. L R Gahan, G A Lawrance, A M Sargeson *Aust. J. Chem.*, 1982, **35** 1119
130. E Mikicuik, B Kotelko, A Szadowska, A Kaminska *Acta Pol. Pharm.*, 1983, **40** 435
131. M Studer, T A Kaden *Helv. Chim. Acta*, 1986, **69** 2081
132. E Kimura *Pure Appl. Chem.*, 1986, **58** 1461
133. E K Barefield, K A Foster, G M Freeman, K D Hodges *Inorg. Chem.*, 1986, **25** 4663
134. D Tschudin, A Basar, T A Kaden *Helv. Chim. Acta*, 1988, **71** 100
135. X Jide, N Shisheng, X Yujnan *Inorg. Chem.*, 1988, **27** 4651
136. N W Alcock, R G Kingston, P Moore, C Pierpoint *J. Chem. Soc., Dalton Trans.*, 1984, 1937
137. N W Alcock, P Moore, C Pierpoint *J. Chem. Soc., Dalton Trans.*, 1984, 2371
138. N W Alcock, E H Cuzzon, P Moore, et al. *J. Chem. Soc., Dalton Trans.*, 1985, 1361
139. N W Alcock, K P Balakrishnan, P Moore *J. Chem. Soc., Chem. Commun.*, 1985, 1731
140. E Kimura, T Koike, M Takahashi *J. Chem. Soc., Chem. Commun.*, 1985, 385
141. Y Iitaka, T Koike, E Kimura *Inorg. Chem.*, 1986, **25** 402
142. E Kimura, T Koike, H Nada, Y Iitaka *J. Chem. Soc., Chem. Commun.*, 1986
143. E Kimura, M Shionoya, T Mita, Y Iitaka *J. Chem. Soc., Chem. Commun.*, 1987, 1712
144. T R Wagler, C J Burrows *J. Chem. Soc., Chem. Commun.*, 1987, 277
145. E Kimura, T Koike, K Uenishi, et al. *Inorg. Chem.*, 1987, **26** 2975
146. E Kimura, K Uenishi, T Koike, Y Iitaka *Chem. Lett.*, 1986, 1137
147. E Kimura, T Koike, H Nada, Y Iitaka *Chem. Lett.*, 1988, **27** 1036
148. N F Curtis, G J Gainford, T W Hambley, et al. *J. Chem. Soc., Chem. Commun.*, 1987, 295
149. E I Sinyavskaya, L V Tsymbal, K B Yatsimirskii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 176
150. N S Poonia, A V Bajaj *Chem. Rev.*, 1979, 389
151. K B Yatsimirskii, M A Konstantinovskaya, E I Sinyavskaya, et al. *Zh. Neorg. Khim.*, 1987, **32**(3) 710 [English translation in *Russ. J. Inorg. Chem.*, 1987(3)]
152. M Kodama, E Kimura *J. Chem. Soc., Dalton Trans.*, 1976, **116** 1720
153. M I Kabachnik, T Ya Medved', N M Dyatlova, et al. *Usp. Khim.*, 1968, **37**(7) 1161 [English translation in *Russ. Chem. Rev.*, 1968(7)]
154. J F Desreux, E Merciny, M F Loncin *Inorg. Chem.*, 1981, **20** 987
155. M P Pasechnik, S P Solodovnikov, E I Matrosev, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, (9) 2080
156. C F G C Geraldes, M C Alpoim, M P M Marques, et al. *Inorg. Chem.*, 1985, **24** 3876
157. T G Appleton, J R Hall, A D Harris, et al. *Aust. J. Chem.*, 1984, **37** 1833
158. R P Carter, R L Carroll, R R Irani *Inorg. Chem.*, 1967, (6) 939
159. K Moedritzer, R R Irani *J. Org. Chem.*, 1966, **31** 1603
160. F I Bel'skii, I B Goryunova, P V Petrovskii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 103
161. T Ya Medved', M I Kabachnik, F I Bel'skii, S A Pisareva *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988 (9) 103
162. P H Smith, K N Raymond *Inorg. Chem.*, 1985, **24** 3469
163. W Linden, G Anderegg *Helv. Chim. Acta*, 1970, **53** 569
164. Y Moriguchi, M Miyazaki, K Ueno *Bull. Chem. Soc. Jpn.*, 1968, **41** 1344
165. B H Wiers *Inorg. Chem.*, 1971, **10** 2581
166. V A Uchtman *J. Phys. Chem.*, 1972, **76** 1304
167. A I Grigor'ev, L V Nikitina, N M Dyatlova *Zh. Neorg. Khim.*, 1974, **19**(12) 4834 [English translation in *Russ. J. Inorg. Chem.*, 1974(12)]
168. N I Voronezheva, A I Grigor'ev, N M Dyatlova *Zh. Neorg. Khim.*, 1976, **21**(8) 2051 [English translation in *Russ. J. Inorg. Chem.*, 1976(8)
169. R J Grabenstetter, W A Cilley *J. Phys. Chem.*, 1971, **75** 676
170. G Gross, T Ya Medved', S Novak, et al. *Zh. Obshch. Khim.*, 1985, **67** 734
171. N M Dyatlova, V V Medyntsev, T Ya Medved', M I Kabachnik *Zh. Obshch. Khim.*, 1968, **38** 1065, 1071, 1076
172. Y Sun, A E Martell, R J Motekaitis *Inorg. Chem.*, 1985, **24** 4343
173. L L Martin, K S Hagen, A Hauger, et al. *J. Chem. Soc., Chem. Commun.*, 1988, 1313
174. P V Bernhardt, G A Lawrance, D F Sangster *Inorg. Chem.*, 1988, **27** 4055
175. H Fujioka, E Kimura, M Kodama *Chem. Lett.*, 1982, 737
176. E Kimura, R Machida, M Kodama *J. Am. Chem. Soc.*, 1984, **106** 5497
177. J-M Lehn, R Ziessel *J. Chem. Soc., Chem. Commun.*, 1987, 1292
178. S Buoen, J Dale, J Krane *Acta Chem. Scand., Ser. B*, 1984, **38** 773
179. Y Sun, A E Martell, R J Motekaitis *Inorg. Chem.*, 1986, **25** 4780
180. N M Dyatlova, V Ya Temkina, I D Kolpakova *Kompleksony* (Complexones), Khimiya, Moscow, 1970, pp 186–189
181. *Assortiment Organicheskikh Kompleksonov: Spravochnik* (Collection of Organic Complexones: A Handbook), IREA, Moscow, 1981, 63 pp
182. G Schwarzenbach, H Senn, G Anderegg *Helv. Chim. Acta*, 1957, **40** 1886

Translated from *Uspekhi Khimii* **61** 456–495 (1992) U.D.C. 547.9+542.95+577.1

Heteroprostanoids: synthesis and biological activity

F A Lakhvich, F S Pashkovskii, E V Koroleva
Institute of Bioorganic Chemistry, Academy of Sciences of Belorussia, Minsk

ABSTRACT. Data on the synthesis and biological activity of the hetero analogues of prostaglandins are examined and systematised. The relationship between the structure and the activity of the heteroprostanoids is discussed.

The bibliography contains 170 references.

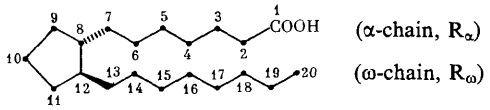
Contents

I. Introduction 243
II. Synthesis of heterocyclic prostanoids 244
III. Heteroanalogues of the α- and ω-chains 249
IV. Heteroanalogues of secoprostanoids 253
V. Heteroanalogues of cyclic endoperoxides 255
VI. Heteroanalogues of prostacyclin 256
VII. Biological activity of the heteroprostanoids 259

I. Introduction

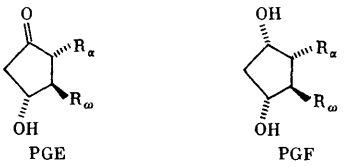
The prostaglandins (PG) are a unique class of natural low molecular bioregulators which are synthesised in practically all tissues and organs of animals and man and play an extremely important role in normal functioning and pathology.

In chemical structure they are unsaturated polyhydroxy acids, derivatives of the hypothetical twenty-atom prostanoic acid.

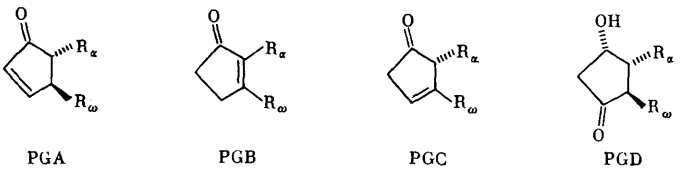


prostanoic acid

The C_7-carboxyalkyl chain of prostaglandins is known as the α-chain and the C_8 alkyl the ω-chain. The character of the functionality of the five-membered ring determines the type of prostaglandins. Prostaglandins of the E and F type are referred to as primary PG and prostaglandins of types A, B, C and D form the group of secondary PG.



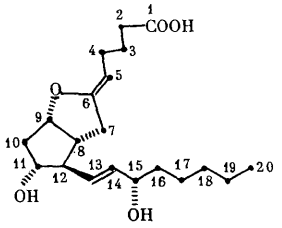
primary PG



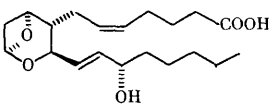
secondary PG

Three series of natural PG can be distinguished. The first is characterised by the presence of one Δ^{13}-*trans*-double bond, the second contains an additional Δ^5-*cis*-double bond. The PG of the third series contain a further Δ^{17}-*cis*-double bond in addition to those mentioned. The number of multiple bonds in the side chains corresponds to the subscript number (PGE_1, PGE_2 etc.).

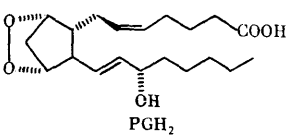
Prostacyclin (PGI_2), 6,9α-epoxy-11α,15α-dihydroprosta-5(*Z*),13(*E*)-dienoic acid, prostaglandin endoperoxides (PGG_2, PGH_2) and thromboxane (TxA_2), like the primary PG, are biosynthetic products of the arachidonic acid cascade and the most important biomolecules of its metabolism.



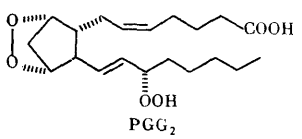
prostacyclin (PGI_2)



thromboxane A_2 (TxA_2)



PGH_2



PGG_2

prostaglandin endoperoxides

The extremely low content of PG, cyclic endoperoxides and prostacyclin in nature, the exceedingly wide spectrum of biological action and the chemical and metabolic instability of preparations based on them, are factors stimulating the development of synthetic

methods for obtaining these and modified compounds (analogues of the natural prototypes) with more specific and prolonged action for the needs of medicine and agriculture.

The heteroprostaglandins occupy an important place among the multitude of analogues synthesised. These are compounds in which one or several carbon atoms of the prostanoid skeleton are replaced by heteroatoms (nitrogen, oxygen, sulphur). The synthesis and biological activity of such compounds form the subject of the present review. Also considered are the heteroanalogues of the cyclic endoperoxides (PGH) and prostacyclin (PGI) in which the oxygen atoms of the endoperoxide and the *cis*-enol ether fragments are replaced in addition to replacing carbon atoms of the skeleton by nitrogen and sulphur.

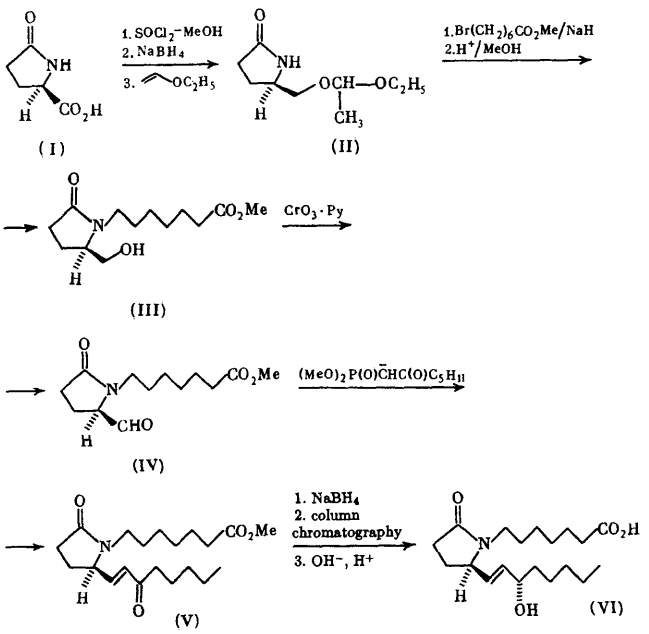
In contrast to the reviews published previously,[1-3] which are devoted mainly to detailed analysis of actual synthetic schemes for PG heteroanalogues, cyclic endoperoxides and prostacyclin, attention is paid in the present review chiefly to an analysis of the methodology of forming the heteroprostanoid skeleton and also to the dependence of biological properties on structure.

II. Synthesis of heterocyclic prostanoids

Construction of the heteroprostanoid skeleton is based on the following main approaches: 1) the regio- and stereoselective introduction of the side chains (R_α and R_ω) or fragments of them into the appropriate heterocyclic compounds, 2) synthesis based on acyclic long chain precursors bearing the side chains or intermediates when the heterocyclic system is formed in one of the intermediate or at the very last stage of the synthesis, 3) regioselective introduction of the heteroatom into the cyclic portion of the prostanoid skeleton of 11-norprostanoids.

1. Heteroprostanoids based on heterocyclic precursors

This approach is widely used in the synthesis of heterocyclic prostanoids. It may be illustrated by the preparation of optically active (12*R*,15*S*)-(−)-11-deoxy-8-aza-PGE_1 (VI) from (*R*)-(+)-pyroglutamic acid (I).[4]



After conversion into the (*R*)-ethoxyethyl ether (II) the latter is alkylated with methyl 7-bromoheptanoate. The alcohol (III) formed by removing protection was oxidised (Collins) to the (*R*)-aldehyde (IV). A Wittig reaction of the synthon (IV) with dimethyl-2-keto-heptylphosphonate gives the (*R*)-enone (V) which on reduction with sodium borohydride leads to a mixture of the 15-epimers of the desired 8-azaprostanoid. Chromatographic resolution of the latter and mild hydrolysis of the ester group in the 15*S*-isomer completes the synthesis of (12*R*,15*S*)-11-deoxy-8-aza-PGE_1 (VI).

Other examples are given in Table 1 of heteroprostanoids obtained using analogous schemes published in the last 10–12 years. In the majority of cases the α-chain in the heterocyclic precursor is introduced using classical methods of *N*- and *C*-alkylation (or acylation). The ω-chains in the alkylation products are formed using the Wittig–Horner–Emmons phosphonate condensation after transformation of the functional groups in position 12 (PG nomenclature) into an aldehyde.

Table 1. Heteroprostanoids from heterocyclic precursors.

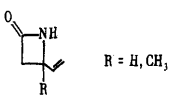
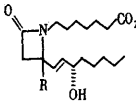
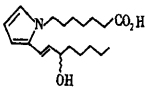
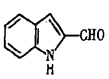
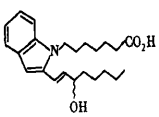
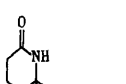
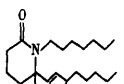
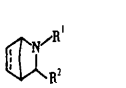
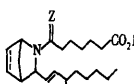
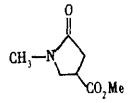
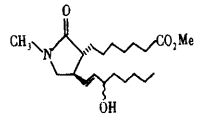
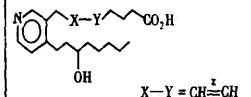
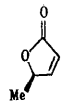
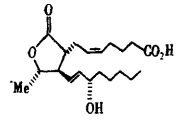
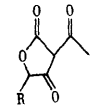
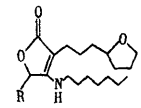
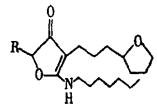
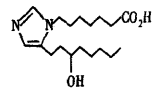
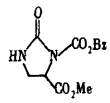
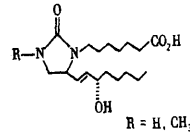
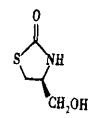
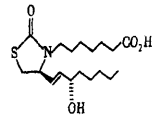
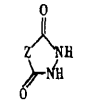
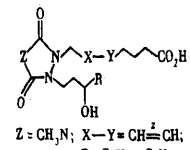
Type of heteroprostanoid	Initial heterocyclic precursor	Structural formula	Reference
8-Aza-	 R = H, CH_3	 R = H, CH_3	[5]
			[6]
			[6]
	 R = H, CH_3	 R = H, CH_3	[7]
	 R^1 = CO_2CF_3, R^2 = CHO R^1 = Ts, R^2 = CO_2Bu	 Z = H_2 Z = O	[8, 9]

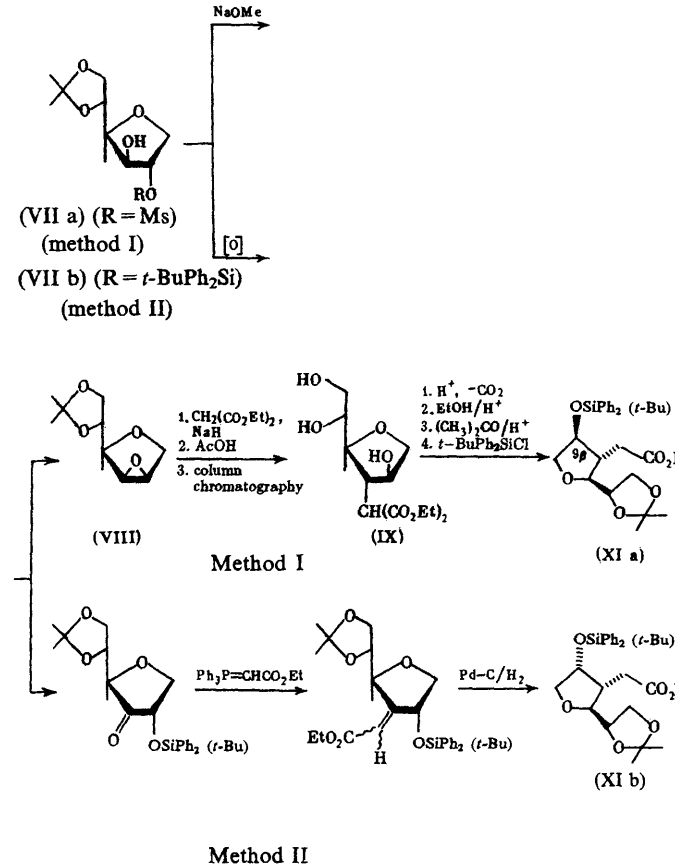
Table 1 (continued).

Type of heteroprostanoid	Initial heterocyclic precursor	Structural formula	Reference
10-Aza-			[10]
		 X—Y = CH=CH, CH_2—CH_2	[11]
10-Oxa-			[12]
10-Oxa-13-aza-			[13]
11-Oxa-13-aza-	R = H, CH_3		
8,10-Diaza-			[14]
		 R = H, CH_3	[15]
8-Aza-10-thia-			[16]
8,10,12-Triaza-		 Z = CH_3N; X—Y = CH=CH; R = C_5H_{11}, C_6H_{13}. Z = S; X—Y = CH_2—CH_2; R = *cyclo*-C_6H_{11}	[17, 18]
10-Thia-8,12-diaza-	Z = CH_3N		

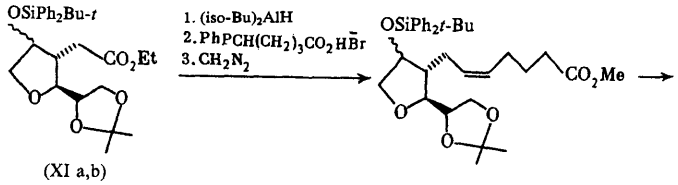
This approach also includes a set of schemes for the synthesis of 11-oxaprostanoids of the $F_{2\alpha(\beta)}$ series from natural heterocyclic compounds, viz. sugars and dihydrosugars.[19–21] The furan ring of the latter is a convenient intermediate for the heterocyclic system for PG 11-oxa analogues. The side chain *cis*-diol, or another analogous group, in the vicinity of the heteroatom of the ring serves as a precursor of the aldehyde function necessary for forming the ω-chain.

The key stage of forming the 11-oxaprostanoid structure from sugars (dihydrosugars) is the replacement of their C(3) hydroxy group by an ethoxycarbonylmethylene group which is an α-chain intermediate. This replacement may be effected by two methods.

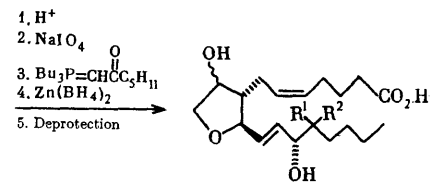
In the synthesis of 11-oxa-$PGF_{2\alpha(\beta)}$ prostanoids (XIIa, b) from derivatives of 1,4-anhydro-D-glucitol (VIIa, b) [19] method I includes the addition of malonic ester to the epoxide (VIII) with isolation of the desired regioisomer (IX) and its subsequent hydrolysis and decarboxylation. Method II comprises the selective oxidation of the C(3) hydroxyl group with subsequent treatment of the resulting 3-keto derivative with the appropriate phosphorane and stereoselective reduction of the exocyclic multiple bond in compound (X). It must be noted that the method of introducing the ethoxycarbonylmethyl group determines the stereochemistry of the chiral centre at position 9 (PG nomenclature).



The diastereomeric synthons (XIa, b) were used for obtaining the desired heteroprostanoids by a sequence of classical conversions.



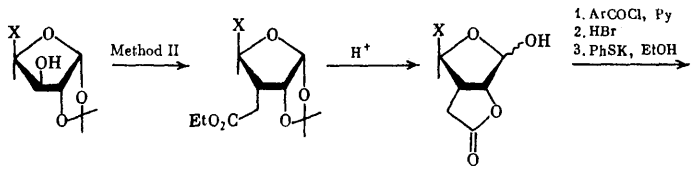
(XI a,b)



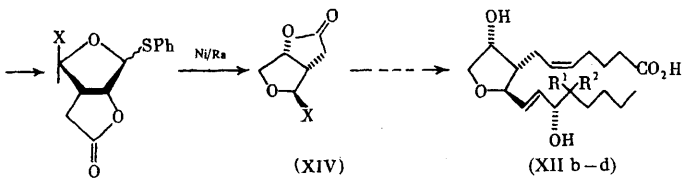
(XII a,b)

a) 9β–OH, b) 9α–OH ($R^1=R^2=H$)

In the synthesis of 11-oxaprostanoids (XIIb–d) from derivatives of D-xylose (XIIIa) and D-glucose (XIIIb),[20] after introducing the ethoxycarbonylmethyl group by method II and acid hydrolysis, the C(1)-glycosidic hydroxyl group was eliminated via the phenylthio derivative by hydrogenolysis over Raney nickel with the formation of oxa analogues of the Corey lactone (XIV).



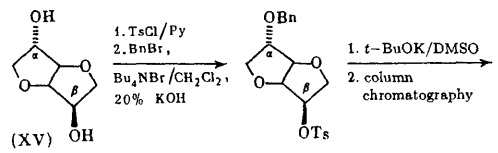
(XIII a,b): a) $X=CH_2OCH_2Ph$, b) X=



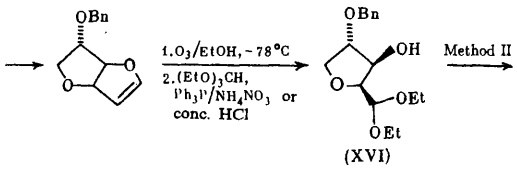
(XIV) (XII b–d)

b) $R^1=R^2=H$, c) $R^1=H$, $R^2=CH_3$, d) $R^1=R^2=CH_3$

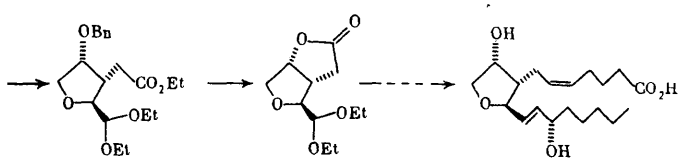
An analogous approach was used in the synthesis of 11-oxa-$PGF_{2\alpha}$ (XIIb) starting from 1,4:3,6-dianhydro-D-sorbitol (XV),[21] which was transformed into furanol (XVI) by a known series of conversions.



(XV) OH



(XVI)



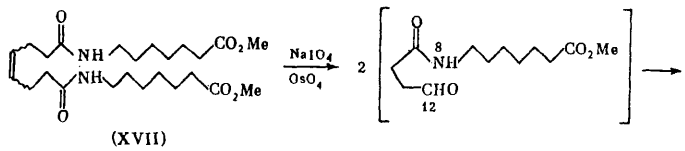
(XII b)

2. Heterocyclic prostanoids from acyclic precursors

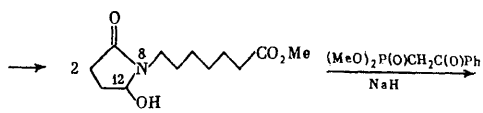
Depending on the molecular fragments used to form the heterocyclic systems, the schemes of synthesis of the heterocyclic prostanoids from acyclic precursors may be subdivided into five main groups, i. e. schemes including 8,12, 8,9, 9,10, 10,11 and 11,12 closure of the heterocycle.

a) Schemes utilising 8,12 closure of the heterocycle

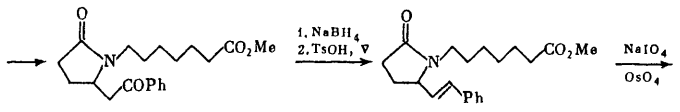
When obtaining the key synthon 11-deoxy-8-azaprostanoids (XXI) from the diamide (XVII), the cyclisation of the long chain precursor occurs after oxidative fission of the (*E,Z*)-multiple bond in the latter. Condensation of the resulting cyclic lactam (XVIII) with the sodium salt of dimethyl phenacylphosphonate gives the ketolactam (XIX). The sequence of conversions (XIX)–(XX)–(XXI) leads to the synthon (XXI).[22]



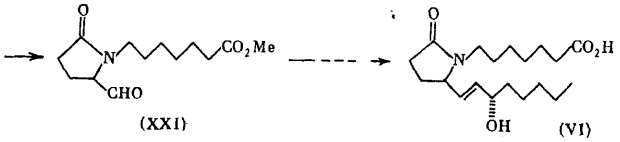
(XVII)



(XVIII)



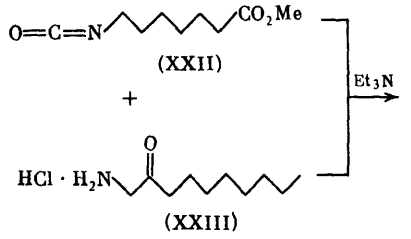
(XIX) (XX)



(XXI) (VI)

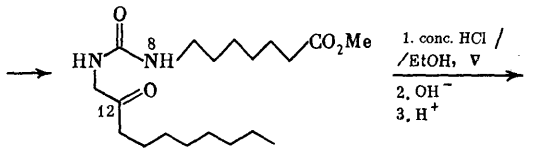
The initial components in the synthetic scheme for the 11,12-dehydro-8,10-diazaprostanoid (XXV) from the isocyanate (XXII) and the β-aminoketone (XXIII) carry the side chains in an already finished form. The formation of the heterocyclic system

occurs in two stages in this case, through the initial formation of the adduct (XXIV) and its subsequent cyclisation.[23]

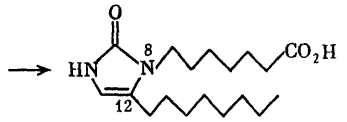


(XXII)

(XXIII)



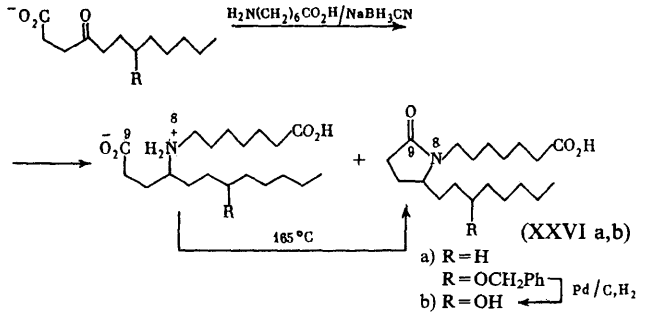
(XXIV)



(XXV)

b) Schemes utilising 8,9 and 11,12 closure of the heterocycle

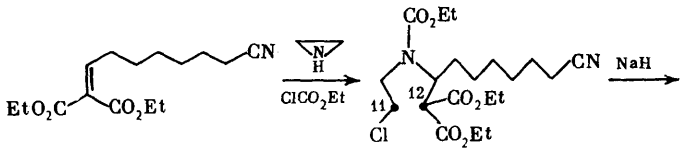
The formation of the heterocycle in the synthesis of 8-aza-9-keto-prostanoic acid (XXVIa) and its 15-hydroxy derivative occurs after the formation (and in part simultaneously with the formation) of the α-prostanoid chain (8,9 closure of the heterocycle).[23]

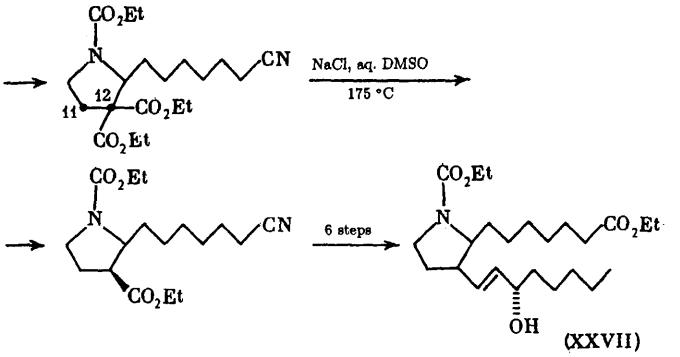


(XXVI a,b)

The 11,12 closure of the heterocycle utilises the previously known schemes of synthesis of the 9-aza- (XXVII) and 9-thia- (XXVIII) prostanoids. The key stages are the following:

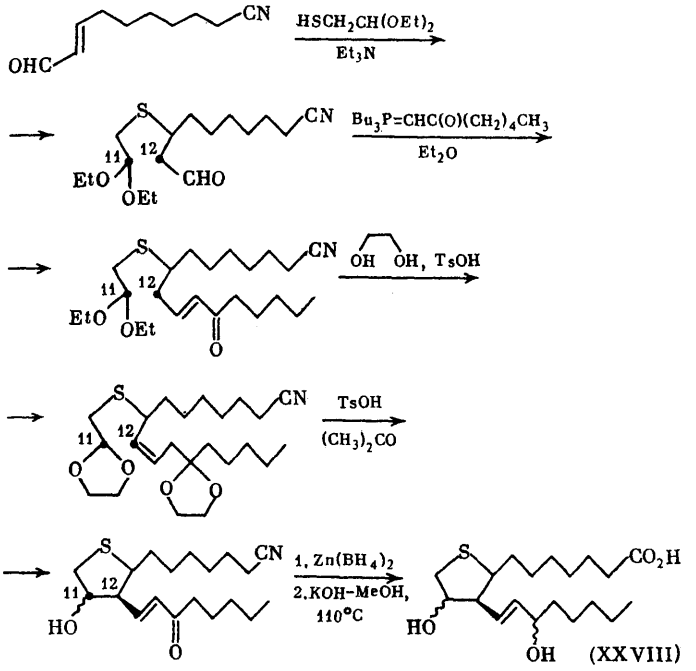
9-*N*-carbethoxy-11-deoxy-PGE$_1$ (XXVII) [24]





(XXVII)

9-deoxy-9-thia-PGE$_1$ (XXVIII) [25]

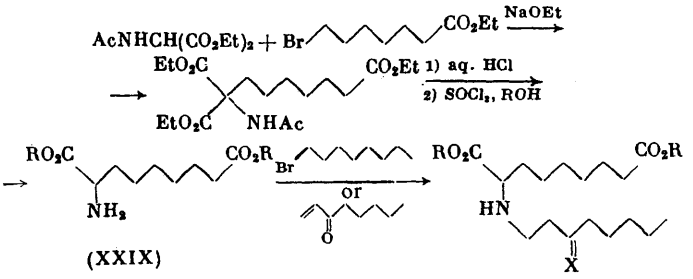


(XXVIII)

As is evident from the schemes the heterocyclic fragment may be formed at various stages of building the prostanoid skeleton.

c) Schemes utilising 9,10 and 10,11 closure of the heterocycle

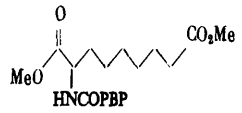
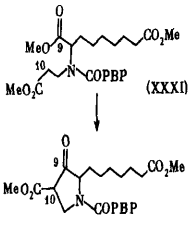
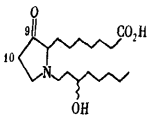
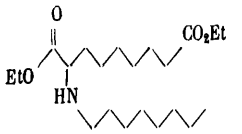
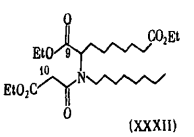
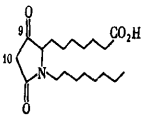
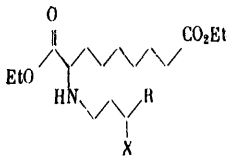
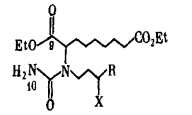
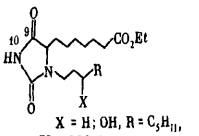
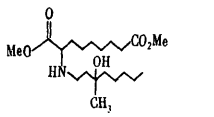
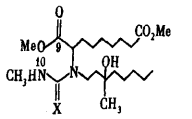
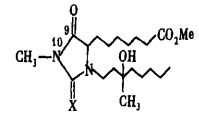
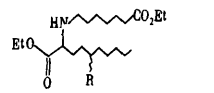
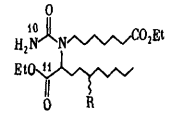
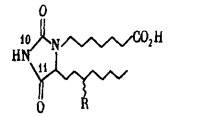
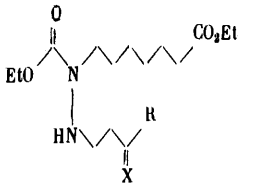
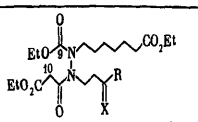
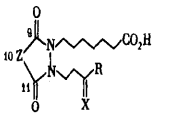
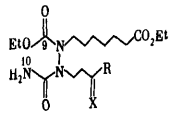
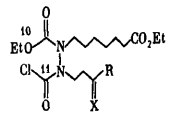
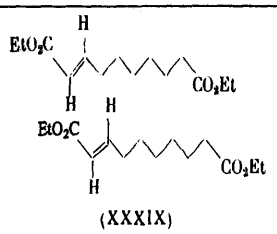
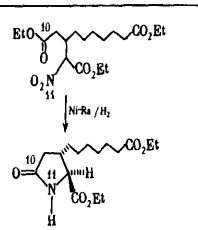
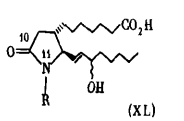
Schemes for obtaining prostanoids with nitrogen atoms at the junction positions of the ring and the side chains mainly belong to this group. The key synthons for these heteroanalogues are long chain α-amino esters and amino diesters, the standard synthetic scheme for which is shown using the examples of amino diesters of azelaic acid (XXIX) and their *N*-alkyl derivatives (XXX).[26]



(XXIX)

(XXX) (X = H_2, O)

Table 2. Synthesis of heteroprostanoids, including 9,10 and 10,11 closure of the heterocycle.

Type of heteroprostanoid	Precursor	Reagent	Condensation product	Structural formula	Reference
12-Aza-			 (XXXI)		[27]
		$HO_2CCH_2CO_2Et$, DCCI	 (XXXII)		[26]
10,12-Diaza-		HCNO	 (XXXIII)	 X = H; OH, R = C_5H_{11}, X = OH, R = *cyclo*-C_6H_{11}	[28–30]
		MeNCO or MeNCS	 X = O, S (XXXIV)	 X = O, S	[31]
8,10-Diaza-		HCNO	 (XXXV)	 R = H; OH	[29]
8,12-Diaza-, 8,10,12-diaza-, 10-oxo-8, 12-diaza-		$EtO_2CH_2CO_2H$, DCCI	 (XXXVI)	 Z = CH_2, NH, O; X = H; H, OH; R = C_5H_{11}, *cyclo*-C_6H_{11}	[18]
		HCNO	 (XXXVII)		
		$COCl_2$	 (XXXVIII)		
11-Aza-	 (XXXIX)	$O_2NCH_2CO_2Me$, Triton B		 (XL) R = H, Me	[32]

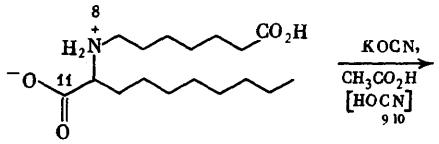
Examples are given in Table 2 of the preparation of heteroprostanoids using these and related synthons.

A characteristic of this group of schemes is the formation of the products (XXXI)–(XXXVIII) by the condensation of a series of reactants at the nitrogen atom of the amino diesters and a cyclisation stage. It must be indicated that for certain schemes, including thermal cyclisation, assignment to this group is arbitrary since the preparation of condensation products and closure of the heterocycle is usually carried out in one step.

The scheme for obtaining 11-azaprostanoids (XL) from the precursor (XXXIX) is also assigned to this type.

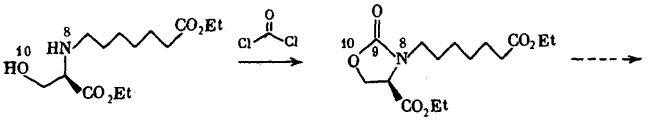
d) Schemes utilising mixed closure of the heterocycle

The synthesis of the 8,10-diaza (XLI), 10-oxa-8-aza (XLII) and 10-oxa (XLIII) analogues does not include the formation of condensation products of type (XXXI)–(XXXVIII). The overall reaction is as though the reagent was inserted between positions 8,11, 8,10 and 10,12 of the long chain prostanoid precursors [(8,9 + 10,11), (8,9 + 9,10) and (10,11 + 11,12) closure of the heterocycle respectively].



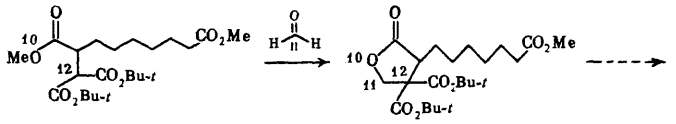
[Ref. 23]

(XLI)



[Ref. 33]

(XLII)



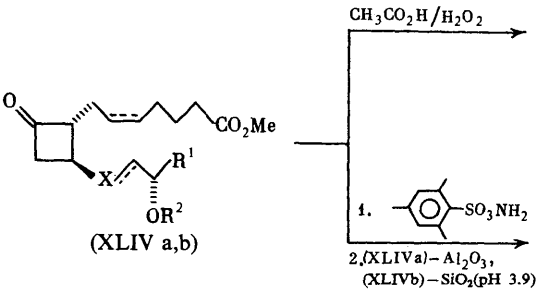
[Ref. 34]

(XLIII)

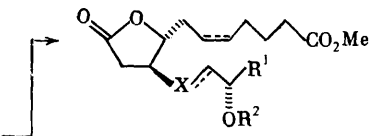
Examples are given in Table 3 of the formation of heterocyclic prostanoid fragments from long chain synthons containing vicinally located functional groups or a double bond in positions 8 and 12 of the future prostanoid structure. Closure of the heterocycles in the analogues being considered are (9,10 + 10,11) and (8,9 + 11,12).

3. Heterocyclic prostanoids from PG 11-nor analogues

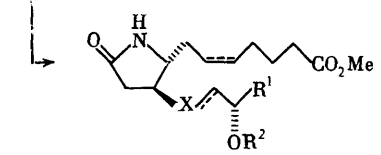
The ring expansion reaction of 11-norprostanoids (XLIVa, b) was used in the synthesis of 9-oxa (XLVa) and 9-aza (XLVIa) analogues of PGE_2 and also 9,13-dioxa- (XLVb) and 13-oxa-9-aza- (XLVIb) prostanoids. In all cases the introduction of the heteroatom into the prostanoid skeleton occurred with complete regioselectivity.[5,41]



(XLIV a,b)



(XLV a,b)



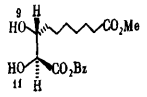
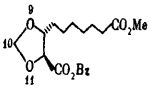
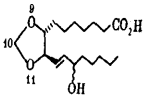
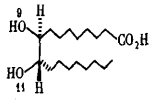
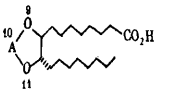
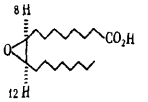
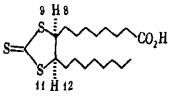
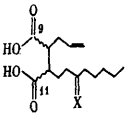
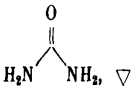
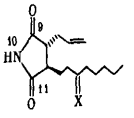
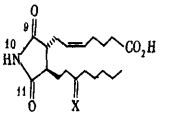
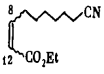
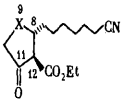
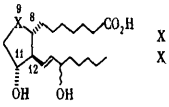
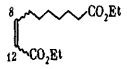
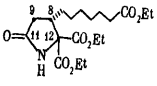
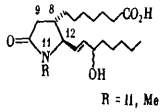
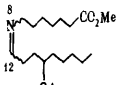
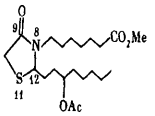
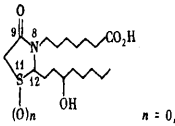
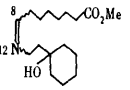
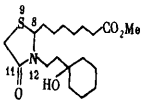
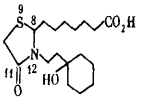
(XLVI a,b)

a) X = CH=, $R^1 = -C_5H_{11}$, $R^2 = -H$;
b) X = O–, $R^1 = -CH_2OPh$, $R^2 = -H$, $-SiMe_2(t\text{-Bu})$

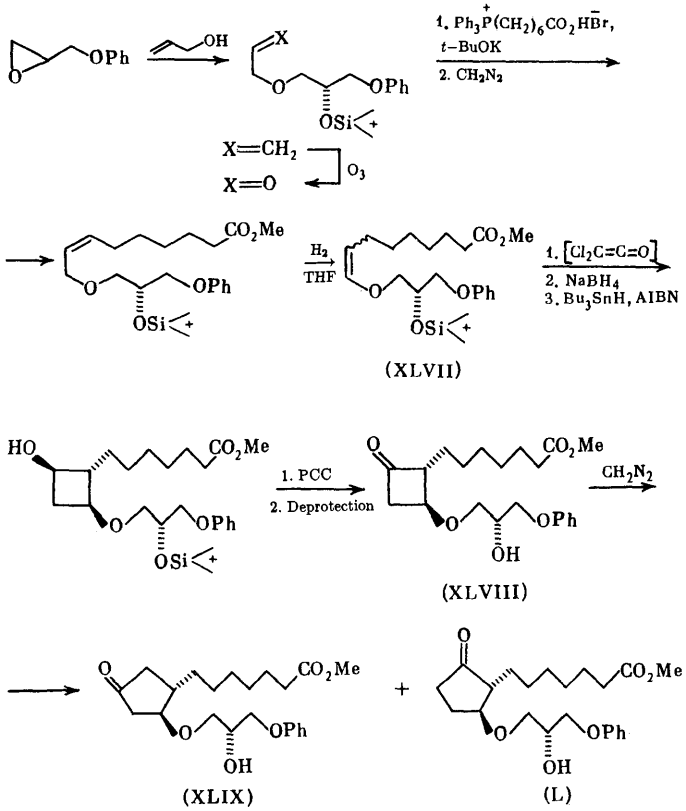
III. Heteroanalogues of the α- and ω-chains

The synthesis of the 13-oxaprostanoids (XLVIII)–(L) is based on the initial formation of the vinyl ether (XLVII) carrying both prostanoid chains with the heteroatom in the appropriate position. Construction of the cyclic portion of prostanoid (XLVIII) occurs as

Table 3. Synthesis of heteroprostanoids by a mixed closing of the heterocycle.

Type of heteroprostanoid	Long-chain bifunctional precursors	Reagents	Cyclisation products	Structural formula	Reference
9,11-Dioxa-		$(CH_2O)_n$			[35]
		$(CH_2O)_n$, $COCl_2$, $CSCl_2$, $POCl_3$/MeOH, $SOCl_2$		 A: CH_2, C(O), C(S), P(O)OCH$_3$, S(O)	[36]
9,11-Dithia-					[36]
10-Aza-	 X = H_2, O		 X = H_2, O	 X = H_2, O	[37]
9-Oxa-(thia)-		$NaXCH_2CO_2Et$, X=O, S		 X = O, X = S	[38, 39]
11-Aza-		$AcNHCH(CO_2Et)_2$, EtONa		 R = H, Me	[32]
8-Aza-11-thia-		$HSCH_2CO_2Me$		 n = 0, 2	[23]
9-Thia-12-aza-					[40]

a result of a [2 + 2] cycloaddition reaction of dichloroketene to the ether obtained.[41]



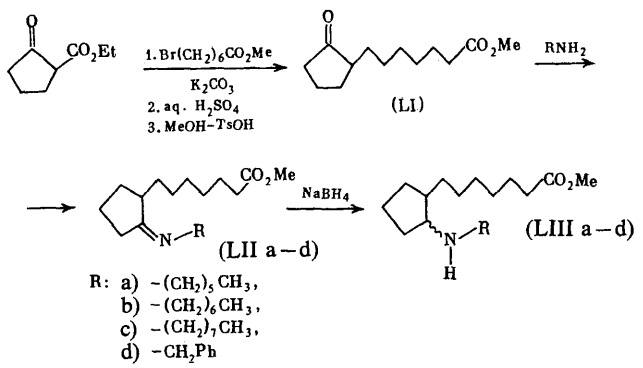
(XLVII)

(XLVIII)

(XLIX) (L)

However functionalised five-membered precursors are used in the majority of schemes for the synthesis of 7- and 13-heteroprostanoids. The heteroatom may be introduced into the composition of the former or into a functional group of a fragment of the prostanoid chains.

The key stage in the formation of the heteroprostanoid fragment of the 13-azaprostanoids (LIIIa–d) is the addition of aliphatic amines at the carbonyl group of the keto ester (LI) with subsequent reduction of the resulting azomethines (LIIa–d).[42]

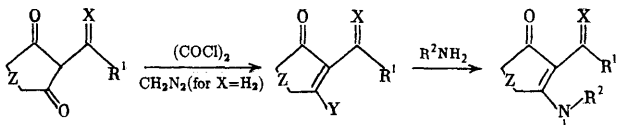


(LI)

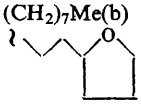
(LII a–d) (LIII a–d)

R: a) $-(CH_2)_5CH_3$,
b) $-(CH_2)_6CH_3$,
c) $-(CH_2)_7CH_3$,
d) $-CH_2Ph$

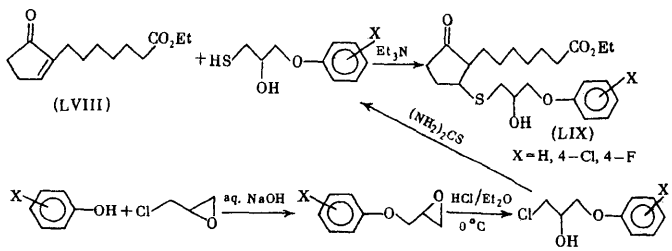
The overall key stage in the synthesis of the 13-aza-, 7-keto-13-aza- and 13-keto-7-azaprostanoids (LVIIa–g) from the cyclic β-di- and β-triketones (LIVa–g) is the addition of an amine to the enol ether (LV) or to the ketovinyl chloride (LVIa–g).[13,43]



(LIV a–g) (LV)(Y = OMe, X = H_2, R^1(c))
(R^1 = a–c) (LVI a–g)(Y = Cl, R^1 = a–c) (LVII a–g)

(LVII)	Z	X	R^1	R^2
a	–	O	$(CH_2)_4CO_2Et$(a)	$(CH_2)_7Me$
b	–	O	$(CH_2)_4CO_2Et$	CH_2Ph
c	–	O	$(CH_2)_7Me$(b)	$(CH_2)_5CO_2Me$
d	–	H_2	 (c)	$(CH_2)_6Me$
e	CH_2	O	$(CH_2)_4CO_2Et$	$(CH_2)_7Me$
f	CH_2	O	$(CH_2)_4CO_2Et$	CH_2Ph
g	CH_2	O	$(CH_2)_7Me$	$(CH_2)_5CO_2Me$

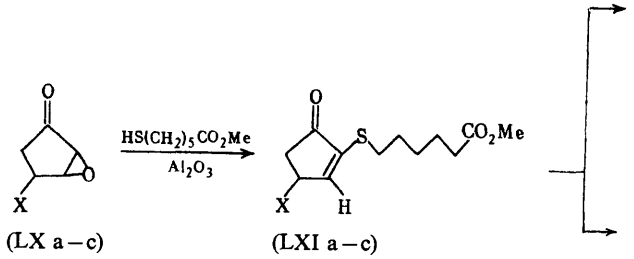
The most widespread method of forming 13-thiaprostanoids includes the addition of mercaptans, corresponding to the ω-chain, to the multiple bond of 2-alkyl substituted cyclopentenones. For example 13-thia-16-aryloxy-17,18,19,20-tetranor-PGE_1 (LIX) was synthesised from the classical synthon (LVIII).[44]



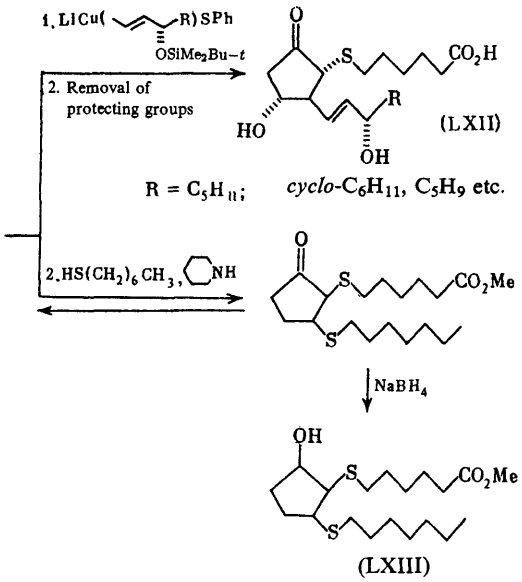
(LVIII) (LIX)
X = H, 4-Cl, 4-F

An analogous scheme was used in the synthesis of the bicyclic 13-thiaprostanoids,[45] and also 11-hydroxy-13-thia analogues.[46]

The 7-thiaprostanoids (LXII) were obtained from the cyclic epoxyketones (LXb, c).[47,48] The addition of a mercaptan corresponding to the structure of the ω-prostanoid chain to the enone (LXIa) leads to a 7,13-dithiaprostanoid of low stability due to a retro-Michael reaction. Reduction of the 9-keto group gives the stable analogue (LXIII).[49]

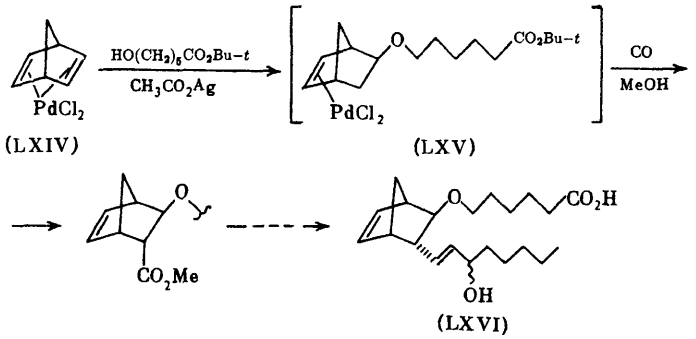


a) X = H,
b) X = OTHP,
c) X = OSiMe$_2$(*t*-Bu)

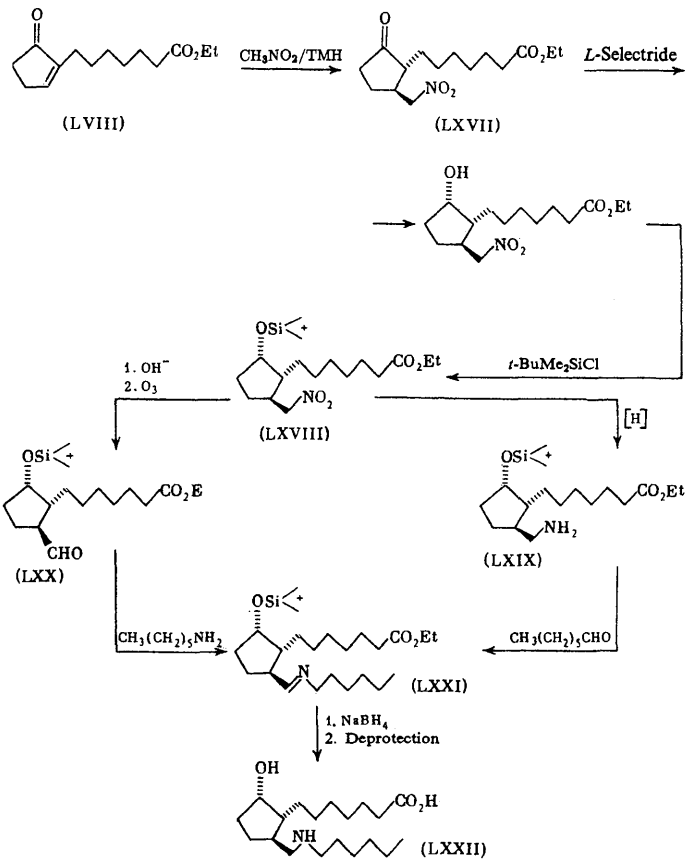


The most widely used approach to obtaining 7-oxa-PG analogues is the alkylation of cyclopentanoid synthons at the 8-hydroxyl function with alkyl halides corresponding to the α-chain structure.[50]

The bicyclic 7-oxaprostanoid (LXVI) was obtained by oxypalladation of the norbornadiene complex (LXIV) with ε-hydroxycaproic ester and subsequent direct carbonylation of the intermediate (LXV).[51]



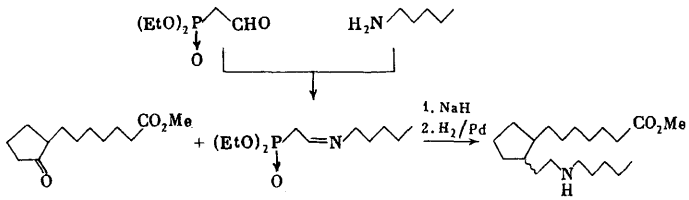
The principle of constructing sidechains analogous to that considered for 7- and 13-heteroprostanoids with other positions of the heteroatom may be illustrated by the example of the synthesis of the 14-azaprostanoid (LXXII).[52] The Michael addition of nitromethane to the cyclopentenone (LVIII) leads to the nitromethyl derivative (LXVII). After the selective reduction of the 9-keto group with L-Selectride and protection of the resulting alcohol, the formation of the ω-chain is effected by two methods. One is by reduction of the nitro group in compound (LXVIII) and subsequent condensation of the amino derivative (LXIX) with hexanal. The other is by the ozonolysis of the nitronate of the ester (LXVIII) with the formation of the aldehyde (LXX) and its further reaction with hexylamine. The final stage of the synthesis is the borohydride reduction of the azomethine (LXXI) formed in both cases.



Methods which have been used to join fragments of the heteroprostanoid chains include nucleophilic substitution of tosylates (mesylates) with the appropriate alkyl sulphides (13, 14 and 15-thiaprostanoids[53]), radical and Michael addition of alkyl mercaptans at a terminal multiple bond (4-thia, 5-thia and 6-thia analogues[48]), alkylation of phenoxides or alkoxides with various alkyl halides (3-oxaprostanoids[54]), alkoxyenamination with a hemiacetal (4-oxa-5-azaprostanoids[55]) and the formation of amide (13- and 14-aza- [56,57]) and sulphonamide bonds (benzenesulphonamidoprostanoids[57–62]).

An alternative approach to prostanoids of this type is the addition of an independently formed heteroprostanoid chain to a

cyclopentanoid synthon as in the synthesis of the 15-azaprostanoid methyl ester (LXXIII).[42]



(LXXIII)

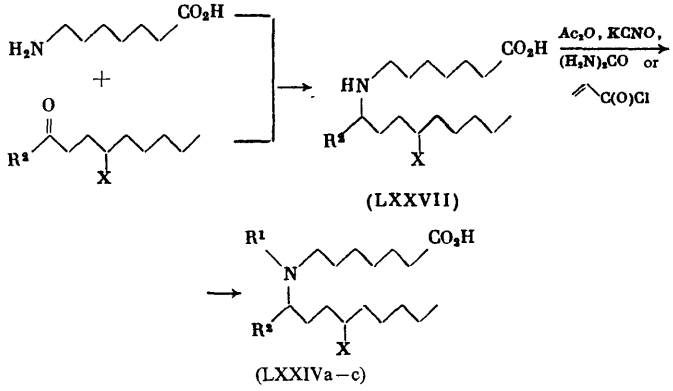
IV. Heteroanalogues of secoprostanoids

From the point of view of structural features the secoprostanoids are as though the acyclic precursors of prostanoids. Nevertheless such 'unfinished prostanoids' display marked prostaglandin-like activity. This group of biologically active compounds did not receive attention in the previous reviews so we saw the need to deal with this problem.

The synthesised heteroanalogues are referred to as 11,12-,[63–67] 8,12-[68,69] and also furan-containing secoprostanoids.[70]

The 11,12-secoprostanoids are mainly *N*-acyl-*N*-alkyl-7-aminoheptanoic acids of the type of (LXXIVa–c), 7-(*N*-alkylmethanesulphonamido)heptanoic acids (LXXIVd), 8-alkylthio(sulphinyl, sulphonyl)-12-hydroxyacids (LXXVa–c), and also 8-acetyl-12-hydroxy-13-aryloxy(thioaryl, alkoxy)tridecanoic acids (LXXVIa, b).

The heteroanalogues (LXXIVa–c) were obtained through the reductive alkylation of 7-aminoheptanoic acid with aldehydes and ketones corresponding to the ω-prostanoid chain and subsequent reaction of the resulting substituted aminoheptanoic acids (LXXVII) with acetic anhydride, potassium cyanide, urea or acryloyl chloride.[63]

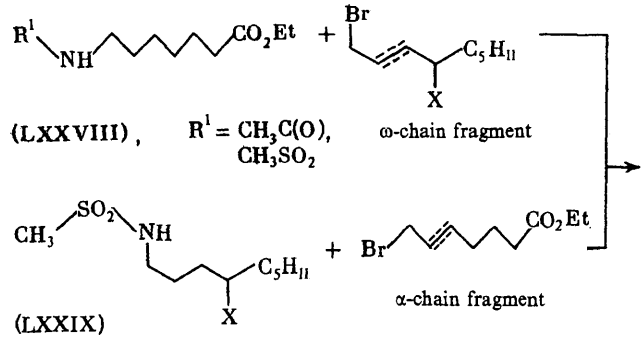


(LXXIVa–c)

a) $R^1 = CH_3C(O)$, b) $R^1 = H_2NC(O)$,

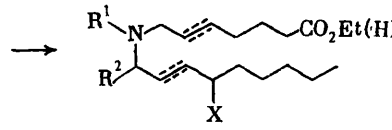
c) $R^1 =$; $R^2 = H, Ph, CH_3$; $X = H$

An alternative variant is the alkylation of the acetyl- and methanesulphonylamides (LXXVIII) and (LXXIX) with halogen derivatives corresponding to the structure of the α- or ω-prostanoid chain.[63,64]



(LXXVIII), $R^1 = CH_3C(O)$, CH_3SO_2; ω-chain fragment

(LXXIX); α-chain fragment

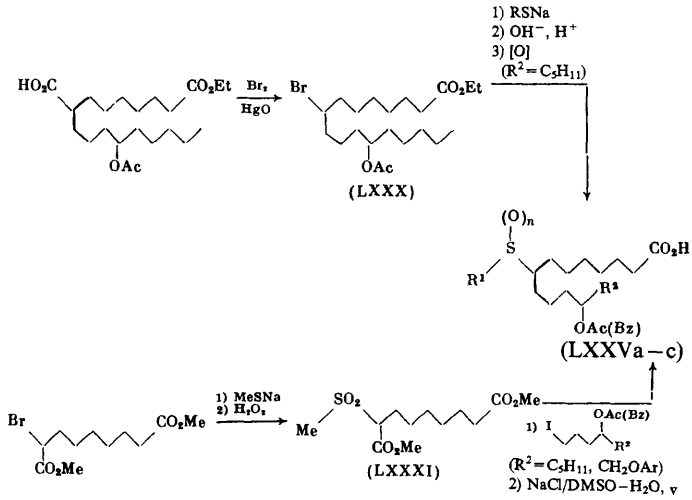


(LXXIV a,d)

a) $R^1 = CH_3C(O)$, $R^2 = H$;

X = H, OAc(OH) d) $R^1 = CH_3SO_2$, $R^2 = H$

The secoprostanoids (LXXVa–c) are formed by the reaction of haloester (LXXX) with various thiolates and also by alkylation of the sulphone (LXXXI).[65]



(LXXXI)

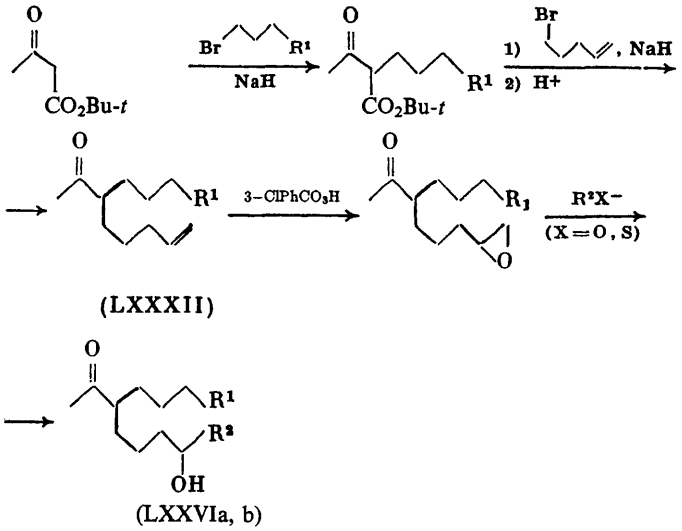
(LXXVa–c)

a) $n = 0$ to 2, $R^1 = Me$, $R^2 = C_5H_{11}$;

b) $n = 0.2$, $R^1 = HO(CH_2)_2$, $R^2 = C_5H_{11}$;

c) $n = 2$, $R^1 = Me$, $R^2 = CH_2OAr$.

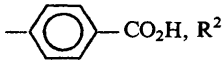
The 8-acetyl-12-hydroxy-13-aryloxy(thioaryl, alkoxy)tridecanoic acids (LXXVIa, b) were obtained from the key synthons (LXXXII) through epoxidation of the latter and fission of the epoxide ring with phenoxides, phenylthiolates and alkoxides.[66,67]



(LXXXII)

(LXXVIa, b)

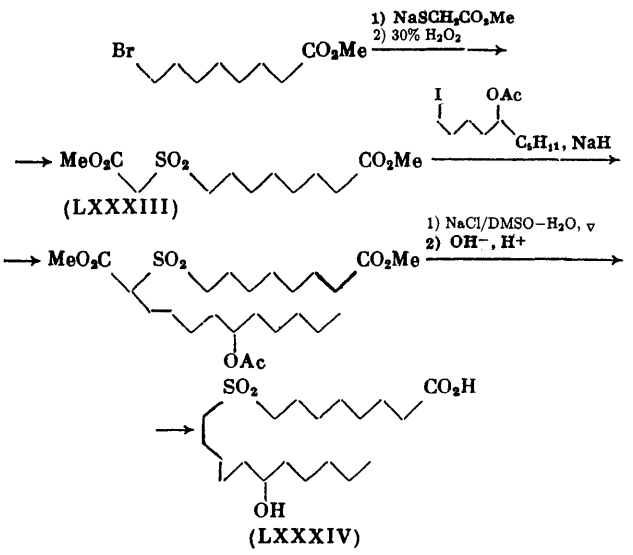
a) $R^1=(CH_2)_3CO_2H$, $R^2=CH_2OAr(CH_2SAr)$;

b) $R^1=$  CO_2H, $R^2=CH_2O(CH_2)_2Me$.

A series of 7-*N*-alkylmethanesulphonamide secoprostanoids, containing *O*- and *S*-phenylene fragments in the ω-chain, was obtained from the methanesulphonamide (LXXVIII), $R^1 = MeSO_2$ using an analogous approach.[66]

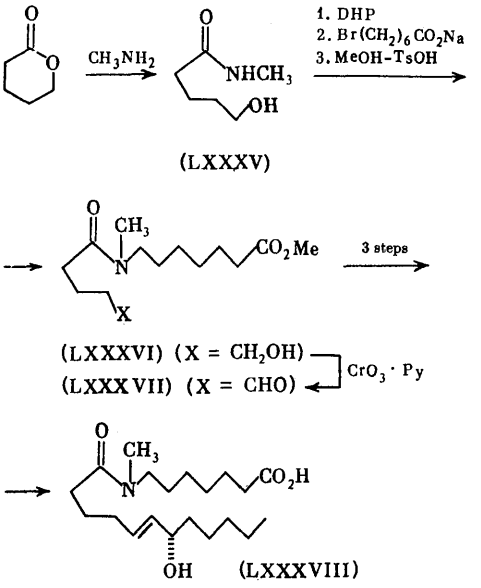
Analogues of 8,12-secoprostanoids synthesised include the 9-sulphonyl (LXXXIV),[65] 8-aza (LXXXVIII), 10-oxa (XC) [68] and the 10-aza and 8-oxa analogues.[69]

The key stage in the formation of the sulphonyl analogue (LXXXIV) is the alkylation of the diester (LXXXIII) in the α-position with an ω-prostanoid chain fragment.[65]



(LXXXIV)

The 8-azasecoprostanoid (LXXXVIII) was obtained through fission of δ-valerolactone with methylamine to form (LXXXV), alkylation of the latter with 7-bromoheptanoic acid, oxidation of the hydroxyl function in the derivative (LXXXVI) and formation of the ω-chain from the aldehyde (LXXXVII) by classical methods.[68]



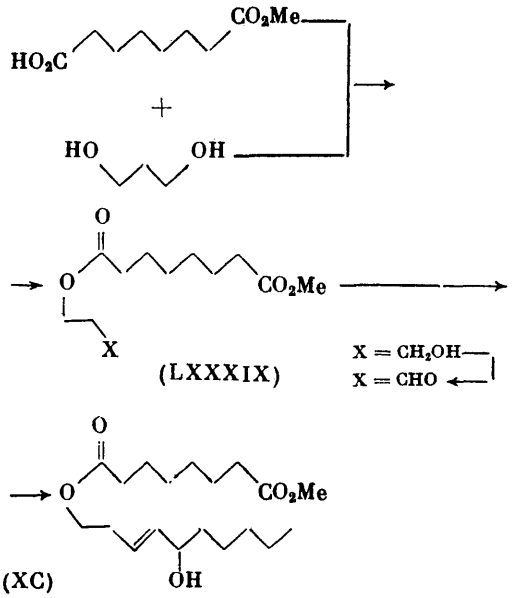
(LXXXV)

(LXXXVI) (X = CH_2OH)

(LXXXVII) (X = CHO)

(LXXXVIII)

The 10-oxa analogue (XC) was synthesised from the hydroxy ester (LXXXIX) to which the ω-chain was attached in an analogous manner.[68]



(LXXXIX)

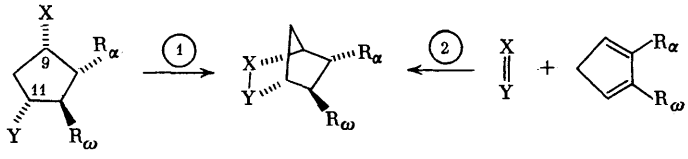
(XC)

The principle of forming the 10-aza- and 8-oxasecoprostanoids was analogous to that considered for the 8-aza and 10-oxa analogues.[69]

V. Heteroanalogues of cyclic endoperoxides

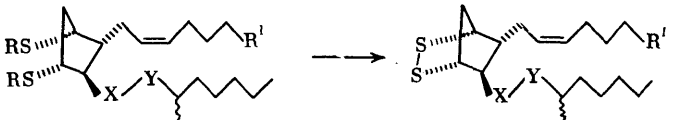
The main problem in the synthesis of heteroanalogues of the cyclic endoperoxides (PGH, PGG) is the replacement of the chemically unstable cyclic endoperoxide group by a more stable one. Of the large number of PGH and PGG analogues obtained up to the present time only those in which one or both oxygen atoms of the endoperoxide grouping are replaced by other heteroatoms (nitrogen, sulphur) are considered in the review.

The formation of the appropriate endocyclic bridging groups of such analogues is effected by two main approaches. The first is through the chemical bond of the functional groups at positions 9,11 of the prostanoid molecule and the second is through a 1,4-cycloaddition of dienophiles, carrying a bridging group in some form or other, to a variously substituted cyclopentadiene.



The first approach was used in the synthesis of dithia, epoxyimino and methyleneimino analogues of PGH.

The key stage in the synthesis of the dithia analogues (XCIIa–c) of PGH is the formation of a disulphide bridge in the appropriate 9,11-dimercapto substituted prostanoids (XCIa–d).[71–73]



(XCI a–d) OH(THP,Ac) (XCII a–c)

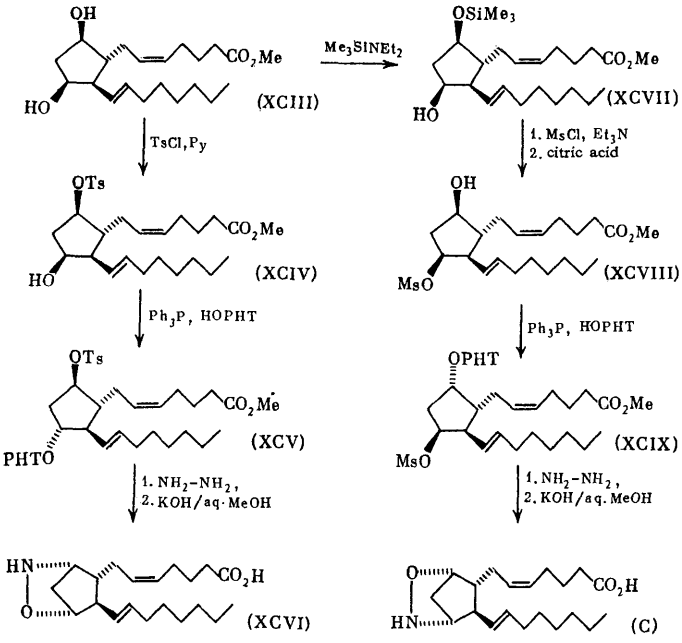
a) $R^1 = CO_2Me$, $X—Y = CH\overset{E}{=}CH$

b) $R^1 = CO_2Me$, $X—Y = C\equiv C$

c) $R^1 = CH_2OAc$, $X—Y = C\equiv C$

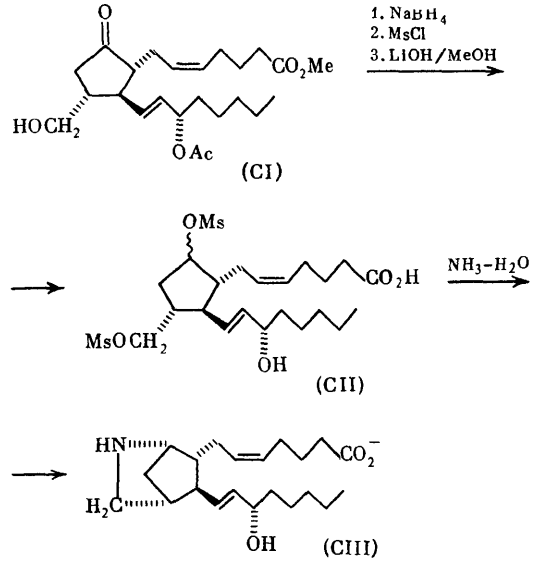
(XCI)	R^1	X–Y	R	Reagent
a	CO_2Me	$CH\overset{E}{=}CH$	H	MnO_2
b			Me	O_2, MeONa/MeOH
c	CO_2Me	$C\equiv C$	Ac	K_2CO_3/MeOH
d	CH_2OAc			

The regioisomeric 9,11-epoxyimino analogues (XCVI) and (C) were obtained from 15-deoxy-11β-$PGF_{2\beta}$ (XCIII).[74] The regioselective tosylation of the less screened 9-hydroxyl group in 11β-$PGF_{2\beta}$ leads to the derivative (XCIV). Subsequently on treatment with triphenylphosphine, *N*-hydroxyphthalimide and diethyl azodicarboxylate compound (XCIV) gave the *N*-alkoxyphthalimide (XCV) from which the epoxyimine (XCVI) was formed on removing the phthalimide protection. In a similar manner the selective trimethylsilyl protection of the 9-hydroxy function of 11β=$PGF_{2\beta}$ leads to the derivative (XCVII). Mesylation of the C(11) alcohol group and removal of silyl protection gives compound (XCVIII) from which the regioisomeric epoxyimine (C) is formed through the alkoxyphthalimide (XCIX).



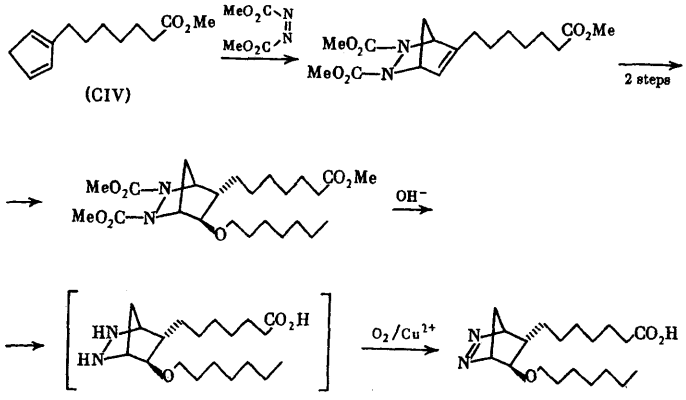
PHT = phthalimido

The methylenimino analogue (CIII) was obtained from the 11-hydroxymethylprostanoid (CI).[75] Reduction of the 9-keto group in the latter and mesylation of the resulting diol leads to the bismesylate (CII), which on reaction with 40% aqueous ammonia gives the ammonium salt of methyleneimino-15-deoxy-PGH_2 (CIII).



A second approach was used in the synthesis of 9,11-azo analogues of the cyclic endoperoxides. The cyclic system of the latter was formed by the Diels–Alder addition of dimethyl(diethyl) azodicarboxylate to a substituted cyclopentadiene of type (CIV). Forming the bridge with the azo group was effected by the alkaline hydrolysis of both methoxycarbonyl(ethoxycarbonyl) groups of the

bicycle and then direct air oxidation of the intermediate hydrazine derivatives in the presence of a divalent copper salt.[76]



VI. Heteroanalogues of prostacyclin

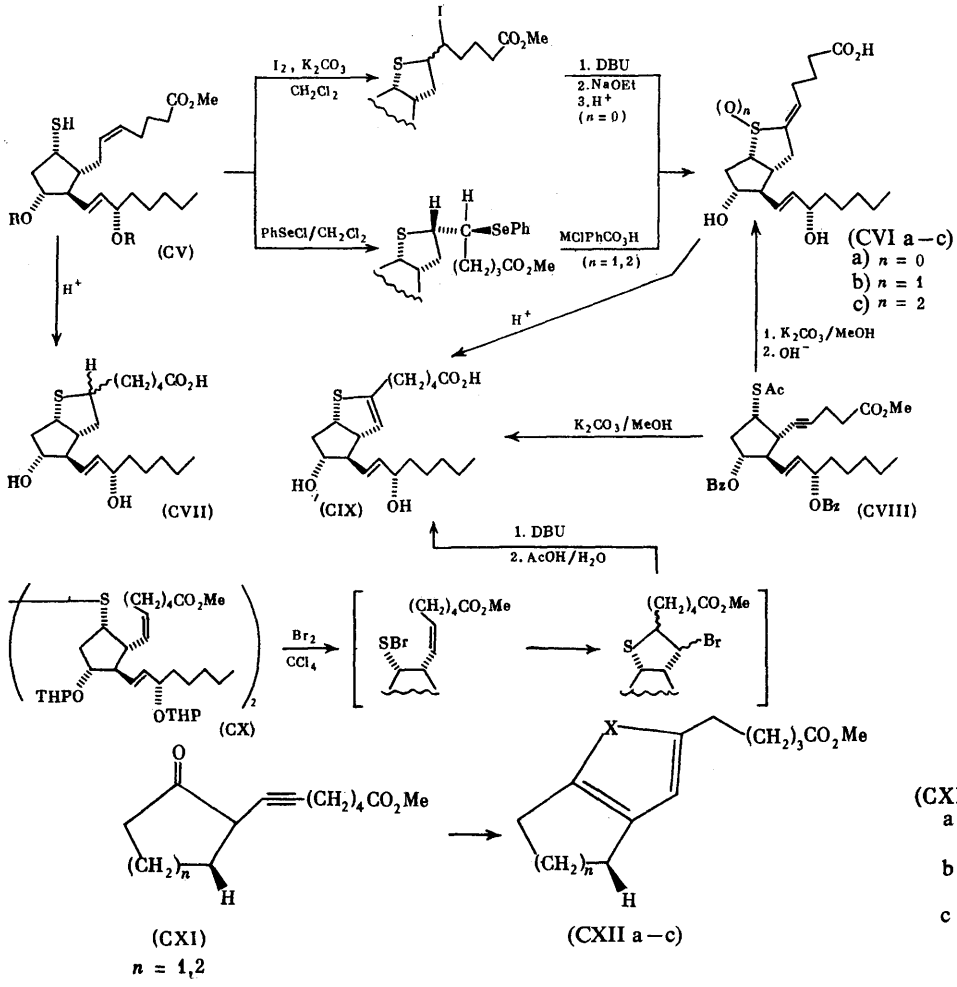
Heteroprostacyclins are described in the literature with heteroatoms at the most varied positions of the molecule. Among those appearing in publications in the last decade it is possible to name 3-oxa,[77–82] 3-aza(thia),[79] 4-thia,[83] 5-aza,[84] 11-oxa,[85] 11-thia,[86] 12-aza,[87] 13-oxa(thia),[88–90] 13-aza[91] and *o*-phenylene analogues.[81,92]

The methods of synthesising such prostacyclin analogues are no different in principle from the methods of forming the basic skeleton of the heteroprostanoids considered above and the synthesis of the *cis*-enol ether system in them is effected by classical means. Consequently in the present review only the modification of the heteroatom of the enol ether fragment is examined. The main purpose of the modification is the replacement of the chemically and metabolically unstable enol ether group by biologically equivalent and/or isosteric structures which are more stable and may have promising use in medicine.

The formation of an enol ether modified with a heteroatom in such heterocyclic PGI analogues was effected using mainly three approaches.

1. Formation of the heterocycle with the participation of the activated multiple bond of the α-chain.

This method is widely used when constructing the enol ether system of natural prostacyclin. Applying it to the 9-mercapto-5,6-*trans* derivatives of $PGF_{2\alpha}$ (CV) leads to the 9-thiaprostacyclins (CVIa–c), (CVII).[93,94] The analogue (CVIa) is also formed by intramolecular attack of the thioacetate grouping at the triple bond in the derivative (CVIII).[95]

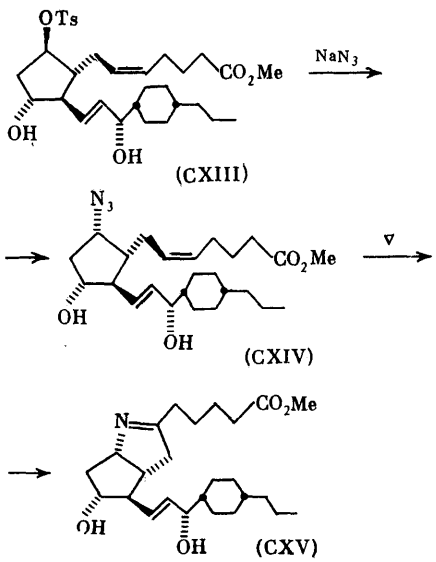


(CXII)	Reagent	X	n
a	H_2S/HCl	S	1,2
	$PhNH_2$,	PhN	1,2
b	Py·HCl, $Hg(O_2CCF_3)_2$	–	–
c	Ac_2O, *p*-TsOH	O	2

The 9-thiaprostacyclin (CIX) was obtained from the disulphide (CX).[96] In this case cyclisation occurs as a result of attack by the Δ^6-double bond at the activated sulphenyl bromide grouping. The same analogue was obtained on cyclisation of the thioacetate (CVIII) by the action of potassium carbonate in methanol,[97] and also on treatment of the 9-thiaprostacyclin (CVIa) with acid.[98]

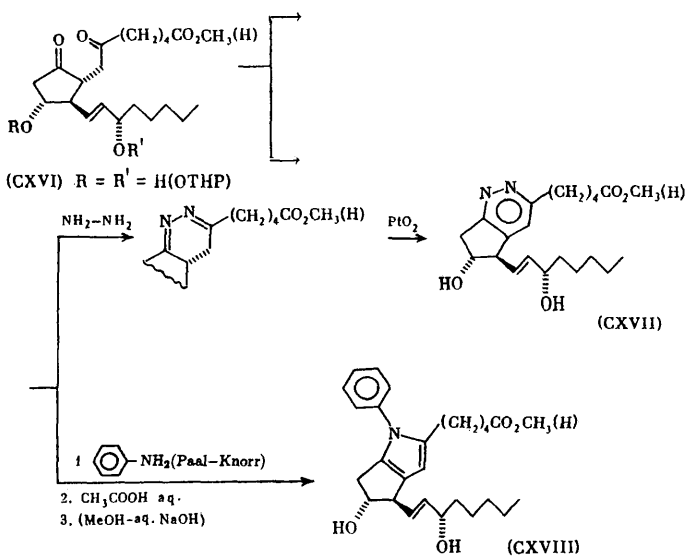
The simplest thiophene (CXIIa), pyrrole (CXIIb) and furan (CXIIc) analogues of prostacyclin were synthesised from the readily accessible 4-alkynylketones (CXI).[99]

The 9-azaprostacyclin (CXV) was obtained using as the key stage the pyrolysis of the azide (CXIV) formed from the tosylate (CXIII).[100]

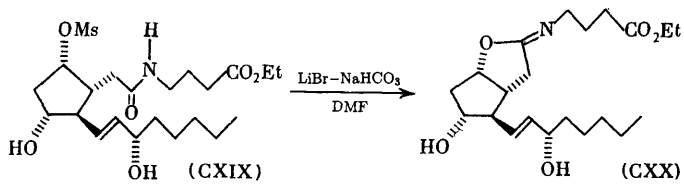


2. Formation of the heterocycle with the participation of other functional groups of the α-chain.

Construction of the heterocyclic systems of the pyridazoprostacyclin (CXVII) and the pyrrole analogue (CXVIII) was effected from the 1,4-dicarbonyl system of 6-keto-PGF_1 (CXVI).[101,102]

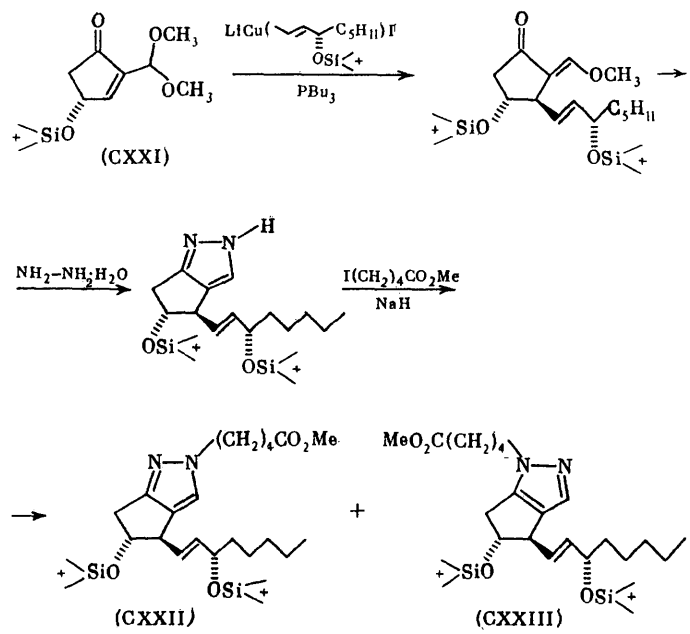


The 5-azaprostacyclin (CXX) was obtained by the cyclisation of the 9-mesyl derivative of the 5-aza-6-ketoprostanoid (CXIX) with a mixture of lithium bromide and sodium hydrogen carbonate.[103]

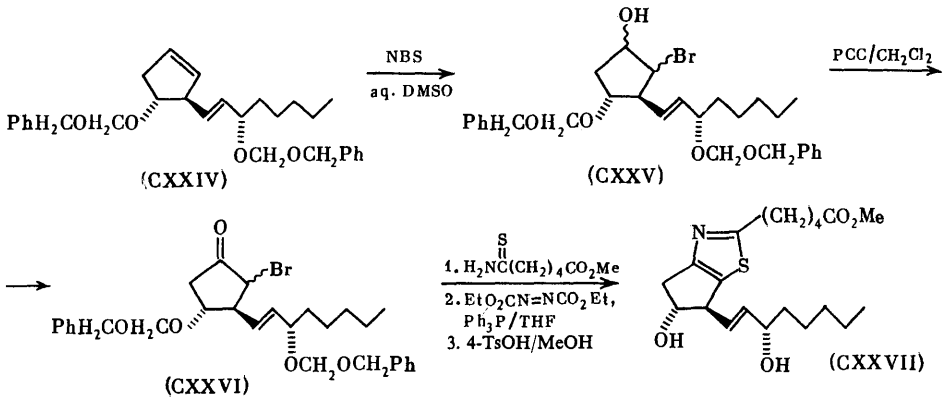


3. Formation of the heterocycle from functionalised derivatives of cyclopentane.

The synthesis of the pyrazole analogues (CXXII) and (CXXIII) from the precursor (CXXI) belongs to this group of schemes.[104]

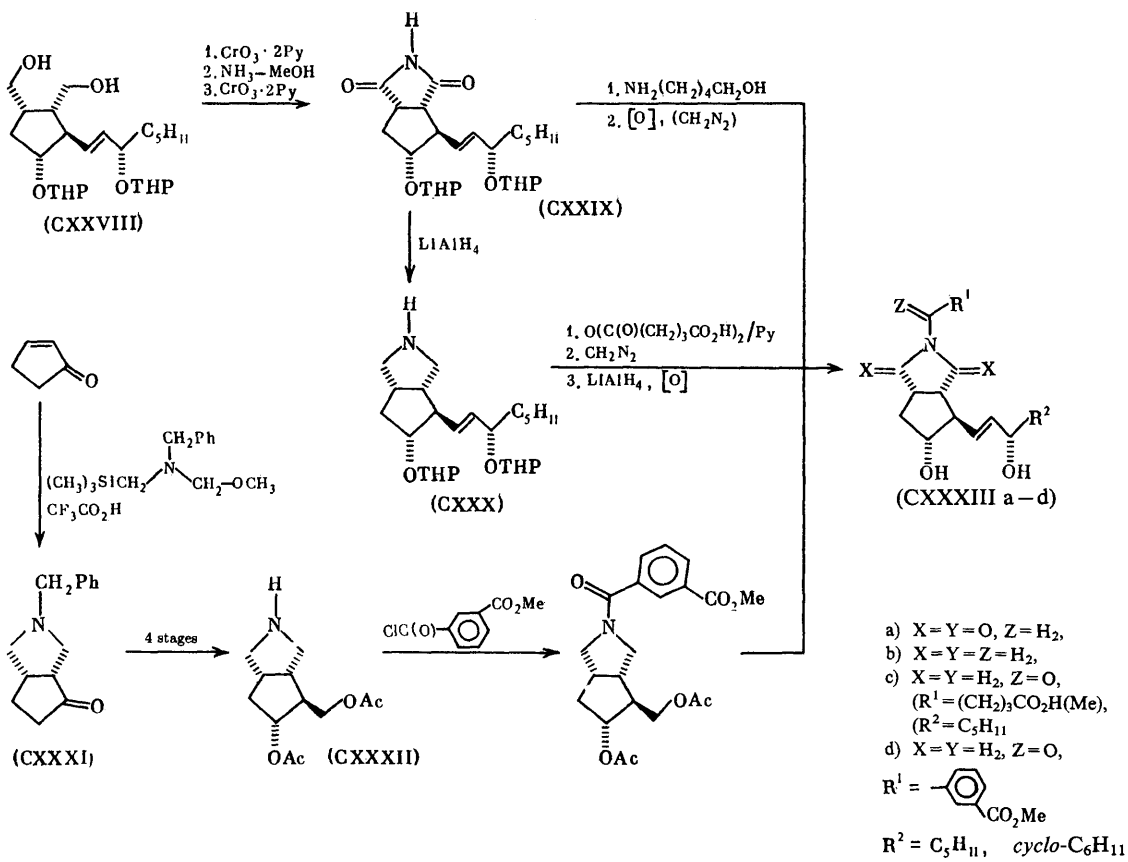


The regiospecific formation of the bromohydrin (CXXV) takes place by the reaction of *N*-bromosuccinimide with compound (CXXIV). Oxidation of the bromohydrin leads to the formation of the bromoketone (CXXVI) which is converted into the thiazolylprostacyclin (CXXVII) by reaction with adipic acid thioamide and subsequent dehydration.[105,106]

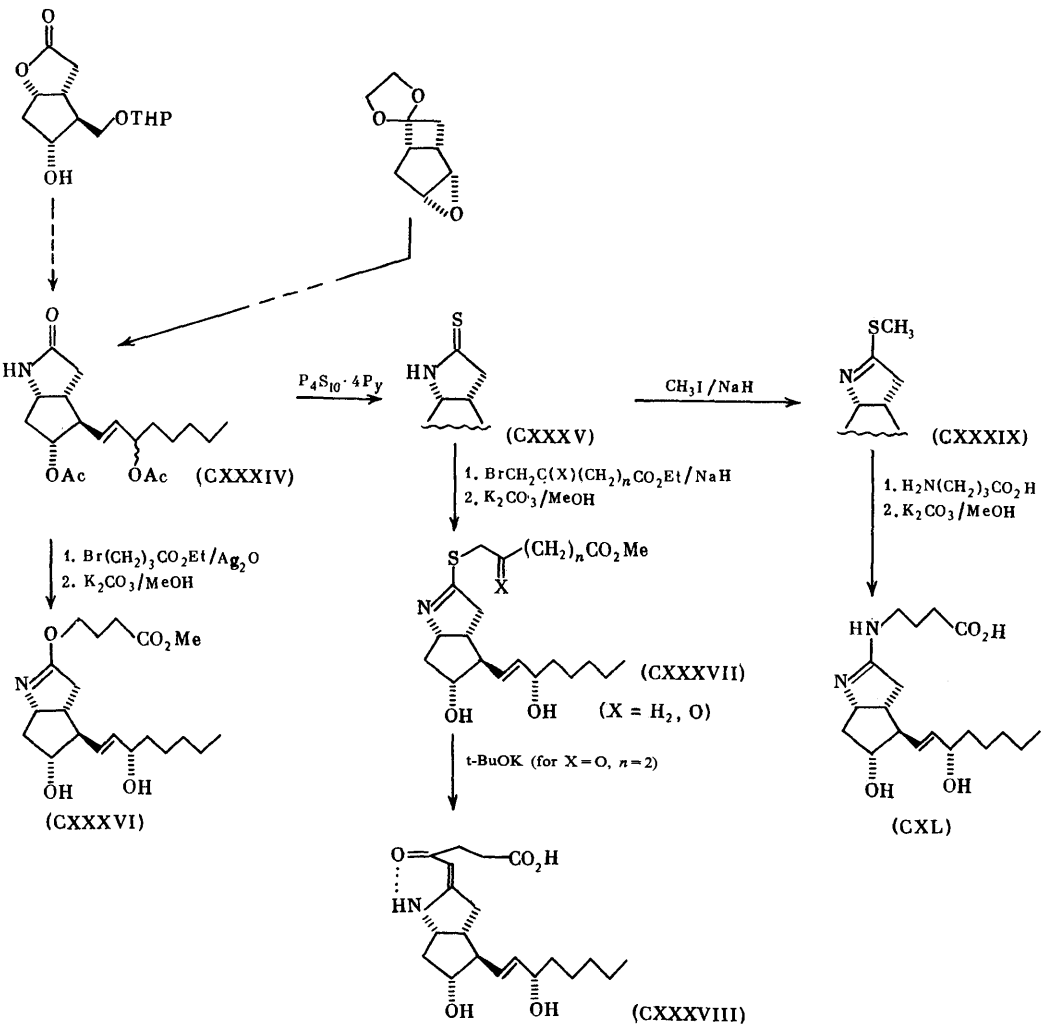


The 6-aza analogues (CXXXIIIa–d) were synthesised by the alkylation (acylation) of the succinimide precursor (CXXIX) [formed from the diol (CXXVIII) in three stages] or from its reduction product (CXXX) and also from the bicyclic diacetate (CXXXII) obtained from the ketone (CXXXI).[107,108]

The β-heteroiminoprostacyclins (CXXXVI)–(CXXXVIII) and (CXL) were synthesised from the lactam (CXXXIV) which may be obtained from the Corey lactone or from the ethylene ketal of 2,3-epoxybicyclo[3.2.0]heptan-6-one. On reaction with the Lawesson reagent the lactam (CXXXIV) was converted into the thiolactam (CXXXV). Alkylation of compounds (CXXXIV) and (CXXXV) leads to the analogues (CXXXVI) and (CXXXVII). The further transformation of compound (CXXXVII) leads to



4-keto-9-deoxy-9-aza-PGI_2 (CXXXVIII). Ammonolysis of compound (CXXXIX) with γ-aminobutyric acid gives the amidine (CXL).[109,110]



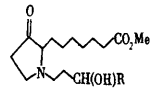
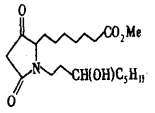
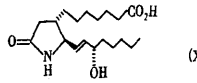
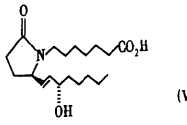
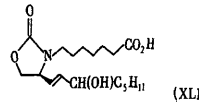
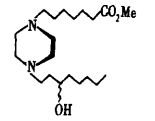
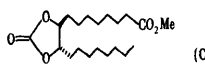
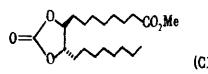
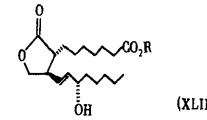
VII. Biological activity of heteroprostanoids

Among the numerous data in the literature on the biological activity of PG heteroanalogues we will discuss chiefly those which refer to the modification of the natural structure affecting the biological properties in a favourable manner, i.e. increasing any form of activity (narrowing the spectrum of action) or increasing the metabolic stability of the compound (prolonging its therapeutic effect).

The biological actions of prostaglandins can be divided into several main types. 1. The effect on the vascular and non-vascular smooth musculature, the contracting or relaxing activity. 2. The gastroprotective effect, including the regulation of secretion of gastric juice both as a result of a change in tone of the smooth muscle tissue and of the effect of PG on water and electrolyte transport in them. 3. The hormonotropic action, including the regulation of gland function by internal secretion stimulating the synthesis of hormones. One of the most important forms of biological activity of PG belongs to this direction, viz. the luteolytic effect, the action on the reproductive system through the regulation of ovarian function. 4. The pro- or anti-inflammatory action. The anti-inflammatory effect is probably linked with the inhibition of natural PG biosynthesis. 5. The induction and inhibition of platelet aggregation. 6. The anti-PG effect of synthetic prostanoids consists of a weakening of the effect of natural PG. The synthetic analogue is, as a rule, an antagonist of the appropriate receptor for the natural PG.

It is assumed that PG acts as a complex with the cell receptor of a given organ on an adenylate cyclase system, increasing or reducing its activity and thereby changing the rate of conversion of ATP into adenosine 3′,5′-phosphate, i.e. changing the content of c-AMP in the tissues of an organ. Consequently PG-like activity is assessed according to the ability to bind to a receptor or according to the change in c-AMP content and a comparison is made with the dose of natural PG equivalent in effect. Tests are used to assess the metabolic stability of a prostanoid which measure the affinity for enzymes responsible for metabolism (15-hydroxy-PG-dehydrogenase, Δ^{13}-PG-reductase, etc.). The anti-PG effect, linked with the action on the process of biosynthesis of prostaglandins from arachidonic acid, is displayed in the ability to inhibit the enzymes of PG biosynthesis (PG-synthetase, PG-isomerase).

Table 4. Types of biological action of the heteroprostanoids.

Heteroprostanoids	Biological action	Active concentration g ml^{-1}	Reference
	Contraction of rat uterus muscle	$0\times5-1\times10^{-7}$	[27]
 PGE$_1$	Ditto	5×10^{-7} 1×10^{-9}	[129]
 (XL) PGF$_{2\alpha}$	Contraction of trachea	4×10^{-6} 4×10^{-7}	[32]
 (VI)	Bronchdilator	1×10^{-6}	[4]
 (XLII)	»	5×10^{-5}	[33]
PGE$_2$ 	Increase of tone of smooth muscle organs Ditto Strengthening of spasmogenic reactions caused by PGE$_2$ Reduction of rat arterial pressure	10^{-9} $10^{-5}-10^{-6}$ $10^{-6}-10^{-7}$ $0\times5-1\times10^{-3}$	[151]
 (CXLI)	Weakening of activity on trachea	$4\times10^{-6}-5\times10^{-4}$	[36]
 (CXLII) PGE	Ditto	$5\times10^{-4}-2.5\times10^{-3}$	
 (XLIII)	Effect on smooth muscle	10^{-8}	[111, 112]

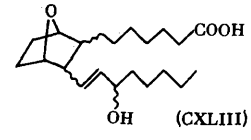
1. Effect on vascular and non-vascular smooth muscle. Gastroprotective, hormonal and pro- or anti-inflammatory activity of heteroprostanoids

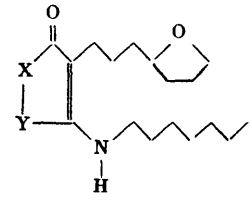
Many synthetic heteroprostanoids show activity on smooth muscle characteristic of PG. However both the size and the sign of the effect depend on the form of the target tissue, which is the specificity of a given prostanoid (Table 4). For example, the 11-aza analogues (XL) do not display a contractive activity on guinea pig and rat ileum but contract the trachea like PGE_2 and also cause rhythmic venous contraction.[32]

The 9,11-dioxa analogues (CXLI) and (CXLII) display strong relaxant activity.[36] The range of active concentrations of these analogues in relaxing the trachea is 0.004 – 2.5 mg ml^{-1}, i.e. they are approximately 100 times more potent than the natural PGs. The given compounds do not exert a relaxant effect on bronchospasm, they do not affect blood pressure and do not cause intestinal disorders (in contrast to PGE_2) in tests *in vivo*. The 10-oxa-11-deoxy analogues (XLIII) are patented as stimulants in certain species, they may be used in gastro-intestinal disorders and are non-toxic.[111]

A link can be traced between structure and activity of the synthetic heteroprostanoids. The methyl esters of the 10-oxa-11-deoxy-PGE analogues are inactive in the interruption of pregnancy,[112] and the acids of the 11-deoxy-E_1 and E_2 series have moderate contracting activity at concentrations of 10^{-7} g ml^{-1} and low toxicity.[34,113] The 11-methyl derivatives of this series inhibit the secretion of gastric juice in dogs and possess anti-hypertensive activity.[114]

The configuration of substituents at the chiral centres of the molecule affect the biological activity even more appreciably. In the 10-oxa-9,9-dicarba analogues of PGH_1 (CXLIII), which possess vasocontracting and broncho-stimulating activity in many tests *in vitro*, the configuration at C(8, 12,15) has a significant effect.[115,116] Thus the 15β-hydroxy derivatives are most active towards the stimulation of the vascular and respiratory musculature and in the case of the 8-isoconfiguration this effect is strengthened. The contracting activity is appreciably reduced in the 15α-hydroxy derivative and in the case of the natural 8,12,15-configuration. a vasodilatation is observed. These same principles are observed in experiments *in vitro* on trachea and smooth muscle. The 11-oxa-13-azaprostanoid (CXLIVa) at a dose of 10 mg kg^{-1} displays a marked antiadrenergic effect (70% relative to control) and also restores the frequency of cardiac contractions and normalises impaired atrioventricular conduction in the adrenaline arrhythmia model in guinea pigs. Compounds (CXLIVb, c) display an antioedemic effect in the carrageenan inflammation model in the rat.[13]


(CXLIII)


a) X = CH_2, Y = O; b) X = O, Y = $CH(CH_3)$; c) X = $CH(CH_3)$, Y = O.

(CXLIVa – c)

Bronchodilating activity is characteristic of numerous derivatives of 3-, 5- and 16-oxa analogues of PGE and PGF. The 3-*O*-hetero analogues have been patented as antiasthmatics,[117] and the 13-thiaprostanoids of the E_1 and E_2 series as hypotensive agents.[46]

A comparative assessment has been carried out of the activity of several synthetic aza and thia analogues in their ability to bind to PG receptors of the appropriate tissues or in the size of the change in c-AMP concentration (Table 5).[23,63] As is seen from the table a hundredfold concentration of the 11,12-seco-aza analogue (CXLV) is necessary for the display of activity comparable to PGE_1. Compound (CXLVI) was the most active among the 8-aza analogues but it was ten times less potent than PGE_1. The most potent of the tested series, the 11,12-seco analogue (CXLVII), was five times less potent than PGE_1 and comparable with tetrahydro-PGA_2 in stimulating c-AMP, although both PGE_1 and tetrahydro-PGA_2 bound more strongly to the receptor of lipocytes than (CXLVII). However on detailed investigation of the biological properties of (CXLVII) it was shown[65] that the compound is not a substrate of 15-hydroxy-PG-dehydrogenase and therefore has enhanced metabolic stability. Furthermore it was established in tests *in vivo* that the analogue (CXLVII) has a higher specificity of action, it is inactive in relation to gastric secretion and is not an antihypertensive agent.

Table 5. Comparative assessment of the activity of synthetic heteroanalogues of the prostaglandins.[23,63,65]

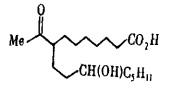
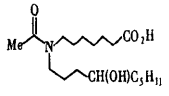
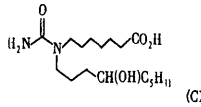
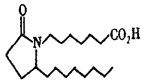
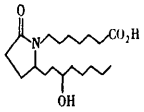
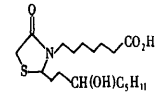
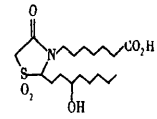
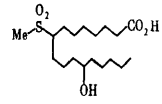
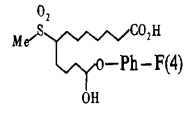
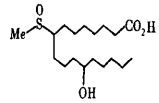
Compound *	c-AMP concentration, mg ml^{-1}				Binding to lipocyte receptor, relative to PGE_1
	1.0	10	25	10^3	
PGE_1	54	60	62	62	1
Dihydro-PGE_1	10	25	26	—	—
Tetrahydro-PGA_1	10	25	26	—	10
	2	11	14	23	833
	—	10	17	17	—
 (CXLV)	2	23	43	40	—
 (XXVIa)	0.7	—	8	13	8300
 (XXVIb)	0.9	—	8	18	4600

Table 5 (contd.).

Compound *	c-AMP concentration, mg ml^{-1}				Binding to lipocyte receptor, relative to PGE_1
	1.0	10	25	10^3	
	1.4	—	8	25	390
 (CXLVI)	5.2	—	27	37	60
 (CXLVII)	14	—	27	38	670
	1	—	23	27	1110
	4	—	40	57	7140

*Activity of PGE_1 at *c*-AMP concentration 10^{-2} mg ml^{-1} was 8, at *c*-AMP 10^{-1} it was 25. Activity of (CXLVII) at 10^{-1} mg ml^{-1} was 2.

The 15α-isomer of (+)-7-oxa-$PGF_{1\alpha}$ (CXLVIII) at a concentration of 100 μg mol^{-1} displays 10% activity of PGE_1 in stimulating adenylate cyclase and has 5% activity of $PGF_{1\alpha}$ in stimulating smooth muscle.[118] The 15β-isomer at a concentration of 1 μg ml^{-1} inhibits the action of $PGF_{1\alpha}$ at a concentration of 250 ng ml^{-1}.

The 9,11-dideoxy (CXLIX) and 9,11,15-trideoxy (CL) derivatives of 7-oxa-PG are antagonists of the action of PGE_1 and $PGF_{1\alpha}$ on smooth muscle.[119] These examples demonstrate the effect on activity of the number of hydroxyl groups and their configuration at C(15). The inhibitory activity is reduced as the degree of hydroxylation of the compound increases.

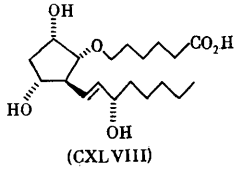
The 7-thia-$PGF_{1\alpha}$ analogue (CLI) shows 10% activity of $PGF_{1\alpha}$ in the extent of binding to the corpus luteum receptor and stimulates adenylate cyclase while its 9β-, 11β-, 8β- and 12α-isomers with unnatural chirality display only 1% of the activity of the analogue with the natural configuration.[120] The 9,11,15-trideoxy-7-thia derivative (CLII) is an inhibitor of contractions and an inhibitor of adenylate cyclase. The values of I_{50} of 15 μM for (CLII) and 5 μM for (CLI) in the inhibition of placenta PG-15-dehydrogenase show that these compounds also regulate the concentration of the natural PG *in vivo*.[120] The relatively little studied group of 9- and

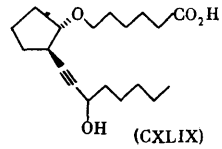
11-oxa-PG analogues which showed 0.05–0.005 of the activity of PGE_2 [121,122] and the 11-thia analogues[123] must be regarded as promising biologically active heteroanalogues.

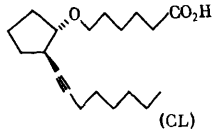
The 10-oxaseco analogue (CLIII) shows high efficiency (approximately equal to the activity of PGE_2 and 30% of that of PGE_1) in the inhibition of gastric juice secretion.[68] The same activity was displayed by the 10,12-diaza analogues of PGE.[124] The 16-phenoxy-PGs proved to be good therapeutic preparations for the treatment of various lesions of the gastro-intestinal tract.[125,126] In preliminary tests the 7,13-dithia analogues of groups E, F and D displayed antiulcer activity without side effects.[49]

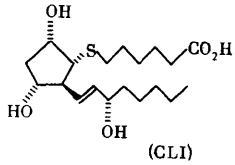
A luteotropic effect among the heteroanalogues of PG was detected only for the 5- and 16-oxa analogues[127,128] although compounds more potent and selective than PGF_2 were discovered amongst them.

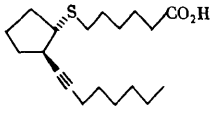
As already mentioned, an inflammatory effect is characteristic of the natural PGs. At the same time certain heteroanalogues display clearly marked anti-inflammatory activity. Thus the 12-aza analogue of PGE (CLIV) is similar in activity to hydrocortisone.[129] The 9,11-dithia analogue (CLV) [36] is nine times more potent than aspirin and is a potential nonsteroidal anti-inflammatory agent. This compound is an inhibitor of PG-synthetase on which apparently the anti-inflammatory effect is based. Anti-inflammatory activity is also possessed by the 9,11-dioxa analogues.[36] A series of heteroanalogues of endoperoxides has been patented as anti-inflammatory agents.[130]

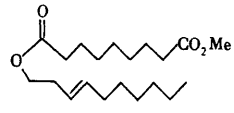

(CXLVIII)

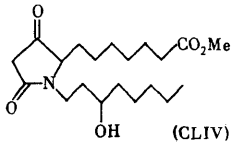

(CXLIX)

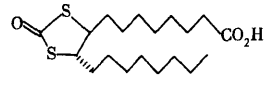

(CL)


(CLI)


(CLII)


(CLIII)


(CLIV)

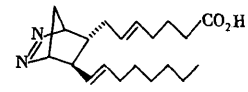

(CLV)

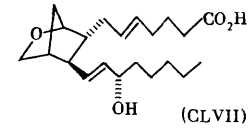
2. The induction and inhibition of platelet aggregation by heteroanalogues of endoperoxides, prostacyclins and PGE

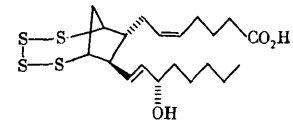
After discovering the fact that the endoperoxides have a significantly stronger effect on the respiratory and vascular smooth muscle than PGE_2 and PGF, the attention of investigators was turned to these unstable intermediate products of the biosynthesis of the primary PGs. Interest in this was strengthened when the ability of endoperoxides to induce rapid and irreversible aggregation of platelets (an action uncharacteristic of the primary PGs) was discovered[131] and it was established that the endoperoxides are metabolised to prostacyclin (PGI_2) and thromboxane A_2 (TxA_2) which are opposite to one another in their action. Prostacyclin is an inhibitor of platelet aggregation and relaxes smooth muscle. Thromboxane A_2, like PGH_2 and PGG_2, is produced in the process of platelet aggregation, but is far more active in inducing aggregation and as an inhibitor of PGE_1-stimulated c-AMP. The extreme instability of these three intermediate prostaglandins, their high potency and reputed role in the biological action of PGs caused the interest in the synthesis of more stable analogues, including heteroanalogues, which might serve as models for studying the mechanism of PG action.

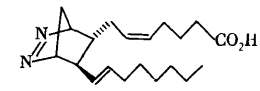
The 9,11-diaza analogues of the endoperoxide (CLVI), like PGG_2, cause a rapid and irreversible platelet aggregation at concentrations of $10^{-5}-10^{-6}$ M. They are almost eight times more potent than PGG_2, seven times more potent than PGH_2, are metabolically more stable and are also 1500 times more potent than PGE_2 in contracting smooth muscle.[132]

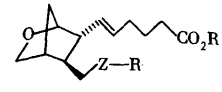
The epoxymethano analogue (CLVII) is an efficient broncho-constricting agent, it is 3–7 times more potent than PGG_2, but less potent in platelet aggregation.[133,134] The 9,11-dithia-PGH_2 analogue (XCIIb) [71,72] is very potent in contraction of the aorta (24 × PGH_2 and 5000 × PGE_2) and is an inducer of platelet aggregation. The endotetrasulphide PHG_2 analogue (CLVIII) causes platelet aggregation in spite of the presence in the structure of the bulky S-containing group which however does not hinder the binding with the endoperoxide receptor.[3] On the other hand the heteroanalogues of PGH_2 without a 15-hydroxy grouping (XCVI), (C) and (CLIX) display inhibitory activity in relation to thromboxane A_2 synthetase and are antagonists of platelet aggregation induced by PGH_2 or by arachidonic acid.[74,135,136] Endoperoxides of such structure have been patented as anti-inflammatory and antithrombotic agents.[137] The epoxymethano (CLX) and the carba analogues of PGH_2 with a heteroatom at position 14 proved to be inhibitors of platelet aggregation.[138]

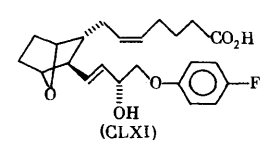

(CLVI)


(CLVII)


(CLVIII)


(CLIX)


(CLX) Z = O, NH


(CLXI)

The oxabicyclo[2.2.1]heptane prostanoids with natural α- and ω-chains are known as potential analogues of thromboxanes. Their analogue (CLXI), containing a 16-fluorophenoxy fragment in the

ω-chain, has high TxA_2-like activity and at a concentration of 4×10^{-11} M is 100 times more potent than the standard agonist, viz. 9,11-epoxymethano-PGH_2.[139] The 12β-isomer is the most active among the isomers with the natural configuration. In the absence of a hydroxyl function from the ω-chain these prostanoids display the opposite activity. Thus the alkyl thioethers of 7-oxabicyclo-[2.2.1]heptane (CLXII) are antagonists of the thromboxane receptor.[53] They possess inhibitory activity towards TxA_2 synthetase and are 30–40 times more potent than ethanol in inhibiting platelet aggregation. The amidocarbamates, amides and diamides of 7-oxabicycloheptanes have also been patented as inhibitors of platelet aggregation.[140] The recently synthesised sulphonamido derivatives of bicycloheptane prostanoids (CLXIII) are also antagonists of the thromboxane receptor.[57,60]

The diametrically opposite biological action of PGI_2 to the action of TxA_2 and the endoperoxides PGH_2 and PGG_2 in platelet aggregation forms a basis to affirm that the balance between the activities of these two groups of arachidonic acid metabolites determines thrombosis and haemostasis. However, in spite of the large number of studies on the biochemistry and physiology of PGI_2 there is still no definite theory on the mechanism of its action. It was shown that like PGE prostacyclin increases the concentration of c-AMP in blood.[141,142] The increase in the c-AMP level, as proposed, must inhibit hydrolysis of arachidonic acid phospholipid ester and thereby moderate the release of arachidonic acid and its metabolism to endoperoxide.

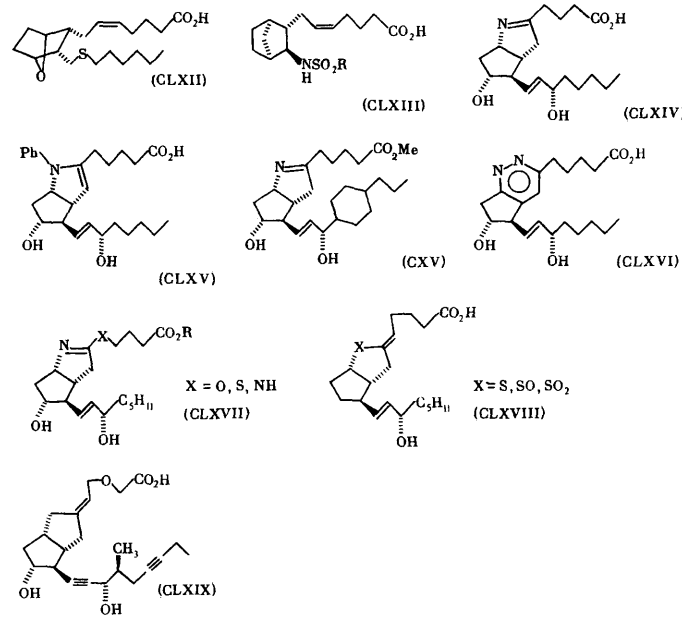
The synthesis of stable analogues of prostacyclin is an urgent problem. Since the instability of PGI_2 is linked primarily with the presence of the enol ether fragment and the carboxyl function near to it, the synthesis of analogues of PGI in which the oxygen of the ring was replaced by nitrogen or sulphur has been effected.

The prostacyclin analogues (CLXIV) and (CLXV) are equivalent to PGI_2 in activity although compound (CLXIV) in contrast to PGI_2 inhibits the synthesis of leucotrienes.[102,143,144] The promise of the recently synthesised azaheteroprostacyclin OP-2507 (CXV) as an anticerebral ischaemic agent is linked with the antithromboxane activity displayed by it.[100] The 6-aza analogues of PGI obtained recently display weak activity.[108] It is considered that among the stable analogues of prostacyclin the greatest activity is possessed by analogues with a sp^2-hybridised atom at C(6), for example compounds (CLXVI)–(CLXVIII).[101] Furthermore the stereochemistry of the upper chain at the Δ^5-double bond affects the activity. The most active proved to be the configuration with a *trans* orientation of the heteroatom and the hydrogen atom at C(5).[93,94,145]

Further modification of the enol ether fragment was effected by the synthesis of 4-keto-9-deoxy-9-aza-PGI analogues.[110]

The potency of these compounds as inhibitors of ADP-induced platelet aggregation was less than a quarter of that of PGE_1 and was 0.01 of the potency of PGI_2. The similarity of the ^1H NMR parameters of this group of compounds and of prostacyclin indicates significant conformational similarity but seemingly, due to the rigidity of the vinyl amide system, the carboxyl group is prevented from reaching the binding centre of the PGI_2 receptor.

The thia analogues are less potent than PGI_2 and the aza-analogues[71,131,132] in platelet aggregation and in contrast to PGI_2 possess vasocontracting activity. It was noted that the inhibitory activity was reduced from the 6,9-thia analogues to the 6,9-sulpho analogues.[93,94]



The most promising among the prostacyclins proved to be its carba analogue, iloprost, consequently synthetic efforts are directed to the further modification of iloprost. In the prostacyclin series, as for PGE, it was discovered that the introduction of a heteroatom into position 3 increases the metabolic stability of a compound[78–80,146,147] since in this case the first metabolic process is blocked, viz. the oxidation in the β-position relative to the carboxyl group.[79] The potency of compounds is reduced at the same time but this is compensated successfully by modification of the lower chain, particularly by introducing alkyl fragments into the ω-chain. The stable and five times more potent 3-oxaprostacyclin (CLXIX) was thus obtained.[78]

In addition to the prostacyclins, 8-aza-11-desoxy-PGE_1,[148] 10-aza analogues,[37] 12-aza-PGE analogues[129] and 9,11-diaza analogues[29] display inhibitory activity in platelet aggregation. The 3-oxa-4,5,6-trinor-3,7-*m*-phenylene analogue of PGE_1 is 30 times more active than PGE in inhibiting platelet aggregation. Anti-aggregatory activity is possessed by azacyclic analogues of the primary PG derivatives, viz. pyrazolidine- and piperazinediones,[18] hydantoin and imidazole derivatives.[28–30]

The reduction in the activity of isomers having an unnatural configuration at the chiral centres 8 and 15 is explained[18,30,116] by the important role of the configuration of the α-chain and the 15-hydroxyl group in anti-aggregatory activity. It must be affirmed that anti-aggregatory activity is observed for the analogues of primary PG identical in configuration to the natural PGs.

13-Azaprostanoic acid (13-APA) possesses unique anti-aggregatory activity and at a concentration of 10^{-5} M is a specific inhibitor of platelet aggregation induced by arachidonic acid, PGH_2 and its epoxymethane analogue.[42,149]

At the same time 13-APA does not inhibit aggregation induced by ADP or thrombin. In a detailed experimental investigation of this unique specificity of 13-APA it was established that 13-APA does not inhibit aggregation by the production of c-AMP, as is assumed for prostacyclin and PGE_1, which in contrast to it are not so

selective in the inhibition of platelet aggregation. Furthermore it was established experimentally that 13-APA is not an antagonist of the action of PGI_2 and PGE_1, since they, although not stimulating adenyl cyclase, do not interfere with the production of c-AMP. In the arachidonic cascade (the metabolic pathway for AA) three places have been proposed at which inhibition of platelet aggregation by 13-APA may occur. There are 1) inhibition of cyclo-oxygenase (PG-synthetase) which transforms AA into the endoperoxide. This action is similar to the action of the non-steroidal anti-inflammatory agents aspirin and indomethacin. 2) Inhibition of thromboxane synthetase and the consequent blocking of the transformation of PGH_2 to TxA_2 like the action of imidazole and the aza analogues of endoperoxide (XCVI), (C) and (CLIX).[74,135,136] 3) Direct inhibition of the thromboxane–endoperoxide receptor. It was established experimentally that 13-APA does not inhibit either the synthesis of endoperoxide or the synthesis of thromboxane but possibly selectively blocks the reaction of TxA_2 and PGH_2 with the platelet receptor. This hypothesis is confirmed by the structural similarity of 13-APA with the unstable PGs, which are active in aggregation, and the sensitivity of the inhibiting activity to molecular and stereochemical modification.[149] When analysing the data on the antiprostaglandin activity and the inhibitory capabilities of the heteroprostanoids it is possible to separate certain structural elements responsible for the development of these properties. Thus the absence of a 15-hydroxyl function is necessary[150] for the development of antagonistic activity or, when discussing isomers, an unnatural configuration for the 15-hydroxyl function.[118–120] The inhibitory action of a compound is also seemingly linked to a significant degree with the absence of a 15-hydroxyl group i.e. anti-inflammatory action,[36,137] inhibition of biosynthesis,[71,74,135,136,150] inhibition of the effect of the natural PGs [29,119] and the inhibition of platelet aggregation.[28,149,150] It has already been mentioned that inhibitory activity is reduced with an increase in the extent of hydroxylation of a compound.[119] From the fairly few examples available it may be suggested that the replacement of the 9,11-carbon atoms by a heteroatom or blocking the free hydroxyl functions in these positions in combination with the absence of a 15-hydroxyl group, will give a compound with anti-inflammatory or other antagonistic activity.[36,74,135,137]

When explaining the appearance of PG-like activity or the activities of PGH_2 and PGI_2 considerable importance is attached to the conformity of the stereochemical configuration of a modified PG to the configuration of the natural PGs.[30,116,118] This applies to any modification of the PG molecule including modification by a heteroatom. To increase metabolic stability it is expedient to modify that part of the molecule which is subject to change in the metabolic process. Seemingly a decisive role in all cases is played by retaining a qualitative similarity between an analogue and the natural PG which itself will be closest to the PG receptor of a cell.

After preparation of the manuscript for publication several publications have appeared on the theme of the review.[152–170]

References

1. E I Levkoeva, L N Yakhontov *Usp. Khim.*, 1977, **46**(6) 1074 [English translation in *Russ. Chem. Rev.*, 1977(6)]
2. V A Dombrovskii, E V Gracheva, P M Kochergin *Usp. Khim.*, 1986, **55**(10) 1720 [English translation in *Russ. Chem. Rev.*, 1986(10]
3. K C Nicolaou, et al. *Angew. Chem. Int. Ed. Engl.*, 1978, **17** 293
4. S Saijo, M Wada, J Himizu, A Ishida *Chem. Pharm. Bull.*, 1980, **28** 1149
5. J-P Depres, A E Greene, P Crabbe *Tetrahedron*, 1981, **37** 621
6. V A Dombrovskii, et al. *Khim. Geterotsikl. Soedin.*, 1986, 40
7. F C Biaggio, E J Barreiro *J. Heterocycl. Chem.*, 1989, **26** 725
8. A Barco, S Benetti, P G Baraldi, et al. *Liebigs Ann. Chem.*, 1982, **5** 960
9. D Blondet, C Morin *J. Chem. Soc., Perkin Trans. 1*, 1984, 1085
10. P A Zoretic, F Barcelos, J Jardin, et al. *J. Org. Chem.*, 1980, **45** 810
11. E J Corey, S G Pyne, A I Schafer *Tetrahedron Lett.*, 1983, **24** 3291
12. J Nokami, T Ono, Y Kajitani, S Wakabayashi *Chem. Lett.*, 1984, (5) 707
13. F A Lakhvich, et al. *Izv. Akad. Nauk Beloruss SSR, Ser. Khim.*, 1988, (6) 53
14. Y Amino, H Eto, C Equchi *Chem. Pharm. Bull.*, 1989, **37** 1481
15. S Saijo, M Wada, J-I Himizu, A Ishida *Chem. Pharm. Bull.*, 1980, **28** 1459
16. N Kubodera, et al. *Heterocycles*, 1982, **18** Spec. Issue, 259
17. D R Adams, et al. *J. Chem. Soc., Perkin Trans. 1*, 1984, (9) 2061
18. P Barraclough, et al. *J. Chem. Soc., Perkin Trans. 1*, 1981, (7) 2096
19. S Hanessian, et al. *Carbohydr. Res.*, 1985, **141** 221
20. R R Arndt, et al . *S. Afr. J. Chem.*, 1981, **34** 121
21. J Thiem, H Luders *Liebigs Ann. Chem.*, 1985, **11** 2151
22. A Barco, S Benetti, G P Pollini *J. Org. Chem.*, 1979, **44** 1734
23. R J Smith, et al. *J. Med. Chem.*, 1977, **20** 1292, 1299
24. G P Rosing, et al. *Heterocycles*, 1976, **4** 719
25. I Vlattas, L D Vecchia *Tetrahedron Lett.*, 1974, (51/52) 4459
26. C J Harris, N Whittaker, G Higgs, et al. *Prostaglandins*, 1978, **16** 773
27. R M Scribner *Tetrahedron Lett.*, 1976, (43) 3853
28. A G Caldwell, et al. *J. Chem. Soc., Chem. Commun.*, 1979, (13) 561
29. A G Caldwell, et al. *J. Chem. Soc., Perkin Trans. 1*, 1980, (2) 495
30. M A Brockwell, A G Caldwell, N Whittaker *J. Chem. Soc., Perkin Trans. 1*, 1981, (3) 706
31. F Cassidy, G Wootton *Tetrahedron Lett.*, 1979, (17) 1525
32. A Barco, S Benetti, G P Pollini, et al. *J. Med. Chem.*, 1981, **24** 625
33. N Kubodera, et al. *Heterocycles*, 1982, **19** 1285
34. A Ishida, S Saijo, K Noguchi, et al. *Chem. Pharm. Bull.*, 1979, **27** 625
35. I T Harrison, V R Fletcher *Tetrahedron Lett.*, 1974, 2729
36. A D Bender, et al. *J. Med. Chem.*, 1975, **18** 1094
37. R W King *Tetrahedron Lett.*, 1981, **22** 2837
38. I Vlattas, L D Vecchia *Tetrahedron Lett.*, 1974, (51/52) 4455
39. I Vlattas, L D Vecchia *Tetrahedron Lett.*, 1974, (48) 4267
40. J B Bicking, et al. *J. Med. Chem.*, 1983, **26** 342
41. E W Collington, et al. *J. Chem. Soc., Perkin Trans. 1*, 1990, (7) 1839
42. D L Venton, S E Enke, G C Le Breton *J. Med. Chem.*, 1979, **22** 824
43. F A Lakhvich, T S Khlebnikova *Izv. Akad. Nauk Beloruss. SSR, Ser. Khim.*, 1989, (4) 39
44. G A Tolstikov, et al. *Zh. Org. Khim.*, 1986, **22** Part 6, 1204
45. N F Bondar', et al. *Zh. Org. Khim.*, 1989, **25** Part 3, 656

46. L Novak, P Kolonits, Cs Szantay, et al. *Tetrahedron*, 1982, **38** 153
47. T Tanaka, et al. *Chem. Pharm. Bull.*, 1985, **33** 2359
48. A Hazato, T Tanaka, K Watanabe, et al. *Chem. Pharm. Bull.*, 1985, **33** 1815
49. S Kurozumi, et al. *Synth. Commun.*, 1977, **7** 169
50. Y Naoshima, et al. *Agric. Biol. Chem.*, 1984, **48** 1123
51. R C Larock, D R Leach *J. Org. Chem.*, 1984, **49** 2144
52. B P Cho, V K Chadha, G C Le Breton, D L Venton *J. Org. Chem.*, 1986, **51** 4279
53. S E Hall, W-C Han, D N Harris, et al. *J. Med. Chem.*, 1989, **32** 974
54. D R Morton, J L Thompson *J. Org. Chem.*, 1978, **43** 2102
55. M I Lopp, et al. *Zh. Org. Khim.*, 1988, **24** 2007
56. F Lieb, U Niewohner, D Wendisch *Liebigs Ann. Chem.*, 1987, (7) 607
57. M Narisada, M Ohtani, F Watanabe, et al. *J. Med. Chem.*, 1988, **31** 1847
58. S Hagishita, K Seno *Chem. Pharm. Bull.*, 1989, **37** 323
59. N Hamanaka, T Seko, T Miyazaki, et al. *Tetrahedron Lett.*, 1989, (30) 2399
60. K Seno, S Hagishita *Chem. Pharm. Bull.*, 1989, **37** 948
61. K Seno, S Hagishita *Chem. Pharm. Bull.*, 1989, **37** 1524
62. M J Martinelly *J. Org. Chem.*, 1990, **55** 5065
63. J H Jones, et al. *J. Med. Chem.*, 1977, **20** 44
64. J H Jones, W J Holtz, J B Bicking, E J Cragoe *J. Med. Chem.*, 1977, **20** 1299
65. R Smith, J B Bicking, N P Gould, et al. *J. Med. Chem.*, 1977, **20** 540
66. J B Bicking, J H Jones, W J Holtz, et al. *J. Med. Chem.*, 1978, **21** 1011
67. J B Bicking, C M Robb, E J Cragoe, et al. *J. Med. Chem.*, 1983, **26** 335
68. P A Zoretic, P Soja, T Shiah *J. Med. Chem.*, 1978, **21** 1330
69. P A Zoretic, P Soja, T Shiah *Prostaglandins*, 1978, **16** 555
70. J Saunders, D C Tipney, P Robins *Tetrahedron Lett.*, 1982, **23** 4147
71. H Miyake, et al. *J. Am. Chem. Soc.*, 1977, **99** 3536
72. A E Greene, A Padilla, P Crabbe *J. Org. Chem.*, 1978, **43** 4377
73. S S Ghosh, J C Martin, J Fried *J. Org. Chem.*, 1987, **52** 862
74. G L Bundy, D C Peterson *Tetrahedron Lett.*, 1978, (1) 41
75. E J Corey, H Niwa *Tetrahedron Lett.*, 1979, (8) 671
76. M F Ansell, M P L Caton, P C North *Tetrahedron Lett.*, 1982, **23** 4113
77. S W Djuric, M Miyano, J P Snyder *Tetrahedron Lett.*, 1986, **27** 4403
78. W Skuballa, et al. *J. Med. Chem.*, 1986, **29** 313
79. K Kojima, et al. *Chem. Pharm. Bull.*, 1987, **35** 4000
80. A Takahashi, M Shibasaki *J. Org. Chem.*, 1988, **53** 1227
81. M Shibasaki, et al. *Chem. Pharm. Bull.*, 1989, **37** 1647
82. S Mori, S Takechi *Heterocycles*, 1990, **31** 1189
83. K Bannai, T Toru, A Hazato, et al. *Chem. Pharm. Bull.*, 1982, **30** 1102
84. B Raduchel *Tetrahedron Lett.*, 1983, **24** 3229
85. P Heath *J. Chem. Soc., Perkin Trans. 1*, 1983, (11) 2675
86. P G Baraldi, A Barco, S Benetti, et al. *Tetrahedron Lett.*, 1983, **24** 4871
87. C L J Wang *Tetrahedron Lett.*, 1983, **24** 477
88. L Novak, J Aszodi, Cs Szantay *Tetrahedron Lett.*, 1982, **23** 2135
89. B F Riefling, H E Radunz, E Merck *Tetrahedron Lett.*, 1983, **24** 5487
90. B F Riefling *Tetrahedron Lett.*, 1985, **26** 2063
91. E W Collington, H Finch, C J Wallis *Tetrahedron Lett.*, 1983, **24** 3121
92. P A Aristoff, A W Harrison *Tetrahedron Lett.*, 1982, **23** 2067
93. K C Nicolaou, et al. *J. Am. Chem. Soc.*, 1981, **103** 3472
94. K C Nicolaou, W E Barnette, R L Magolda *J. Am. Chem. Soc.*, 1981, **103** 3486
95. K Shimoji, Y Arai, M Hayashi *Chem. Lett.*, 1978, 1375
96. M Shibasaki, Y Torisawa, S Ikegami *Chem. Lett.*, 1980, 1247
97. M Shibasaki, Y Torisawa, S Ikegami *Tetrahedron Lett.*, 1982, **23** 4607
98. H Yokomori, et al. *Heterocycles*, 1982, **18** Spec. Issue, 251
99. K A Richardson, et al. *Tetrahedron Lett.*, 1985, **26** 1171
100. S Iguchi, Y Miyata, S Okuyama, et al. *Chem. Pharm. Bull.*, 1988, **36** 1128
101. K C Nicolaou, et al. *J. Am. Chem. Soc.*, 1979, **101** 766
102. H W Smith, et al. *Prostaglandins*, 1982, **24** 543
103. B Raduchel *Tetrahedron Lett.*, 1983, **24** 3229
104. M Suzuki, S Sigiura, R Noyori *Tetrahedron Lett.*, 1982, **23** 4817
105. R H Bradbury, K A M Walker *Tetrahedron Lett.*, 1982, **23** 1335
106. R H Bradbury, K A M Walker *J. Org. Chem.*, 1983, **48** 1741
107. H Nakai, et al. *Tetrahedron Lett.*, 1979, (9) 805
108. K Miyajima, M Takemoto, K Achiwa *Heterocycles*, 1988, **27** 643
109. U Bartmann, G Bek, D Knolle, R Rann *Sovremennye Napravleniya v Organicheskom Sinteze* (Modern Directions in Organic Chemistry) (Edited by I P Beletskii), Mir, Moscow, 1986, p. 29
110. A Guzman, E Martinez, E Velarde, et al. *Can. J. Chem.*, 1987, **65** 2164
111. German P. 2 229 225; *Chem. Abs.*, 1973, **78** 111 102q
112. F I Carrol, et al. *J. Med. Chem.*, 1978, **21** 321
113. A Ishida, S Saijo, J-I Himizu *Chem. Pharm. Bull.*, 1980, **28** 783
114. A G Pernet, et al. *Tetrahedron Lett.*, 1979, (41) 3933
115. T A Eggelte, et al. *J. Chem. Soc., Perkin Trans 1*, 1978, (9) 980
116. D R W Hall, A B Funcke, K D Jaitly *Prostaglandins*, 1979, **18** 317
117. German P. 2 813 305; *Chem. Abs.*, 1979, **90** 86 849b
118. J Fried, M M Mehra, W L Kao *J. Am. Chem. Soc.*, 1971, **93** 5594
119. J Fried, et al. *Nature (London)*, 1969, **223**(5202) 208
120. J Fried, M M Mehra, Y Y Chan *J. Am. Chem. Soc.*, 1974, **96** 6759
121. I T Harrison, V R Fletcher, J H Fried *Tetrahedron Lett.*, 1974, (32) 2733
122. US P. 3 883 659; *Chem. Abs.*, 1976, **84** 30 855j
123. I T Harrison, et al. *Tetrahedron Lett.*, 1975, (13) 1165
124. Europ. P. 20 039; *Chem. Abs.*, 1981, **94** 191 785h
125. A K Banerjee, et al. *Br. J. Pharmacol.*, 1981, **73** 225
126. A K Banerjee, et al. *Prostaglandins*, 1981, **22** 167
127. M Hayashi, Y Arai, H Wakatsuka, et al. *J. Med. Chem.*, 1980, **23** 525
128. M Hayashi, H Miyake, S Kori, et al. *J. Med. Chem.*, 1980, **23** 519
129. R M Scribner *Prostaglandins*, 1977, **13** 677
130. German P. 4 174 456; *Chem. Abs.*, 1980, **92** 146 336k

131. M Hamberg, J Svensson, T Wakabayashi, B Samuelsson *Proc. Natl. Acad. Sci. USA*, 1974, **71** 345
132. E J Corey, K C Nicolaou, Y Machida, et al. *Proc. Natl. Acad. Sci. USA*, 1975, **72** 3355
133. G L Bundy *Tetrahedron Lett.*, 1975, (24) 1957
134. C Malmsten *Life Sci.*, 1976, **18** 169
135. G R Gorman, et al. *Proc. Natl. Acad. Sci. USA*, 1977, **74** 4007
136. F A Fitzpatrick, et al. *Nature (London)*, 1978, **275**(5682) 764
137. US P. 4 575 512; *Chem. Abs.*, 1986, **105** 42 538y
138. Japanese P. 8 145 465; *Chem. Abs.*, 1981, **95** 150 445z
139. N H Wilson, et al. *Eur. J. Med. Chem.*, 1989, **23** 359
140. US P. 4 607 048; *Chem. Abs.*, 1986, **105** 226 172f
141. R R Gorman, S Bunting, O V Miller *Prostaglandins*, 1977, **13** 377
142. J E Tateson, S Moncada, J R Vane *Prostaglandins*, 1977, **13** 389
143. G L Bundy, J M Baldwin *Tetrahedron Lett.*, 1978, (16) 1371
144. M K Bach, et al. *Prostaglandins*, 1987, **23** 759
145. D R Morton, F C Brokaw *J. Org. Chem.*, 1979, **44** 2880
146. K Kojima, et al. *Chem. Pharm. Bull.*, 1985, **33** 948
147. G Bundy, F Lincoln, N Nelson, et al. *Ann. N. Y. Acad. Sci.*, 1977, **180** 76
148. P A Zoretic, P Soja *J. Heterocycl. Chem.*, 1977, **14** 1267
149. G C Le Breton, et al. *Proc. Natl. Acad. Sci. USA*, 1979, **76** 4097
150. R R Gorman, et al. *Fed. Proc. Fed. Am. Soc. Exp. Biol.*, 1981, **40** 1997
151. E I Levkoeva, T Ya Shvarts, M D Mashkovskii, L N Yakhontov, et al. *Khim. Farm. Zh.*, 1976, **10**(12) 64
152. A P Kalnin'sh, Ya F Freimanis, K I Dikovskaya, M P Gavars *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, 1990, (1) 78
153. E V Dozha, et al. *Zh. Org. Khim.*, 1990, **26**(5) 1024
154. G A Tolstikov, et al. *Zh. Org. Khim.*, 1990, **26**(2) 451
155. G A Tolstikov, et al. *Zh. Org. Khim.*, 1990, **26**(7) 1484
156. M Murata, S Ikoma, K Achiwa *Chem. Pharm. Bull.*, 1990, **38** 2329
157. US P. 4 861 913; *Ref. Zh. Khim.*, 1990, (22) 220 132P
158. R B Garland, M Miyano, D Piren, et al. *J. Org. Chem.*, 1990, **55** 5854
159. B Buchmann, et al. *Tetrahedron Lett.*, 1990, **31** 3425
160. R C F Jones, J Schofield *J. Chem. Soc., Perkin Trans. 1*, 1990, (2)
161. M J Kelley, et al. *J. Chem. Soc., Perkin Trans. 1*, 1990, (8) 2352
162. T Arima, T Shiramatsu, M Matsuura, et al. *Prostaglandins*, 1990, **39** 319
163. K Suzuki, N Saito, Y Sakata, et al. *Prostaglandins*, 1990, **40** 463
164. S Kamata, N Haga, T Tsuri, et al. *J. Med. Chem.*, 1990, **33** 229
165. M Ohtani, M Narisada *J. Med. Chem.*, 1990, **33** 1027
166. K Ezumi, M Yamakawa, M Narisada *J. Med. Chem.*, 1990, **33** 1117
167. J Das, S E Hall, M Nakane, et al. *J. Med. Chem.*, 1990, **33** 1741
168. M Nakane, J A Reid, W C Han, et al. *J. Med. Chem.*, 1990, **33** 2465
169. F A Dakhvich, et al. *Zh. Org. Khim.*, 1991, **27**(1) 96
170. M Ohtani, et al. *J. Org. Chem.*, 1991, **56** 2122

Translated from *Uspekhi Khimii* **61** 497–522 (1992) U.D.C. 543.544

Supercritical fluid chromatography

M S Vigdergauz, A L Lobachev, I V Lobacheva, I A Platonov

ABSTRACT. The characteristic features of supercritical fluid chromatography (SCFC) are examined and there is a brief historical note concerning the development of the method. Information concerning the use of supercritical fluid chromatography in the analysis of objects of different nature is presented in the form of a table. The roles of the mobile and stationary phases in the separation process and the characteristic features of the apparatus and of the use of the method in physicochemical research are discussed.

The bibliography includes 364 references.

Contents

I. Introduction 267
II. Historical note 267
III. The mobile phase 267
IV. The stationary phase 268
V. Apparatus 273
VI. Qualitative and quantitative analyses 274
VII. Extraction by the supercritical fluid 274
VIII. Physicochemical aspects of the use of supercritical fluid chromatography 274

I. Introduction

In the classification of chromatographic methods in terms of the state of aggregation of the mobile phase (MP) employed, one speaks of gas and liquid chromatography. Supercritical fluid chromatography (SCFC) occupies an intermediate position since a supercritical fluid differs in its properties from those of both a liquid and a gas.

Depending on the nature of the eluent and the conditions under which it operates, one can distinguish the following versions of chromatographic separation:[1] gas chromatography proper (the eluent consists of the usual gases at pressures close to atmospheric); barochromatography (the mobile phase consists of the usual gases at elevated pressures); vapour chromatography (using vapours of volatile liquids); supercritical fluid chromatography (the pressure and temperature of the mobile phase exceed somewhat the critical parameters); density chromatography (the pressure amounts to hundreds and thousands of atmospheres).

The transition to fluid chromatography can be achieved also by transforming the liquid eluent by means of the appropriate changes in temperature and pressure. The distinctive features of the SCFC method are determined mainly by the state of the mobile phase. The following may be included among them:

(1) Specificity of the apparatus (possibility of using individual units comprising liquid and gas chromatographs).

(2) The use of additional devices ensuring the transition of the fluid to the liquid state (employing detectors traditional for liquid chromatography) or gas state (employing gas-chromatographic detectors).

(3) The high solvent power of the fluid which limits the number of suitable stationary phases (SP).

(4) The sharp alteration of the properties of the mobile phase in the vicinity of the critical points, which makes it difficult to obtain stable results for small changes in the separation parameters.

(5) The need to attain effective hermetic seals in all parts of the chromatograph and in the connections.

Examination of the driving and inhibiting factors as well as of the elementary step underlying the separation show that in supercritical fluid chromatography the more detailed classification used in gas and liquid chromatography is also possible.[2]

In all cases (gas and liquid chromatography and SCFC) the driving factor is the stream of mobile phase and the inhibiting factor is physical sorption.

Like gas and liquid chromatography, SCFC can be divided into fluid-adsorption and fluid-liquid chromatography.†

II. Historical note

The first study using a mobile phase in the supercritical state was carried out in 1962.[3] Freons (150–170 °C, pressure up to 136 kg cm^{-1}) were used as the mobile phases. Porphyrins, which are not susceptible to gas-chromatographic analysis because of their thermal instability, were eluted under supercritical conditions. Later the range of eluents employed was expanded, making it possible to analyse polynuclear aromatic hydrocarbons with boiling points up to 600 °C.[4] However, the method was not widely used for many years. a sharp increase in interest in SCFC occurred in the 1980's–1990's. Thus, since 1985 about 400 studies have been published, including two monographs[5,6] and about 20 reviews[7–26]. A number of communications were devoted to the use of the method for the analysis of biologically important organic compounds,[27] its advantages and disadvantages,[28] and also its role in analytical chemistry.[22,28–31] Numerous communications[27,32–127] about the method were delivered at the St. Petersburg Conferences starting in 1985. The first symposium on SCFC was held in 1987.[128]

III. The mobile phase

Substances which are thermally stable above the critical temperature, which undergo no changes on contact with the stationary phase (the latter has a large surface area and can exhibit a

† As in other versions of partition chromatography, in fluid-liquid chromatography adsorption by the solid carrier may make a significant contribution to the separation.

catalytic activity), and which have suitable critical parameters (pressure and temperature) can be used as mobile phases in SCFC. There exists a fairly large list of substances which can be employed as eluents in fluid chromatography.[129] However, in practice only a few of them are commonly used (Table 1). Eluents whose transition to the critical state requires a high temperature or pressure (water with P_{cr} = 226.8 kg cm^{-2} and T_{cr} = 374.4 °C; benzene with P_{cr} = 43.8 kg cm^{-2} and T_{cr} = 288.9 °C) are hardly employed in practice. Many hydrocarbons, for example pentane, isomerise or undergo other reactions when adsorbents with a large surace area are used as the stationary phase[1] (changes occur also in the sorbates), which affect significantly the separation characteristics. Being in the supercritical state, the mobile phase acquires a high solvent power and the diffusion coefficients of the substances dissolved in it are also high under these conditions. This makes it possible to treat the fluid as a mobile phase combining the advantages of the solvent in liquid chromatography with those of the carrier gas in gas chromatography. The main requirements which must be met by the mobile phase in SCFC, as in gas and liquid chromatography, are inertness towards the substances analysed, the stationary phase, and the material of the column and the connections and also compatibility with the detector. The most widely used mobile phase is CO_2 (Table 2). Ethane,[211] butane,[145,176] n-pentane,[25,26,138,176,182,187,203,245] nitrogen oxides,[26,184,189,202,205,215,237,290] fluorine derivatives of sulphur,[186,215,241307,320] hydrocarbons,[126,193] and the intert gases[185,267] are more rarely used. The preferential employment of the non-polar CO_2 as the mobile phase can be accounted for both by the low values of its critical parameters (31.3 °C, 72.9 atm), which makes it possible to carry out the analysis at the usual temperatures, and by the possibility of controlling its selectivity by introducing modifying agents of different nature using a number of procedures:[309,311] methanol,[148,170,179,182] isopropyl alcohol,[156,159,163,170,182] chloromethanes,[159] nitromethane,[163] dioxane,[187] etc. Another advantage of CO_2 as the mobile phase is also the possibility of using virtually all the classical types of detector in conjunction with it (the ionisation-flame detector, the UV detector, mass spectrometers, IR spectrometers, etc.—Table 2). The absence of such advantages in other mobile phases is evidently one of the reasons for their limited application. The difficulties arising in the analysis of polar compounds, which are not fully removed even when modifying agents are employed, must be included among the disadvantages of CO_2. The possibility of obtaining inverted micelles in supercritical fluids such as ethane and propane has been investigated.[311–314] The core of the micelle is capable of being solvated by water, which gives rise to the possibility of the solubilisation in it of polar compounds and their subsequent effective separation during partition between the water-solvated micelles and the non-polar stationary phase. Polar compounds (such as a neutral azo-dye and a protein—cytochrome *c*), which do not dissolve in the pure fluid and in the water-saturated fluid, can dissolve in such a mobile phase. The maximum separation in CSFC is attained with programmed temperature and pressure. It is to be expected that the properties of the mobile phase can vary appreciably over a wide temperature and pressure range and the behaviour of the fluid resembles the behaviour of the mobile phase in liquid or gas chromatography. At the critical pressure and temperature, the mobile phase passes from one state of aggregation to another, which is accompanied by a sharp alteration in the nature of the separation. Fig. 1 presents the dependences of the logarithms of the relative retentions of naphthalene and anthracene on the reciprocal of the absolute temperature using hexane as the mobile phase.[315] It is seen that, on attainment of critical conditions, there is a sharp jump in the relative retention, indicating a change in the state of aggregation of the mobile phase. Thus, contrary to the traditional ideas about the passive role of the mobile phase in the gas-chromatographic process, one may claim that the change in the state of aggregation of the mobile phase alters also the selectivity of the separation. The posibility of controlling the selectivity by altering the state of aggregation of the mobile phase was also noted previously. Solid—liquid, mesomorphous, etc. transitions were achieved in this connection.

Table 1. Properties of certain mobile phases used in supercritical fluid chromatography.[129]

Compound	T_b, °C	T_{cr}, °C	P_{cr}, kg × cm^{-2}	ρ^*, g cm^{-3}
Carbon dioxide	—78.5	31.3	72.9	0.448
Nitrous oxide	—89.0	36.5	71.4	0.457
Ethane	103.6	9.9	50.5	0.227
Butane	—0.5	152.0	37.5	0.228
Pentane	36.3	196.6	33.3	0.232
Methanol	64.7	240.5	78.9	0.272
Isopropyl alcohol	82.5	235.3	47.0	0.279
SF_6	—	45.6	37.1	0.750

*ρ = density of supercritical fluid.

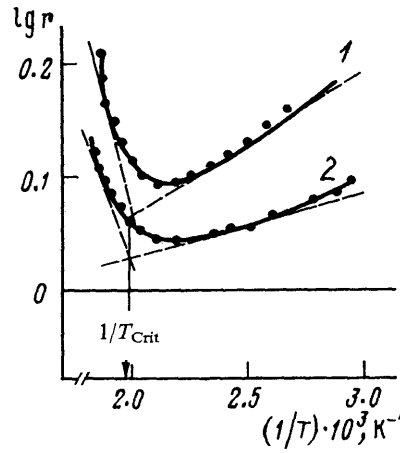


Figure 1. Dependence of the logarithms of the relative retentions of naphthalene (curve *1*) and anthracene (curve *2*) (with benzene as the standard) on the reciprocal of the absolute temperature (average pressure in the column 10 kg cm^{-2}, mobile phase—hexane, 15 × 0.4 cm stainless steel column filled with Silasorb 600).[315]

IV. The stationary phase

Packed columns are used in the fluid-adsorption version and both packed and capillary columns are used in the fluid-liquid version. In the case of capillary columns, cross-linked polysiloxanes are most

often employed as the stationary phase (Table 2): diphenylsiloxane, methylphenylsiloxane, methylsiloxane,[131,153] OC-17,[133,137] OV-225,[137] polysiloxane with grafted *N*-naphthylaminoacid ester,[155] etc. Azo-t-butane[131] or other compounds of a similar type are used as cross-linking agents. Adequate attention has been devoted to problems of the synthesis of stationary liquids for SCFC satisfying the requirements of the virtually complete insolubility in the fluid and thermal stability. Such liquids are cyanoethylphenylvinylmethylpolysiloxane,[316] oligoepoxyethane-containing polysiloxane phases,[317] and chiral stationary phases.[149,166,179] Studies on the swelling of the stationary phases, used in the SCFC with capillary columns, in the fluid and the influence of this process on the retention characteristics are of special interest. In particular, the dissolution of a number of individual mobile phases (pentane, CO_2) and binary mobile phases (methanol–pentane, CO_2–2-propanol) in polysiloxane stationary phases with different ratios of the phenyl and methyl components (OV-1, DV-5, SE-54, OV-17, SE-33) has been investigated.[318–321] In all cases, the soluiblity and adsorbability of the mobile phase diminish with increase in pressure. On raising the pressure above a certain value (which is 260 °C for pentane[320]), the influence of the pressure becomes insignificant. The high solvent power of the mobile phase makes more stringent the requirements as regards the technique of the preparation of the capillary columns.[322–324] Thus it has been shown[322] that the stability of the stationary phase film is directly proportional to the viscosity of the solution. In order to improve the quality of the columns, it is recommended that volatile solvents be employed, raising the temperature of the column during the deposition of the liquid. It is also proposed that a modifying agent can be used to maintain the required viscosity. However, stringent requirements must also be met by such a modifying agent. In experiments with packed columns in the fluid-adsorption version, stationary phases based on silicon dioxide are generally employed: silica gel,[126,180,182,184–186,196,237,255] LiChrosorb Si,[175,183] LiChrosorb Si60,[26,187,197,217,263] LiChrosorb Si 100,[214,224,245,252] PSG porous glass beads,[226] and PRP-I polymeric sorbent.[125] Alumina is hardly used,[295] evidently because of its high catalytic activity under the conditions of the existence of the fluid. In experiments with packed columns, preference is given to grafted sorbents. In this case the sorbents consist of various silica gels with grafted NH_2,[125,173,180,193,233] C_{18},[64,125,175,218] CN,[125,196] and chiral groups,[194,198] as well as others used traditionally in liquid chromatography.

Table 2. Conditions in the separation of mixtures in a stream of supercritical fluid.

System analysed	Mobile phase	Stationary phase, column, detector	Refs
Chlorine-containing compounds, pesticides, n-alkanes, polybutadiene (M = 500), triacylglycerides	Pentane, CO_2	Quartz columns more than 15 m long and with an internal diameter less than 100 μm coated with polymethylphenyl-siloxane ethers (5 or 50% of phenyl)	[Ref. 25]
Polyaromatic hydrocarbons, PS-800 polystyrene	1,4-Dioxane, pentane, C_2H_6, CO_2, N_2O	25 cm × 4.6 mm columns with LiChrosorb Si60; UV detector	[Ref. 26]
Mixture of N,N'-dimethyl aniline, *N*-methylaniline aniline, quinoline, 1,2,3,4-tetrahydroquinoline		IRFT	[Ref. 121]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column, detector	Refs
Lipids	CO_2	IRFT	[Ref. 122]
Fluorocarbon grease	CO_2	9.4 m × 30 μm columns with a 0.20 μm layer of DV-1; FID	[Ref. 123]
Various organic substances	Fluid with 1–2% Ar	Chromatographic separation with subsequent condensation on a cooled (12 K) gold-plated cylinder; the component (argon) matrix formed is analysed on an IR spectrometer	[Ref. 124]
Altemaria toxins in produce (grain, fruit, vegetables)	CO_2 + methanol, CO_2 + isopropyl alcohol	Packed columns filled with SG containing grafted C_1, C_8, C_{18}, NH_2, CN, and other groups; UV detector	[Ref. 125]
Ferrocene derivatives, mixtures of metal acetylacetonates	CO_2 and Freon 23 modified with methanol	Packed columns filled with SG, SG containing grafted C_{18} and phenyl groups or PRP-1 polymeric sorbent; UV detector	[Ref. 126]
Polyphenyls: *o*-, *m*-, and *p*-terphenyls, *o*, *o'*-quaterphenyl, *m*, *m'*-quaterphenyl	CO_2	19.5 m × 100 μm quartz columns coated with a 0.4 μm layer of DV-5 (5% phenylmethylsiloxane); IRFT	[Ref. 130]
Napthalene, phenanthrene, pyrene, and benzopyrene	CO_2	5 m × 25(50) μm quartz columns coated with a 0.15 μm layer of cross-linked SE-54; IRFT	[Ref. 131]
Involatile and thermally unstable compounds	CO_2	MS	[Ref. 132]
n-Alkanes, alcohols	CO_2	20 m × 50 μm quartz columns coated with a 0.25 μm layer of OV-17 SP; FID	[Ref. 133]
Lipids, wax, siloxane oligomers, urine extracts	CO_2	10 m × 50(100) μm quartz columns coated with a 0.2 μm layer of DV-1701 (lipids, urine extracts) or a 0.2 μm layer of DV-5(wax); 20 m × 100 μm quartz columns with a 0.4 μm layer of DV-5 (oligomers)	[Ref. 134]
Triglycerol esters	CO_2	10 m × 50 μm quartz columns with a 0.1 μm layer of methyl-phenyl siloxane 50% phenyl) and a 0.2 μm layer of methyl siloxane	[Ref. 135]
Carbamates and acid pesticides, mixtures of alkanes, triacylcylcerides, oils	CO_2	Quartz columns 2–5 m long with an internal diameter less than 75 μm coated by a 0.15 μm layer of cross-linked SE-54	[Ref. 136]
Triglycerides (T_{36}, T_{48}, T_{42}, T_{54})	CO_2	10 m × 100 μm quartz columns (in a steel tube with a 0.2 μm layer of SE-54, RSL-300, OV-225, and poly(ethylene glycol); FID	[Ref. 137]
Azoaniline and anthraquinone dyes	Pentane	20 m × 50 μm quartz columns with a 0.25 μm layer of cross-linked SE-54; UV detector	[Ref. 138]
Labile carboxylic acids, prostaglandins	CO_2	12 m × 50 μm quartz columns with a 0,25 μm layer of cyanopropylpolysiloxane (and 15 m × 50 μm columns); FID	[Ref. 139]
Glycerol tetraesters	CO_2	10 m × 75 μm columns with a 0.25 μm layer of cross-linked methylphenylpolysiloxane; FID	[Ref. 140]
Medicinal preparations (steroids, therapeutic antibiotics, cannabinoids)	CO_2	13–18 m × 50 μm columns with cross-linked SE-33; FID	[Ref. 141]
Polyaromatic nitrocompounds (polar fraction of diesel extracts)	CO_2	15 m × 50 μm columns with a 0.25 μm layer of cross-linked n-octylpolysiloxane and biphenylpolysiloxane; nitrogen-selective detector	[Ref. 142]
Mono, di, and triglycerides	CO_2	5 and 19 m × 100 μm columns with a 0,25 μm layer of dimethyldiphenylpolysiloxane and cyanopropylmethyldiphenylpolysiloxane: FID	[Ref. 143] [Ref. 144]
Napthalene, phenanthrene, chrysene, picene	Butane, CO_2	Quartz columns of different lengths and with different diameters with a 0.5 μm layer of cross-linked methylsiloxane; fluorescent detector	[Ref. 145]
Isomers of antioxidants, caffeine, sodium arachidonate, testosterone, cholesterol	CO_2	3 m × 0.1 mm columns with a 0.4 μm layer DV-5; redox-chemiluminescent detector	[Ref. 146]
Components of wax, metabolites of triazine pesticides, high-molecular-weight polyaromatic compounds, abietic acid	CO_2	10 m × 50 μm columns with a 0.5 μm layer of SB-phenyl-5; MS	[Ref. 147]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column, detector	Refs
49 compounds used in agro-chemistry	CO_2 modified with methanol	20 m × 100 μm columns with SE-33 and SB-cyanopropyl-25; UV detector	[Ref. 148]
N-pentafluoro-propionylisopropyl esters and the D- and L-isomers of methionine	CO_2	20 m × 200 μm columns with a 0.15 μm layer of polysiloxane cotaining 7% of a chiral amide; FID	[Ref. 149]
Extract of acid herbicides, mixture of volatile and involatile components	CO_2	19.5 m × 100 μm columns with a 0.4 μm layer of DV-5; FID	[Ref. 150]
Oligo- and poly-saccharides (18 glucose fragments)	CO_2	10 m × 65 μm columns with a 0.2 μm layer of DV-1; FID	[Ref. 151]
Squalane (lipid standard), 1,3-distearin, 1,2-dipalmito-stearin	CO_2	10 m × 75 μm columns with cross-linked methylphenylpoly-siloxane (50% of phenyl); FID and MS	[Ref. 152]
Pyrrolizidine alkaloids	CO_2	10 m × 50 μm columns with SB-biphenyl-30; MS	[Ref. 153]
C_{10}, C_{24}, and C_{36} normal hydrocarbons, crude petroleum, napthalene, hydrogenated triglycerides	CO_2	16.5 m × 50 μm columns with a 0.25 μm layer of SE-54 deactivated by polymethyl-hydrosiloxane	[Ref. 154]
Norephedrine derivatives, amino acids	CO_2	10 m × 50 μm columns with *N*-napthyl--amino acid ester grafted on polymethyl--siloxane; FID	[Ref. 155]
Mixture of hydrocarbons, caffeine, polyethylene-propylene	CO_2	10 m × 50 μm columns with a 0.25 μm layer of SB-biphenyl-30; extraction with supercritical fluid; FID	[Ref. 156]
Mixture of glycerides, mixture of hydrocarbons	CO_2 with $HCOOH + H_2O$	10 m × 50 μm columns with a 0.2 μm layer of polysiloxanes; FID	[Ref. 157]
Pesticides and metabolites, dimpylatodiisocyanato-toluene, Triton X-100, tetrahydrocannabinol	CO_2	15 m × 50 μm columns with a 0.25 μm layer of SB-methyl-100; FID; thermionic detector	[Ref. 158]
Phenanthrene, chrysene, picene, coronene, naphthalene and their derivatives	CO_2, CO_2 + + 2-propanol, $CO_2 + CH_2Cl_2$	10 m × 50 μm columns with a 0.25 μm layer of 100% methylpolysiloxane; UV detector	[Ref. 159]
Coal tar, polymeric additives	CO_2	Columns with methylpolysiloxane (10 m × 50 μm) and SG containing grafted C_{18} groups (25 × 4.6 mm); FID	[Ref. 160]
Pyrethrin	CO_2	IR spectrometer	[Ref. 161]
Caffeine, cocaine, codeine, sulphonamides, pesticide carbamates	CO_2	Columns of different lengths with an internal diameter of 50 μm; MS	[Ref. 162]
Coal tar extract, pyrene, ovalene	CO_2 CO_2 + + 2-propanol, CH_3NO_2	10 m × 50 μm columns with a 0.25 μm layer of 100% cross-linked methylpoly-siloxane; UV detector	[Ref. 163]
Surfactants, polyglycols (M = 1200), dimethyl-polysiloxane	CO_2	3–20 m × 50 μm columns with SB-bi--phenyl-30 and SB-methyl-100; FID	[Ref. 164]
Wax, crude petroleum	CO_2	20 m × 100 μm columns with a 0.1 μm layer of cross-linked VR-1; FID	[Ref. 165]
Isopropyl esters of 3,5-dinitrobenzamides	CO_2	5–10 m × 50 μm columns with a cross-linked polymeric chiral SB; FID	[Ref. 166]
Sulphur-containing poly cyclic compounds	CO_2, CO_2 + + N_2O	10 m × 50 μm columns with a cross-linked SE-30; plasma detector	[Ref. 167] [Ref. 168]
Explosive (traces)	CO_2	6.8 m × 0.05 mm columns with a 0.25 μm layer of super-cross-linked SB-octyl-50; thermoenergetic detection	[Ref. 169]
Polycyclic aromatic hydrocarbons and their nitro-derivatives	CO_2, CO_2 + + methanol	25 cm × 1.3 mm columns with Spher C_{18}; UV detector	[Ref. 170]
Poly(ethylene oxide), Triton X-305, polycaprolactone diol, epoxy-polymers	CO_2, CO_2 + + methanol, CH_3CN	25 cm × 4.6 mm columns, polystyrene SP, PRP-1, and LiChrosorb Si 100; UV detector	[Ref. 171]
Mixture of polyaromatic hydrocarbons	CO_2, CO_2 + + 7 modifying agents	20 cm × 4.6 mm columns with SG containing grafted diol groups; 15 cm × × 4.5 mm columns with SG containing grafted octyl groups; UV	[Ref. 172]
Polyaromatic hydrocarbons extracted from coal tar	CO_2	Series-connected packed columns filled with silica gel containing grafted amino-groups and octadecyl groups	[Ref. 173]
Coffee extract from roasted coffee grains, coffee grain powder	CO_2	Extraction with supercritical fluid followed by separation; UV detector	[Ref. 174]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column detector	Refs
Mixture of polyaromatic hydrocarbons, mixture of phenol derivatives, mixture of unsaturated mono-aromatic hydrocarbons	CO_2, CO_2 + + polar modi-fying agents	15–25 cm × 4.6 columns filled with SG containing grafted C_{18} groups and LiChrosorb Si 60; UV detector	[Ref. 175]
Polyaromatic hydrocarbons	Propane, butane pentane, iso--butane	UV detector	[Ref. 176]
High-boiling residues from North Sea petroleums	CO_2	25 cm × 1.3 columns with CP-Spher Si; 30 cm × 2.1 mm columns with Spher-5 containing grafted cyano-groups; 25 cm × 1.3 mm columns with SG impregnated with 1% $AgNO_3$ solution; FID	[Ref. 177] [Ref. 178]
Phosphine oxide enantiomers	CO_2, CO_2 + + alcohols, CO_2 + alcohol mixtures	10 cm × 4.6 mm steel columns filled with the chiral Pirkle phase (LiChrosorb with grafted NH_2 groups); UV detector	[Ref. 179]
Unpurified urine extract, medicinal drugs, multi-component mixtures of polar and non-polar substances	CO_2	20 cm × 2.1 mm columns filled with SG or Spherosorb containing amino- and nitrile groups; MS	[Ref. 180]
Sucrose polyethers in a mixture with aliphatic acids	CO_2	10 m × 65 μm columns with a 0.20 μm layer of DV-1; FID	[Ref. 181]
Aromatic hydrocarbons	CO_2, CO_2 + + methanol	Packed columns filled with SG, Develosil ODS, and a chiral SP; UV detector	[Ref. 182]
Mixture of xanthines, carbamates, sulphon-amides, steroids, and ergot alkaloids	CO_2, CO_2 + + methanol or methoxyethanol	10 cm × 4.6 mm columns filled with LiChrosorb or Spherosorb containing grafed NH_2 groups; MS	[Ref. 183]
Group analysis of petroleum	NO, CO_2	3 columns with Spheri-5-cyano-MPLC, SG CP-Spher, SG impregnated with $AgNO_3$; FID	[Ref. 184]
Polyaromatic hydrocarbons in extracts of aerosol particles in diesel engine exhaust gases	CO_2	Extraction with supercritical fluid followed by separation on 15 cm × 4.6 mm columns with Develosil ODS-5; UV detector	[Ref. 127]
2-Methyl-1, 4-naptho--quinone, acenapthene--quinone phenan-threnequinone	CO_2 + methanol	25 cm × 1 mm columns filled with SG; IRFT	[Ref. 185]
Group analysis of petrols and petroleum products (up to 350 °C)	SF_6 CO_2	25 cm × 1 mm columns with SG; FID 25 cm × 4.6 mm columns with SG and SG impregnated with $AgNO_3$; FID	[Ref. 186] [Ref. 178]
Oligostyrene PS 800 (M = 810), mixture of napthalene, anthracene, pyrene, and chrysene	Pentane, 1,4-dioxane	25cm × 4.6 mm columns with LiChrosorb Si 60; UV detector	[Ref. 187]
Polyaromatic hydrocarbons from diesel fuel exhaust gases	CO_2, CO_2 + + methanol	Extraction with supercritical fluid followed by gas-chromatographic analysis	[Ref. 188]
Aromatic aldehydes and ketones, polyaromatic hydrocarbons, epoxy-acrylate oligomers	Xenon	17 m × 150 μm columns coated by cross-linked SE-54; IRFT	[Ref. 189, 190, 191]
Mixtures of petroleum and coal origin	CO_2	Semi-preparative SCFC, columns with an internal diameter of 30–70 μm filled with SG containing grafted NH_2 groups; UV detector, FID	[Ref. 192]
Mixture of aniline and its derivatives, mixture of phenols, ethers, and alcohol	CO_2, CO_2 + + methanol, Freon-23	25 cm × 4.6 mm columns filled with SG containing grafted NH_2 and phenyl groups; UV detectors, IRFT	[Ref. 193]
Racemic mixtures of t-butyl esters of *N*-acetylamino-acids	CO_2, CO_2 + + methanol, methyl ether	25 cm × 4 mm columns filled with a chiral sorbent (*N*-formyl-L-valylaminopropyl grafted to SG); UV detector	[Ref. 194]
Polydimethylsiloxane, acenapthenequinone	CO_2	19.5 m–100 μm columns with a 0.4 μm layer of DV-5; IRFT	[Ref. 195]
Polyaromatic hydrocarbons, aromatic amines, alkyl-benzenes, chlorobenzenes, dialkyl phthalates, azo-compounds	CO_2 + modifying agents	Packed columns filled with SG and SG containing grafted diol and CN groups; FID	[Ref. 196]
Oligostyrenes PS 8000	CO_2 + 1,4--dioxane	25 cm × 4.6 mm columns with LiChrosorb Si 60	[Ref. 197]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column, detector	Refs
Optical isomers of α-aminoacid derivatives	CO_2, methanol	20 cm × 4 mm columns with a chiral SP (SG with grafted *N*-formylvaline); UV detector	[Ref. 198]
Sulphur-containing heterocyles in vacuum cracking residues	CO_2	Extraction with supercritical fluid followed by gas -chromatographic analysis	[Ref. 199]
Liquid crystal mixtures	CO_2	Packed columns with SG containing grafted C_{18} groups; UV detector	[Ref. 200]
8 esters	CO_2	12.5 cm × 5 mm columns filled with Spherisorb ODS-2; UV detector	[Ref. 201]
Polyaromatic hydrocarbons in ash, dust, and river bottom deposits	N_2O, CO_2, N_2O + methanol	Extraction with supercritical fluid followed by gas-chromatographic determination	[Ref. 202]
Polystyrene oligomers	Pentane	1 m × 260 μm columns with Develosil ODS; UV detector	[Ref. 203]
Polyaromatic hydrocarbons	CO_2	22 cm × 4.6 mm columns filled with SG containing grafted C_{18} groups and 15 cm × 4.6 mm columns with Develosil ODS-5	[Ref. 204]
Polyaromatic hydrocarbons, nicotine, and related compounds in cigarette ash, etc.	CO_2 or N_2O	Extraction with supercritical fluid followed by gas-chromatographic determination	[Ref. 205]
Polyaromatic hydrocarbons	CO_2, CO_2 + + modifying agent	25 cm × 4.6 mm columns filled with LiChrosorb Si 100; UV detector	[Ref. 206]
Anthraquinone in paper and wood	CO_2	Extraction with supercritical fluid followed by HPLC analysis	[Ref. 207]
Styrene oligomers A500 and A1000, components of OU-17 Nonidet P-40 detergent	methanol, diethyl ether	Columns with Develosil-100-5 and Develosil ODS-5; UV detector	[Ref. 208]
Racemic amides and phosphine oxides	CO_2, CO_2 + CH_3OH, C_2H_5OH	25 cm × 4.6 mm columns (SP with grafted β-cyclodextrin); 25 cm × 4.6 mm columns with Pirkle covalent phase [(*R*)-*N*-3, 5-dinitro-benzoylphenylglycine]; UV detector	[Ref. 209]
Ferrocenes	CO_2	25 cm × 1 mm columns with Shimpak Diol-150; detector—emission spectrometer with atomisation in a plasma	[Ref. 210]
Polystyrene standard (M = 1574)	CO_2, ethane	UV detection	[Ref. 211]
n-Alkanes, alkyl aryl ketones, terpenes, polyaromatic hydrocarbons	CO_2	20 cm × 3 mm columns with Spherisorb ODS-2; FID	[Ref. 212]
Polyaromatic hydrocarbons	CO_2	Extraction with supercritical fluid followed by gas-chromatographic analysis	[Ref. 213]
Polyaromatic hydrocarbons	alkanes, CO_2	25 cm × 4.6 mm columns with LiChrosorb Si 100	[Ref. 214]
Aerosols in a stream of eluent	CO_2, N_2O, pentane, benzene, SF_6	Detection by laser light scattering method	[Ref. 215]
Mixtures of docosane and pyrene, triacylglycerides, fructose and sucrose, opium alkaloids	CO_2, CO_2 + polar modifying agents	10 – 20 cm × 4.6 mm columns filled with Sorbax BP Sil, Micropak MCH, Spherisorb containing grafted NH_2 groups, SG containing grafted C_{18} groups	[Ref. 216]
Polyaromatic hydrocarbons, petroleum products	CO_2	15 – 50 cm × 1 mm columns (Sorbax BP Sil); 15 cm × 4.6 mm columns (LiChrosorb Si 60); 15 cm × 4.6 mm columns (Spherisorb ODS-2); 15 cm × 4.6 mm columns (SG XOA 800); FID	[Ref. 217]
Phthalates, styrene oligomers, polyaromatic hydrocarbons	CO_2	10 cm × 0.3 mm columns filled with Develosil ODS-3K and ODS-5K; UV detector	[Ref. 218]
Binary mobile phases	CO_2 with organic modifying agents	20 cm × 4.6 mm columns filed with Sg containing diol groups; UV detector and detection in the visible region of the spectrum	[Ref. 219]
Complex organic compounds on various adsorbents; resins, foil, dust, Spherocarb, etc.	CO_2, isobutane, methanol and binary MP	Extraction with supercritical fluid	[Ref. 220]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column, detector	Refs
Baldenon (a steriod preparation), medicinal drugs with a COOH group	CO_2	10 m × 5 μm and 5 m × 25 μm columns with grafted SB-methyl and SB-octyl phases; MS	[Ref. 221]
Napthalene, fluorene, phenanthrene, pyrene	CO_2	25 cm × 4.6 mm columns filled with grafted Spherisorb ODS-2 carrier	[Ref. 222]
Polyaromatic hydrocarbons	CO_2	Packed columns having an internal diameter of 4.6 mm with SG and SG containing grafted C_{18}, diol, diphenyl[biphenyl], and napthyl-ethyl groups; UV detector	[Ref. 223]
Polystyrene standards, mixture of aromatic hydrocarbons	Pentane, dioxane	25 cm × 4.5 mm columns filled with LiChrosorb Si 100; UV detector	[Ref. 224]
Thermolabile herbicides from sandy, loamy soils	CO_2, CO_2 + + methanol	Extraction with supercritical fluid	[Ref. 225]
Styrene and methylphenylsiloxane oligomers	Methanol, diethyl ether	Packed columns with PSG-10 porous glass beads (d = 11.5 μm, pore size 178 Å)	[Ref. 226]
Benzyl chloride	CO_2	15 cm × 4 mm columns with Silasorb 600 Silasorb containing grafted C_{18} groups	[Ref. 227]
Solid samples	CO_2	Extraction with supercritical fluid	[Ref. 228]
"Maoming" oil shale		Extraction with supercritical fluid	[Ref. 229]
Polyethylene PE-70	CO_2	10 cm × 1 mm and 20 cm × 1 mm columns SG containing grafted poly--siloxane	[Ref. 230]
Steroids, benzodiazepines opiates	CO_2	16 m × 100 μm SCFC columns with SPB-1; 30 m × 250 μm gas-liquid chromatographic columns with DV-5; detection based on ionic mobilities	[Ref. 231]
Sulphonoamide preparations and antibiotics	CO_2, CO_2 + isopropyl alcohol	10 cm × 1 mm columns with cyanodeltabond; 15 cm × 1 mm columns with Spherisorb 5ODS2; 7 m column with SB-cyanopropyl-25, SB-methyl-100, and SB-biphenyl-30	[Ref. 232]
Amines, Azaarenes	CO_2	25 cm × 4.6 mm and 25 cm × 1 mm columns with grafted amino-groups and nitrile groups; FID, IRFT	[Ref. 233]
Enantiomers of 3-thienylcyclohexylglycollic acid	CO_2, CO_2 + + methanol	25 cm × 4.6 mm columns with Cyclobond CSP and chiral OB gel; UV detector	[Ref. 234]
Phenmedipham, aldicarb	CO_2	10 m × 100 μm columns with SB-methyl-100; IRFT, FID	[Ref. 235]
Alkaloids from the leaves of *Catharanthus roesus*	CO_2 + methanol	10 cm × 4.5 mm columns with Spherisorb; UV detector, MS	[Ref. 236]
Ketoacids from urine	NO	10 m × 50 μm columns with cross-linked SE-30; thermionic detector	[Ref. 237]
Siloxane liquids, fats	CO_2	10 m × 50 μm columns with a 0.2 μm layer of DV-5 and 25 m × 100μm columns with a 0.2 μm layer of SE-24; FID	[Ref. 238]
Herbicides, pharmaceutical preparations	CO_2	6 m × 50 μm columns with a 0.25 μm layer biphenylyl-siloxane; MS	[Ref. 239, 240]
Group analysis of petrols and middle distillates of fuel	SF_6 + CO_2	25 cm × 1 mm columns with SG; 25 cm × × 2.1 mm columns with $AgNO_3$-treated Nucleosil SA; FID	[Ref. 241]
Hydroxyethylated alcohols	CO_2	Columns 5 m long containing methylpolysiloxane; FID	[Ref. 242]
Polystyrene oligomers, pyridine, phenol	CO_2	Packed columns with SG of diferent porosity (70 – 1100 Å) containing grafted C_{18} groups (2 – 17%); UV detector	[Ref. 243]
Solid samples containing organic compounds		Extraction with supercritical fluid followed by gas-chromatographic analysis	[Ref. 244]
Napthalene, anthracene, pyrene, chrysene	Pentane	24 cm × 4.6 mm columns with LiChrosorb Si 100; UV detector	[Ref. 245]
Group separation of petroleum components	CO_2	8 – 10 and 15 m × 200 μm columns with a 0.15 μm layer of liquid crystal poly--siloxane	[Ref. 246]
Enantiomers of 1,2-aminoalcohols	CO_2 + ASCCI	10 × 30 cm × 4.6 mm columns with CS, GN phase; UV detector	[Ref. 247]
Mixtures of polymers, aldicarb and its metabolites, mixtures of monomers, dimers, and trimers of diisocyanatotoluene	CO_2	15 m × 50 μm columns with SB-biphenyl--30; 12 m × 50 μm columns with 50% cyanopropyl-siloxane; 20 m × 50 μm columns with SE-63;FID	[Ref. 248]
Analysis of traces of organic substances	CO_2	Capillary columns with poly-siloxane SP; all types of detectors	[Ref. 249]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column, detector	Refs
Group and individual analysis of petrols	CO_2	SCFC and gas chromatography, 25 cm × 4.6 mm columns with SG; 25 cm × 4.6 mm columns with SG impregnated with $AgNO_3$; 10 cm × × 4.6 mm columns with cation-exhange SG; 25 cm × 4.6 mm columns with SG containing grafted amino-groups; FID	[Ref. 250]
Palladium β-diketonates	CO_2 + methanol	Series-connected 5 cm × 4.6 mm and 30 cm × 4.6 mm columns with LiChrosorb Si 60 and a 25 cm × 4.6 mm column with SG containing grafted C_{18} groups; UV detector	[Ref. 251]
Caprolactonediol and methyl methacrylate oligomers	$CO_2 + CH_3CN$	25 cm × 4.6 mm columns with LiChrosorb Si 100; UV detector	[Ref. 252]
Polyaromatic hydrocarbons in marine deposits	CO_2	25 cm × 1 mm columns with Spherisorb-5; FID photoionisation detector, MS	[Ref. 253]
Oil from lemon peel	CO_2	Extraction with supercritical fluid; MS	[Ref. 254]
8 organophosphorus pesticides	CO_2, CO_2 + + 2-propanol	10 cm × 1 mm columns with SG and SG containing grafted amino-groups and C_{18} groups;MS	[Ref. 255]
Chemical additives to polymers (21 compounds)	CO_2	15 m × 100 μm columns with a 0.5 μm layer of phenylmethylpolysiloxane; FID, IRFT	[Ref. 256]
Components of the smell of natural produce	CO_2	Extraction with supercritical fluid followed by gas-chromatographic analysis	[Ref. 257]
Free aliphatic acids	$CO_2 + H_2O$	10 cm × 1 mm column filled with 7 different SP; FID	[Ref. 258]
Oligosaccharides	CO_2	10 m × 50 μm columns with a 0.2 μm layer of DV-5; MS	[Ref. 259]
Essential oils, petroleum products	CO_2	Extraction with supercritical fluid	[Ref. 260]
Herbicides based on sulphonylurea and their metabolites	CO_2 + polar modifying agents	Extraction with supercritical fluid followed by SCFC analysis	[Ref. 261]
Homologous series of alkylarenes and n-alkanes	CO_2, CO_2 + + methanol, CH_3CN	15 cm × 4.6 columns with styrene–di--vinyl-benzene copolymer (PLRP-S); UV detector	[Ref. 262]
Metal carbonyls, highly viscous motor oils, standard aromatic hydrocarbons	CO_2, CO_2 + + methanol, CH_3CN	Extraction with supercritical fluid followed by SCFC analysis	[Ref. 263]
Ecdysteroids, phytoecdysteroids	CO_2 + methanol	2 cm × 4.6 mm columns with SG; UV detector, MS	[Ref. 264, 265]
Basic nitrogen-containing substances	CO_2, CO_2 + + methanol	25 cm × 1 mm columns with Deltabond; FID	[Ref. 266]
Terpenes	Xenon	40 cm × 100 μm columns with Spherosil--XOA-800 SG; UV detector	[Ref. 267]
Methyl palmitate	CO_2, CO_2 + + 1-hexanol	10 m × 100 μm columns with a 0.5 μm layer of SB-methyl-100; IRFT	[Ref. 268]
Aromatic hydrocarbons	CO_2	10, 15, and 25 cm × 2.1 and 4.6 mm columns filled with SG containing grafted C_{18} groups	[Ref. 269]
Poly(methyl-3,3,3-tri--fluoropropyl)siloxane	CO_2, CO_2 + + 2-propanol	MS	[Ref. 270]
Mixtures of nitro-derivatives of diphenylamine and aniline	CO_2	10 cm × 1 mm columns with a sorbent containing cyano-propyl groups, 10 m × 100 μm column with a 0.25 μm layer of SB-cyano-propyl-25; IRFT	[Ref. 271]
Diuron and its metabolites	CO_2 + methanol	15 cm × 4.6 mm columns filled Rosil C_{18}; UV detector	[Ref. 272]
Benzene derivatives (6 compounds)	CO_2, CO_2 + + methanol	30 cm × 4.6 mm columns filled with SG containing grafted C_{18} groups; 17.5 cm × 4.6 mm columns with a polydivinyl--benzene sobent containing C_{18} groups; UV detector	[Ref. 273]
Polychlorinated biphenyls, polyaromatic hydrocarbons, heterocycles, $C_{12}-C_{24}$ alkanes	CO_2	Extraction with supercritical fluid from polyurethane foam followed by chromatograph-linked mass-spectrometric analysis	[Ref. 274]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column, detector	Refs
Pesticides	CO_2	Extraction with supercritical fluid followed by HPLC analysis	[Ref. 275]
Explosives, side products	CO_2	25 cm × 1 mm columns with Deltabond containing cyano-groups: IRFT	[Ref. 276, 277]
8 nitro-derivatives	CO_2	1.5–2.5 cm × 1 mm columns, Deltabond containing grafted cyano-groups	[Ref. 277]
Aminoacids	$CO_2 + CH_3OH$, H_2O, CH_3NH_2	15 cm × 4.6 mm columns filled with SG of the Nucleosil-100 type	[Ref. 278]
Docosanol and palmitic acid	CO_2 + methanol	15 cm × 4.6 mm columns filled with Sorbax ADS and LiChrosrob RP-18; vaporisation light scattering-based detection	[Ref. 279]
Mixtures of steroids	CO_2	10 m × 100 μm column with SB-cyano--propyl-25;IRFT	[Ref. 280]
α-Pinene and its oxidation products	CO_2	Extraction with supercritical fluid followed by SCFC analysis	[Ref. 281]
Oil triacylglycerides	CO_2	5 m × 50 μm columns with a 0.2 μm layer of DV-5; MS	[Ref. 282]
Anthracene, dichlorobi--phenyl sulphone, triazopan,vitamins, steroids	CO_2	Packed 10 cm × 1 mm and capillary 6 m × 50 μm columns; photoionisation detector	[Ref. 283]
Tocopherols from wheatgerm	CO_2 + alcohol	Extraction with supercritical fluid followed by HPLC analysis of fractions	[Ref. 284]
Complex organic compounds	CO_2 + methanol	15 cm × 4.6 mm columns filled with Nucleosil containing grafted C_{18} groups or with Rosil containing aminopropyl groups; MS	[Ref. 285]
Sulphor-containing antioxidants and heterocycles isolated from objects in the environment	CO_2	3.5 m × 100 columns with a 0.4 μm layer of DV-5; chemiluminescence detector of atomic sulphur	[Ref. 286]
Sesquiterpenes	CO_2	25 cm × 4.6 mm columns filled SG of the Nucleosil-100 or Spherisorb type; IRFT	[Ref. 287]
Ethoxyethylated alcohols, inositol triphosphate, peroxides	CO_2	10 m × 50 μm columns with a 0.5 μm layer SB-methyl-100; FID and MS	[Ref. 288]
Phenylthiohydantoin derivatives of aminoacids (24 compounds)	CO_2 + modifying agent	25 m × 4.6 mm columns filled with Sorbax containing grafted cyano-groups; UV detector	[Ref. 289]
Steroids in plasma and urine	N_2O	10 m × 50 μm columns with polymethyl--hydrosiloxane; thermionic detector	[Ref. 290]
Sulphur-containing organic compounds	CO_2	20 m × 100 μm columns with a 0.2 μm layer of DV-1701; flame-photometric detector	[Ref. 291]
Polyaromatic hydrocarbons	CO_2	10 m × 50 μm columns with a 0.5 μm layer of SB-phenyl-5; MS	[Ref. 292]
Trimethoprim, hexoestrol, diethylstilboestrol, dienoestrol, sulphamethazine in pig kidneys	CO_2	Extraction with supercritical fluid followed by SCFC analysis	[Ref. 293]
Biphenylylmethylsiloxane	CO_2	4 m × 0.5 mm columns with SB-phenyl-5; UV or fluorimetric detector	[Ref. 294]
C_{21}, C_{24}, C_{26}, C_{28}, C_{31} n-alkanes, caffeine	CO_2	10 cm × 1 mm columns filled with Al_2O_3 in the alcoholic form and Deltabond containing grafted cyano-groups	[Ref. 295]
Organic components of river or ground water	CO_2	1.8 mm × 0.25 mm columns with Spheri--sorb ODS, 10 m × 50 μm columns with a 0.25 μm layer of cross-linked SE-30, concentration on Sep-PAK C_{18}; UV detector, FID	[Ref. 296]
Organic isocyanates	CO_2	Columns with an internal diameter of 10 μm SP: SB-methyl-100 (0.5 μm), SB-biphenyl-30 (0.25 μm), SB-octyl-50 (0.5 μm)	[Ref. 297]
Napthalene, biphenyl, phenanthrene, n-alkanes	CO_2	10 m × 100 μm columns with BP-1 and 12 m × 100 m columns with BP-10; FID	[Ref. 298]
Aromatic hydrocarbons from furnace and diesel fuel	CO_2	Columns filled with SG; FID	[Ref. 299]
Azaarenes	CO_2 + methanol	SG with grafted amino-groups UV	[Ref. 300]
Polymethylphenylsiloxane oligomers	Alcohol + C_6H_{14}	detector 10 cm × 0.35 mm columns; IRFT	[Ref. 301]
Herbicides and pesticides ($\overline{M}$ = 200–350)		Comparison of the characteristics of the determination by the HPLC and SCFC methods using capillary and packed columns; FID, UV detector , selective detector of nitrogen and phosphorus	[Ref. 302]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column, detector	Refs
Aromatic hydrocarbons	CO_2	25 cm × 4.6 mm columns filled with SG containing grafted C_{18} groups; UV detector	[Ref. 303]
Up to C_{90} n-alkanes from Polywax 655, oil, triglycer--ides esters of cholesterol and aliphatic saturated and unsaturated acids	CO_2	5–25 m × 0.2–0.53 mm columns with a 0.1–0.25 μm layer of polymethyl- and polymethylphenyl-siloxanes (comparison with gas-liquid chromatography on capillary columns)	[Ref. 304]
Mixtures of mineral oils, polydimethyl-siloxanes, etc	CO_2	10 m × 0.1 mm capillary columns; FID	[Ref. 305]
Benzoic and isophthalic acids and their methyl esters	11 different MP	Capillary columns with internal diam-eters of 77 and 100 μm with DV-5 and Carbowax; UV detector, IRFT	[Ref. 306]
1-Decanol and its deriva-tives (7 compounds)	SF_6	5 m × 100 μm columns with methylpoly-siloxane; FID	[Ref. 307]
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin from specimens of aqueous deposits	CO_2 + methanol	Extraction with supercritical fluid	[Ref. 308]

Note. SG = silica gel; FID = flame-ionisation detector, MS = mass spectrometer, IRFT = IR spectrometer with Fourier transform, ASCCI = acetonitrile solution of the counterion and the $N(C_2H_5)_3$ $[N(C_2H_5)_3H^+?]$ competing ion, HPLC = high performance liquid chromatography.

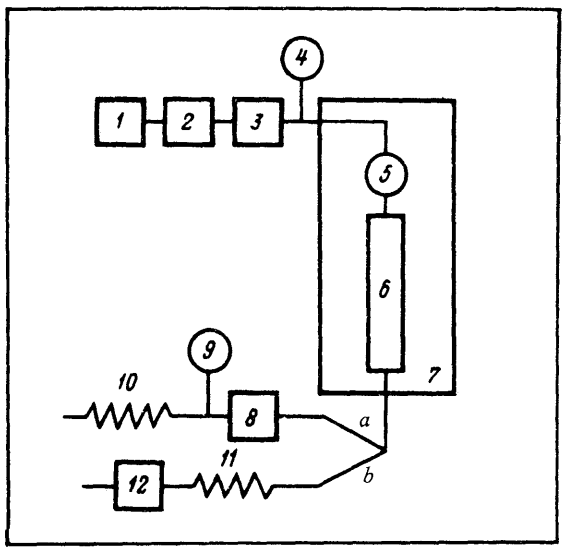


Figure 2. Block diagram of the fluid chromatograph: *1*, cylinder; *2*, pressure reducer; *3*, pump; *4*, manometer; *5*, metering tap; *6*, chromatographic column; *7*, column thermostat; *8*, UV detector; *9*, reference manometer; *10* and *11*, restrictors; *12*, ionisation detector.

V. Apparatus

The formation of the fluid can be regarded as transition from one state of aggregation of the mobile phase to another (from liquid to gaseous and conversely). The separation of various mixture requires the correct combination of individual units comprising liquid or gas chromatographs. Here it is necessary to ensure, on the one hand, a stable high pressure in the system and, on the other, the possibility of detection in the fluid flow. A block scheme of an SCF chromatograph is illustrated in Fig. 2. One may note two principal aspects of the construction of the apparatus: the improvement of the design of the detectors and of the intermediate devices for the connection of the SCF chromatograph to other instruments for physicochemical research and also the development of the restrictor technology and of the technique for the injection of the sample.[325,326] The technique of the injection of the sample in SCFC with capillary columns is approximately the same as in gas chromatography: sample injection with stream splitting, injection with stream splitting and maintenance for a period of time, direct injection, and injection with extraction by the supercritical fluid.[327] In view of the small diameter of the capilliary columns in SFC (50–100 μm compared with 200–500 μm in gas chromatography), the use of automated systems with a programmed sample injection cycle (from 50 μs to 2 s) is promising.[328] The loop-type metering taps with stream splitting generally adopted in high performance liquid chromatography, are widely used.

The high pressure necessary to maintain the mobile phase in the supercritical fluid state hinders the application of detectors traditionally employed in high performance liquid chromatography (HPLC) or gas chromatography. Flame-ionisation detectors (FID) and UV detectors are most often used for detection in SCFC (Table 2). The columns are connected to the detecting systems via a restrictor which is placed before or beyond the detector in order to prevent a sharp change in the pressure in the system. For detection in a stream of liquid, the restrictor is placed beyond the detector (for example, in the case of UV detection). If a FID is used in the chromatograph, the placing of the restrictor beyond the column makes it possible to direct the stream of the mobile phase immediately into the detector. Quartz capillaries (straight capillaries, tapering capillaries,[329] and capillaries coiled into a helix) and partly fused ends of the columns (the so called integral restrictors[134]) can function as restrictors. The study of the effectiveness of capillary restrictors[329–331] showed that the restrictor must be heated, which makes it possible to eliminate the losses of the compounds being analysed and to control the linear flow rate of the mobile phase in the column by programming the temperature. The FID are used in SCFC virtually without any modifications. Certain complications arise when UV detectors are employed because their cell is not always designed for the necessary pressure. A detecting device for SCFC designed for pressures up to 500 kg cm^{-2} has been proposed.[332] Its working cell consists of a section of a capillary with a remote polyimide coating and three optical wave guides perpendicular to its axis. UV beams are directed into the cell through one of them but the other two are used for the simultaneous observation of the fluorescence and the absorption of UV radiation. For the combination of the SCF chromatograph with a mass spectrometer,[333–338] an appropriate interface is essential. Judging from the existing reviews,[334] there is reason to believe that appreciable advances have been made in this field. As in the classical versions of chromatography, in the analysis of sulphur and phosphorus compounds by SCFC a flame-photometric detector is used[339] which makes it possible to detect nanogramme amounts of sulphur and phosphorus. IR spectrometers, as a rule combined with Fourier transformation, play a notable role as detectors.[340–342] Such detectors are most convenient in experiments with CO_2 as the mobile phase. Carbon dioxide is transparent over a wide range,

which permits the determination of many organic compounds. An advantage of the use of CO_2 is also that the sensitivity of the detection can be greatly increased by combining the IR spectrometer with a microcope.[130] The pure sorbate is introduced onto the surface of a ZnSe plate transparent in the IR region (under normal conditions, CO_2 is converted into the gaseous state), after which its IR spectrum is recorded. Plasma detectors,[168,343,344] ion-conducting polymer membranes,[345] ion mobility spectrometers,[346,347] and ^1H NMR spectrometers[348] are less widely used. As in classical gas chromatography, in certain cases double detection is resorted to in order to obtain universal (for example, using a FID) and specific (using a photometric detector) chromatograms.[349] The use of a combination of these detectors is particularly convenient in the analysis of mixtures with a complex composition. Thus the application of equipment traditional for gas and liquid chromatography in SCFC requires only the construction of special units whereby the columns can be connected to the detectors.[344,350]

VI. Qualitative and quantitative analyses

The development of gas chromatography made it possible to achieve considerable advances in the identification of substances: (1) it became possible to compare directly the signal received from the object analysed with the signal from a standard specimen; (2) an identification system based on the determination of the retention indices of the mixture components was developed.

The use of liquid chromatography for qualitative analysis involves problems caused by the difficulty of determining the retention time of the non-sorbed component.

Most of the problems arising in liquid chromatography are retained in the SCFC, occupying an intermediate position, while the achievements of gas chromatography are little used. One of the main disadvantages of SCFC is the difficulty of maintaining reproducible separation conditions, which is associated with the sharp alteration of the properties of the fluid near the critical point. Another disadvantage is caused by the necessity to use adsorbents and sorbents with grafted groups, whose characteristics are not as satisfactorily reproducible as in gas chromatography. Reference specimens are most often employed for the purpose of identification.[150,151,153,157] In the analysis of complex objects of unknown composition, group separation with subsequent individual analysis of the fractions, for example, by gas chromatography with capillary columns[199,213,231] or HPLC,[153,275] is frequently employed. In the latter case, the approaches adpted in HPLC are used in SCFC. Attempts have been made to set up standard retention index scales. In particular, compounds belonging to the homologous series of alkyl aryl ketones (ranging from acetophenone to octaphenone) and normal alkanes (from dodecane to tetracosane) have been used for this purpose.[262] The application of both scales leads to comparable results, but the former must be regarded as more universal because it can be employed when polar modifying agents are added to the mobile phase (for example, CO_2). Modified Kovac indices, calculated from the formula[351]

$$RI = \frac{\lg t'_{R(x)} - \lg t'_{R'(\text{decane})}}{\lg t'_{R'(\text{pentadecane})} - \lg t'_{R(\text{decane})}},$$

where $t'_{R(x)}$ is reduced retention time of the substance analysed, were proposed for estimation of retentions of different kinds.

Smaller difficulties arise in quantitative analysis. The calibrating plot[167,216,230] and internal standard[202] methods are most often used in SCFC for the treatment of the signal. The calculation is based either on the area of the chromatographic peak or on its height.

VII. Extraction by the supercritical fluid

The supercritical fluid has a number of characteristic features as an extractant: (1) its viscosity is virtually identical to that of the gas and its diffusion coefficient is greater and its density is smaller than those of the liquid (this makes the extraction time several times shorter); (2) its solvent power depends greatly on the temperature and pressure, which permits its deliberate alteration.

Such properties of the fluid promote the rapid extraction of a wide range of organic compounds (polyaromatic hydrocarbons, diuron, linuron, caffiene, medicinal drugs, insecticides, herbicides, etc.) from ash, town dust, soil, river and sea bottom deposits, etc.[188,202,205,207,213,220,225,229,244,254,257,260,261,274,275,281,284,308,352]

Table 3 presents certain examples of the use of extraction by a supercritical fluid. As a rule a degree of extraction of 80–95% is attained after only 20–30 min from the start of extraction. The change in pressure and temperature (and hence in the solvent power of the extractant) during the extraction process gives grounds for the assumption that extraction by the supercritical fluid is an additional separation stage during which individual fractions of the substances analysed may be isolated. Thus fractions comprising sulphur-containing heterocycles (with different numbers of rings) have been isolated from the vacuum residues in the catalytic cracking of petroleum,[199] caffeine has been isolated from coffee extract and coffee grains,[174] polyaromatic hydrocarbons have been isolated from town dust,[220] etc. Extraction by the supercritical fluid can be carried out after preliminary concentration of the substance to be analysed on different adsorbents (synthetic resins, polyurethane foil, carbon sorbents, Tenax GT,[188,220,274] and glass wool[275]), which makes it possible to reduce the detection limit. A convenient feature of the use of a supercritical fluid for extraction also consists in the fact that the extract may be analysed not only by SCFC but also by HPLC [174,207,275,284] or gas chromatography.[199,205,213,244,257,281] The gas-chromatographic analysis of the extract as a rule presupposes the cryogenic concentration of the sample at the inlet to the column[205,244,257] or the absorption of the substances present in the sample by an appropriate solvent into which an internal standard has been introduced.[150] The subsequent analysis is performed by the usual gas-chromatographic procedure. In the extraction of mixtures of known composition, the regime permitting the attainment of the maximum extraction and separation can be selected on the basis of preliminary calculations of the solubilities of the substances analysed in the supercritical fluid using the available formulae.[353] The employment of extraction by a supercritical fluid for the automatic preparation of samples for analysis not only by chromatographic but other (for example spectroscopic) methods is likewise promising. Thus extraction by a supercritical fluid can be included in any multistage analytical scheme.

VIII. Physicochemical aspects of the use of supercritical fluid chromatography

The study of the equilibrium in the fluid-sorbent system, which makes it possible to determine the thermodynamic characteristics of the dissolution of a number of substances, is of considerable

interest.[342,353,354] Special versions of fluid chromatographs have been proposed for physicochemical research.[355] They can be used also for analytical purposes. The diffusion coefficients (simple and binary) of compounds such as unsaturated aliphatic acid esters and benzene and its derivatives have been determined in supercritical CO_2 [355,356] and chlorotrifluoromethane and sulphur hexafluoride.[357] The heats of desorption of toluene, phenol, naphthalene, anthracene, and other aromatic hydrocarbons have been determined in the temperature range 307–353 K and at pressures up to 200 kg cm^{-2} using CO_2 as the mobile phase.[358] The heat of desorption increment per C_2H_4 group is $\sim$2.507 kJ mol^{-1}. The effect of density on the enthalpy and entropy of transfer in SCFC has been investigated[359] using CO_2 as the mobile phase and the cross-linked SE-54 and OV-17 stationary phases. The change (decrease) in the enthalpy of transfer of the test substance with increase in the density of the mobile phase (CO_2) has been confirmed for sorbates such as normal alcohols and normal alkanes. The enthalpies found by the authors[359] (−24.7 to −35.2 kJ mol^{-1} for OV-17 and −16.3 to −36.0 kJ mol^{-1} for SE-54) agree with the literature data obtained by liquid chromatography (for high densities) and gas chromatography (for low densities). The intermediate position of SCFC was yet again confirmed. An attempt was made to devise a single theory of adsorption chromatography using homogeneous adsorbents and adsorbents characterised by a discrete distribution on their surface of energetically or structurally different adsorption centres.[264,360–363] The mobile phase can be a gas, a liquid, or a supercritical fluid.

Table 3. Extraction with supercritical fluid.

Object analysed	Isolation and determination conditions, extractant	Refs.
Plastic materials, corn ears, control mixtures of hydrocarbons	CO_2, subsequent analysis—SCFC (10 m × 50 μm columns with a 0.25 μm layer of SB-biphenyl-30)	[Ref. 156]
Coffee extract (roasted grains)	CO_2, subsequent analysis—HPLC (SG and SP) with grafted C_{18} groups, $CH_3OH + H_2O$ as MP	[Ref. 174]
Contaminants in the environment preadsorbed on TENAX GC (SRM 1650 standard and polyaromatic hydrocarbons from diesel fuel up to coronene inclusive)	CO_2 and $CO_2 + CH_3OH$. Direct extraction from adsorbing cartridge (30 min); subsequent analysis—gas chromatography (cryogenic concentration at inlet to 30 m × 320 μm column with a 1 μm layer of DV-5)	[Ref. 188]
Polyaromatic hydrocarbons from ash, town dust, and river bottom deposits	Ethane, CO_2 and N_2O, CO_2 and N_2O with CH_3OH, the extract is collected in a vessel with a solvent containing the internal standard; analysis on 60 m × 250 μm columns with a 0.25 μm layer of DV-5	[Ref. 202]
Anthraquinone from kraft-paper, pine wood fillings	CO_2 (20 min), analysis–HPLC using 15 cm × 3.5 mm columns with Bondapak C_{18}, CH_3CN–pH 6.8 buffer mixture as MP	[Ref. 207]
Polyaromatic hydrocarbons (SRM 1649 standard)	CO_2; possibility of extraction of all the substances from the matrix, quantitative extraction and concentration of traces, selective extraction of individual fractions, and multistage extraction. Analysis—gas chromatography (15 m × 250 μm column with a 0.25 μm layer of SE-54)	[Ref. 213]
Chrysene, benzanthrone, 1-nitro-pyrene, dibenzocarbazole, coronene etc, SRM 1649 standard)	CO_2, isobutane, and $CH_3OH - CO_2$ from adsorbents (KhAD-2, polyurethane foil, Spherocarb); desorption of polar compounds with $CO_2 + CH_3OH$ mixture and desorption of high molecular-weight compounds with isobutane; analysis—gas chromatography (15 m × 250 μm with cross-linked SE-54)	[Ref. 220]
Herbicides from loamy soils	CO_2, $CO_2 + CH_3OH$; analysis—SCFC (capillary columns with SB-cyanopropyl-25 and packed columns with Partisil-5, ODS-3)	[Ref. 225]
Natural products, aromatic hydrocarbons	CO_2; automatic isolation of substance from matrix and sample preparation (Milton Roy SPA system)	[Ref. 228]
"Maoming" oil shale	Supercritical liquid in the presence of H_2O and toluene with subsequent collection of individual fractions (soluble in cyclohexane, toluene, etc)	[Ref. 229]
Polyaromatic hydrocarbons (in impregnated wood, town dust, river deposits), phenols from aerosols in forest fires, nicotine from tobacco, scent components, biological markers	CO_2, N_2O, ethane; subsequent analysis—gas chromatography (30 m × 320 μm columns with a 1 μm layer of DV-5 and 60 m × 250 μm columns with a 0.25 μm layer of DV-5); cryogenic concentration of the sample is carried out at the inlet to the column	[Ref. 244]
Oil from lemon peel	CO_2; extractor—empty 35 mm × 4.6 mm column; analysis—gas chromatography (25 m × 200 μm column with CBP 20)	[Ref. 254]
Components of the smell of natural products	CO_2, extractor (0.1 ml) combined with the gas chromatograph evaporator, after reduction of pressure, the extract is subjected to cryogenic concentration at the inlet to a 30 m × 320 μm column with a 1 μm layer of DV-5	[Ref. 257]
Standard aromatic hydrocarbons (in heptane)	CO_2, $CO_2 + CH_3OH$; extractor connected to a 6-way metering tap in place of metering loop and is provided with autonomous heating; no "memory" effect	[Ref. 263]
Polyaromatic hydrocarbons (from napthalene to perylene), polychlorinated biphenyls	CO_2; sample extracted from filter, extract concentrated to 1 ml and analysed (20 m × 250 μm columns with a 0.25 μm layer of DV-5)	[Ref. 274]
Pesticides from glass wool (5 substances)	CO_2; CO_2 passed through extractor, the eluate being directed to series-connected 18 × 1.5 mm column with RP-18 or 14 × 1.5 mm columns with Si 60 on which the sample is fractionated	[Ref. 275]
Tocopherols from wheat germ	CO_2 + alcohol; extract concentrated on a 50 × 10 mm column with SG from which it is directed to seperation (20 cm × 20 mm column); the collected fractions are analysed by HPLC	[Ref. 284]
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDBD)	CO_2, NO, and their mixtures with CH_3OH; 100% extraction from bottom TCDBD deposits achieved, gas chromatographic analysis (30 m × 250 μm columns with a 0.17 μm layer of cross-linked SE-54)	[Ref. 308]

Note. SG = silica gel.

The development of the SCFC method confirms the view that chromatographic separation is a single process occurring over a broad spectrum of experimental conditions (with a gas, a supercritical fluid, or a liquid as the mobile phase). The chromatographic separation of any objects can be achieved using the same apparatus. By varying the experimental conditions (pressure and temperature), it is possible to select an effective procedure for the solution of a specific analytical problem.

References

1. M S Vigdergauz, A V Garusov, V A Ezrets, et al. *Gazovaya Khromatografiya s Neideal'nymi Elyuentami* (Gas Chromatography with Non-ideal Eluents), Nauka, Moscow, 1980, p. 128
2. M S Vigdergauz *Chromatographia,* 1988, **25** 681
3. E Klesper, A H Corwin, D A Turner *J. Org. Chem.,* 1962, **27** 700
4. S T Sie, G W A Rijnders *Sep. Sci. Technol.,* 1967, **2** 729
5. C M White (Editor) *Modern Supercritical Fluid Chromatography,* Alfred Huthig, Heidelberg, 1988, 239 pp
6. B A Carpenter, M R Sevenante (Editors) *Supercritical Fluid Extraction and Chromatography. Techniques and Application,* Royal Society of Chemistry, London, 1988, 253 pp
7. H J Cortes (Editor) *Multidimensional Chromatography. Techniques and Applications. Chromatographic Science Series,* Marcel Dekker, New York–Basel, 1990, Vol. 50, 357 pp
8. T Maeda, T Hobo *Bunseki,* 1988, (5) 332
9. C M White, R K Houck *J. High Resolut. Chromatogr, Commun.,* 1986, **9** 4
10. M Saito, T Hondo *Yukagaku,* 1986, **35** 273
11. H M Widmer *Modern Supercritical Fluid Chromatgraphy* (Edited by C M White), Alfred Huthig, Heidelberg, 1988, p. 211
12. M Novotny *Microcolumn Separaration: Columns, Instruments, and Ancillary Techniques,* Amsterdam, 1985, p. 105
13. S Rokushika *Hyomen,* 1988, **25** 92
14. R Kallasorg, K Punnyng, T Symer *Uch. Zap. Tartussk. Gos. Univ.,* Tartu, 1989, (844) 93
15. C F Pool, S K Pool *Anal. Chim. Acta,* 1989, **216** 109
16. R D Smith, B W Wright, C R Yonker *Anal. Chem.,* 1988, **60** 1323
17. V G Berëzkin, M A Koshevnik, E Yu Sorokina, et al. *Zavod. Lab.,* 1989, **55**, 1
18. C H Lochmuller *J. Chromatogr. Sci.,* 1987, **25** 583
19. M Saito, Y Yamauchy *Kagaku Kogaku,* 1988, **52** 498
20. D Leyendecker, D Leyendecker *GIT,* 1987, **31** 920
21. W Ecknig, H-J Polster *Mutteilunsbl. Chem. Ges. DDR,* 1986, **33** 225
22. P R Griffiths *Anal. Chem.,* **60** 593
23. F P Schmitz *GIT,* 1989, **33** 530
24. K Nurmela, M-L Rikkola *Kemi-Kemi,* 1987, **14** 1071
25. R D Smith, B W Wright, H R Udseth *Advances in Capillary Chromatography,* Heidelberg, 1986, p. 56
26. E Klesper, F P Schmitz *J. Chromatogr.,* 1987, **402** 1–39
27. I Trummer *Proc. 2nd Int. Conf. Biochem. Separ. Keszthely, Oct. 2–7 1988, 2nd IGBS: Full Pap. and Abstr. Budapest, 1988,* p. 481
28. D J Hawkos *Int. Labmate,* 1987, **12** 15
29. M Poeck *Chem.-Techn. (BRD),* 1987, **16** 134
30. H M Widmer *Chimia,* 1987, **41** 402
31. D Leyendecker, D Leyendecker *Lab. Pract.,* 1988, **12** 658
32. P Jusforques, M Perrut *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, 25 Feb.–1 March, 1985,* p. 542
33. M Novotny, S R Springston, S V Olesik, et al. *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, 25 Feb.–1 March, 1985,* p. 535
34. J L Hensley, H M McNair *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, 25 Feb.–1 March, 1985,* p. 537
35. D R Gere *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, 25 Feb.–1 March, 1985,* p. 534
36. M Perrut *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, 25 Feb.–1 March, 1985,* p. 540
37. B E Richter *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986,* p. 514
38. E G Klesper *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986,* p. 513
39. B W Wright, C R Yonker, H T Kalinoski, et al. *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986,* p. 517
40. P Jusforguea, M Perrut *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986,* p. 755
41. K E Markides, R S Johnson, B J Tarbet, et al. *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986,* p. 746
42. E J Cuthrie *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986,* p. 747
43. M L Lee, S M Flieds, M Nishioka, et al. *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986,* p. 516
44. R U Qerter *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986,* p. 907
45. D W Later *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986,* p. 486
46. S L Pentoney, K H Shafer, P R Griffiths, et al. *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986,* p. 473
47. S Beale, C Borra, F Andreolini, et al. *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986,* p. 900
48. J W Jordan, Taylor, M Ashraf-Khorassani, et al. *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986,* p. 751
49. J Henioh, E Lee *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986,* p. 518
50. T L Chester *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986,* p. 515
51. K G Owens, J P Reilly *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986,* p. 753
52. R G Brownlese H E Schwartz, H H Lauer *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9–13, 1987,* p. 1045
53. F C Knopf, Pang Tien-Hai, K M Dooley *Abstr. Pap. 194th ACS Nat. Meet. (Am. Chem. Soc.), New Orleans, Aug. 30–Sept.4, 1987,* Washington, 1987, p. 486
54. S L Pentoney, G J Pariente, P R Griffiths *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9–13, 1987,* Pittsburg, 1987, p. 816
55. H H Lauer, H E Schwartz, P J Barthel *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9–13, 1987,* Pittsburg, 1987, p. 1049

56. F J Yang, D Later, B Richter, et al. *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9–13, 1987*, Pittsburg, 1987, p. 1026
57. I J Burkes, G D Owens, M P Lacey, et al. *Abstr. Pap. Pittsburg Conf. and Expo Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9–13, 1987*, Pittsburg, 1987, p. 1046
58. B E Richter, D E Knowles, M A Andersen, et al. *Abstr. Pap. Pittsburg Conf. and Expo Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9–13, 1987*, Pittsburg, 1987, p. 1021
59. J Frasier, H McNair, L Cerruti *Abstr. Pap. Pittsburg Conf. and Expo Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9–13, 1987*, Pittsburg, 1987, p. 1024
60. J Henion, E Lee, S H Hsu, et al. *Abstr. Pap. Pittsburg Conf. and Expo Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9–13, 1987*, Pittsburg, 1987, p. 671
61. D R Luffer, P A David, M Selby, et al. *Abstr. Pap. Pittsburg Conf. and Expo Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9–13, 1987*, Pittsburg, 1987, p. 1023
62. J Henion, E Lee *Abstr. Pap. Pittsburg Conf. and Expo Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9–13, 1987*, Pittsburg, 1987, p. 798
63. E M Fujinari, M E McNally, J R Wheeler *Abstr. Pap. Pittsburg Conf. and Expo Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9–13, 1987*, Pittsburg, 1987, p. 815
64. S Yoclovich, S O'Neill, J Guthrie, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 744
65. S Yoclovich, S O'Neill, J Guthrie, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 278
66. S E Moring, H E Schwartz, P J Barthel, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 278
67. J Henion, E Lee, L McLaughlin, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 307
68. K Kempfert *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 522
69. J D Buchner, R C Willoughly, S Ketkar *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 257
70. A J Berry, D E Games, S Mahatheeranont, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 248
71. M L Lee, E C Huang, K E Markides, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 297
72. J D Pinkston, G D Owens *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 65
73. M E McNally, J R Wheeler, W R Melander *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 420
74. P R Griffiths *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 32
75. N L Porter, B E Richter, D E Knowles, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 160
76. S E Moring, H E Schwartz, P J Barthel, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 743
77. R D Smith, H K Jones, B W Wright, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 628
78. M R Andersen, B E Richter *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 160
79. D J Bornhop, B E Richter, D W Later *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 72
80. R J Skelton, K E Markides, P B Farnsworth, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 399
81. G P Williams, M L Kumar, R K Houck, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 72
82. E C Huang, B J Jackson, K E Markides, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 1072
83. P J Rudewicz, J W Hurst, I Mylcreest *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 1074
84. R P Khosah *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 232
85. S Trestianu, F Munari, P Mapelli, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 595
86. A C Roselli, R K Houck, R M Ravey *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 1065
87. L A Pekay, S V Olesik *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 1159
88. W T Foreman, R E Sievers, B Wenclawiak *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 1066
89. H E Schwartz, S E Mering, J M Levvy, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 597
90. R J Skelton, K E Markides, P B Farnsworth, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 1067
91. H-C K Chang, S R Sumpter, K E Markides, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 749
92. R C Wieboldt, G E Adams *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 790
93. L T Taylor, T Berger, J Dye *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 599
94. M Novotny *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 792
95. M Ashraf-Khorassani, L T Taylor *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 1157

96. N S Johansen *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 593
97. R P Khosah, H A Bryant *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 745
98. A C Rosselli, F Pacholec, R Ravey *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 742
99. C W Saunders, L T Taylor, L J Mulkahey *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988, Pittsburg, 1988*, p. 421
100. E D Sexton, S M Rule *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 1010
101. C R Powley *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 539
102. P A David, M Novotny *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 592
103. C A Rouse, B J Tarbet, K Jones, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 746
104. E C Huang, B J Jackson, K E Markides, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 401
105. D E Raynie, K E Markides, M L Lee *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 422
106. J W King, K Eskins, J P Friedrich, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 596
107. E R Campbell, B E Richter, D W Later *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 423
108. M R Andersen, B E Richter *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 425
109. N L Porter, B E Richter, D E Knowles, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 426
110. B E Richter, N L Porter, D E Knowles, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 424
111. F J Yang, D W Later, B E Richter *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 741
112. E A Bruijn, P Sandra, F David, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 600
113. M Saito, Y Yamauchi, Hondo, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 1071
114. R D Sith, B W Wright, H R Udseth *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 304
115. C W Saunders, L T Taylor, L J Mulcahey *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 158
116. J R Wheeler, M E McNally *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 747
117. J W Huber, W G Eugelhart, R W Egan *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 759
118. B E Richter, N L Porter, D E Knowles, et al. *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 159
119. J L Hedrick, E M Calvey, L T Taylor *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 1068
120. M L Kumar, R M Ravey, A C Rosselly *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 1070
121. C C Jonson, J W Jordan, R J Skelton, et al. *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, 25 Feb.–1 March, 1985*, p. 538
122. M E Hunger, J L Fasching *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, 25 Feb.–1 March, 1985*, p. 657
123. M L Kumar, C P Wagner, R M Ravey, et al. *Abstr. Pap. Pittsburg Conf. and Expo. Anal Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986*, p. 748
124. A S Boparai, D C Ettinger, J F Schneider *Abstr. Pap. Pittsburg Conf. and Expo. Anal Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986*, p. 337
125. E M Calvey, Ch W Thorpe, A E Pohland, et al. *Abstr. Pap. Pittsburg Conf. and Expo. Anal Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986*, p. 750
126. M Ashraf-Khorassani, J W Hellgeth, L T Taylor *Abstr. Pap. Pittsburg Conf. and Expo. Anal Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986*, p. 752
127. K Jinno, T Hoshino, T Honto, et al. *Abstr. Pap. Pittsburg Conf. and Expo. Anal Chem. and Appl. Spectrosc., Atlantic City, March 10–14, 1986*, p. 844
128. V Berry, L T Taylor *Am. Lab.*, 1988, **20** 23
129. B A Rudenko, M A Baidarovtseva, M A Agaeva *Zh. Anal. Khim.*, 1975, **30** 1191
130. S L Pentony, K H Shafer, P R Griffiths *Chromatogr. Sci.*, 1986, **24** 230
131. R D Smith, E G Chapman, B W Wright *Anal. Chem.*, 1985, **57** 2829
132. J Cousin, P J Arpino *Analysis*, 1986, **14** 215
133. C R Yonker, B W Wright, R C Petersen, et al. *J. Phys. Chem.*, 1985, **89** 5526
134. E J Guthrie, H E Schwartz *J. Chromatogr. Sci.*, 1986, **24** 236
135. T L Chester, D P Innis *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1986, **9** 178
136. B W Wright, R D Smith *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1986, **9** 73
137. M Proot, P Sandra, E Geeraert *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1986, **9** 189
138. Wm P Jackson, D W Later *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1986, **9** 175
139. K E Markides, S M Fields, M L Lee *J. Chromatogr. Sci.*, 1986, **24** 254
140. S J Deluca, K J Voorhees, T A Langworthy, et al. *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1986, **9** 182
141. D W Later, B E Richter, D E Knowles, et al. *J. Chromatogr. Sci.*, 1986, **24** 249

142. W R West, M L Lee *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1986, **9** 161
143. C M White, R K Houck *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1985, **8** 293
144. M Lafosse, M Dreux, L Morin-Allory *J. Chromatogr.*, 1987, **404** 95
145. S R Springston, M Novothy *Anal. Chem.*, 1986, **58** 2699–2704
146. W T Foreman, R E Sievers, B W Wenclawiak *Fresenius Z. Anal. Chem.*, 1988, **330** 231
147. S B Hawthorne, D J Miller *Fresenius Z. Anal. Chem.*, 1988, **330** 235
148. J R Wheeler, M E McNally *Fresenius Z. Anal. Chem.*, 1988, **330** 237
149. J S Bradshaw, S K Aggarwal, C A Rouse, et al. *J. Chromatogr.*, 1987, **405** 169
150. S L Pentoney, A Giorgetti, P R Griffiths *J. Chromatogr. Sci.*, 1987, **25** 93
151. T L Chester, D P Innus *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1986, **9** 209
152. G Holzer, S Deluca, K J Voorhees *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1985, **8** 528
153. G Holzer, L H Zalkow, C F Asibal *J. Chromatogr.*, 1987, **400** 317–322
154. S M Fields, M L Lee *J. Chromatogr.*, 1985, **349** 305
155. F-J Ruffing, J A Lux, W Roeder, et al. *Chromatographia*, 1988, **26** 19
156. K Anton, R Menes, H M Widwer *Chromatographia*, 1988, **26** 221
157. H E Schwartz, P J Barthel, S E Moring, et al. *Fresenius Z. Anal. Chem.*, 1988, **330** 204
158. D W Later, B E Richter, W D Felix, et al. *Am. Lab.*, 1986, **18** 108
159. S M Fields, K E Markides, M L Lee *J. Chromatogr.*, 1987, **406** 223
160. K D Bartle, I K Barker, A A Clifford, et al. *Anal. Prog.*, 1987, **24** 229
161. D Wiaboldt, G Adams *Int. Labmate*, 1987, **12** 11
162. M E Rose *Mass Spectrom. London*, 1987, **9** 264
163. S M Fields, K E Markides, M L Lee *Anal. Chem.*, 1988, **60** 802
164. D E Knowles, L Nixon, E R Campbell, et al. *Fresenius Z. Anal. Chem.*, 1988, **330** 225
165. B W Wenclawiak *Fresenius Z. Anal. Chem.*, 1988, **330** 218
166. W Roder, F-J Ruffing, G Schomburg, et al. *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1987, **10** 665
167. D R Luffer, L J Galante, P A David, et al. *Anal. Chem.*, 1988, **60** 1365
168. L J Galante, M Selby, D R Luffer, et al. *Anal. Chem.*, 1988, **60** 1370
169. J M F Douse *J. Chromatogr.*, 1988, **445** 244
170. A L Blilie, T Greibrokk *J. Chromatogr.*, 1985, **349** 317
171. B Gemmel, B Lorenschat, F P Schmitz *Chromatographia*, 1989, **27** 605
172. J M Levy, W M Ritchey *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1985, **8** 824
173. R G Christensen *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1985, **8** 503
174. K Sugiama, M Saito, T Hondo, et al. *J. Chromatogr.*, 1985, **332** 107
175. P Mourier, M Caude, R Rosset *Analysis*, 1985, **13** 299
176. D Leyendecker, F P Schmitz, D Leyendecker, et al. *J. Chromatogr.*, 1985, **321** 273
177. E Lundanes, T Greibrokk *J. Chromatogr.*, 1985, **349** 439
178. T A Norris, M G Rawdon *Anal. Chem.*, 1984, **56** 1767
179. P A Mourier, E Eliot, M H Caude, et al. *Anal. Chem.*, 1985, **57** 2819
180. J B Crowther, J D Henion *Anal. Chem.*, 1985, **57** 2716
181. T L Chester, D P Innis, G D Ovens *Anal. Chem.*, 1985, **57** 2243
182. T Takeuchi, Y Hashimoto, D Ishii *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, 1986, 965
183. A J Berry, D E Games, J R Perkins *J. Chromatogr.*, 1986, **363** 147
184. E Lundanes, B Iversen, T Greibrokk *J. Chromatogr.*, 1986, **366** 391
185. K H Shafer, S L Pentoney, P R Griffiths *Anal. Chem.*, 1986, **58** 58
186. H E Schwartz, R C Bownlee *J. Chromatogr.*, 1986, **353** 77
187. F P Schmitz *J. Chromatogr.*, 1986, **356** 261
188. S B Hawthorne, D J Miller *J. Chromatogr. Sci.*, 1986, **24** 258
189. S B French, M Novotny *Anal. Chem.*, 1986, **58** 164
190. M W Raynor, G F Shilstone, K D Bartle, et al. *J. High Resolut. Chromatogr.*, 1989, **12** 300
191. M A Healy, M Poliakoff, J J Turner *Pittsburg. Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22–26, 1988*, Pittsburg, 1988, p. 1092
192. R M Campbell, M L Lee *Anal. Chem.*, 1986, **58** 2247
193. J W Jordan, L T Taylor *J. Chromatogr. Sci.*, 1986, **24** 82
194. S Hara, A Dabashi, K Kinoshita, et al. *J. Chromatogr.*, 1986, **371** 153
195. S L Pentoney, K H Shafer, R P Griffiths *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1986, **9** 168
196. J M Levy, W M Ritchey *J. Chromatogr. Sci.*, 1986, **24** 242
197. D Leyendecker, D Leyendecker, F P Schmitz, et al. *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1986, **9** 525
198. S Hara, A Dobashi, T Hondo, et al. *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1986, **9** 249
199. M Nashioka, D G Whiting, R M Campbell, et al. *Anal. Chem.*, 1986, **58** 2251
200. P J Schoenmakers, C C J G Verhoeven, H M Van den Bogoert *J. Chromatogr.*, 1986, **371** 121
201. A Wilsch, G M Schneider *J. Chromatogr.*, 1986, **357** 239
202. S B Hawthorne, D J Miller *Anal. Chem.*, 1987, **59** 1705
203. Y Hirata, F Nakata, S Murata *Chromatographia*, 1987, **23** 633
204. K Jinno, M Kuwajima *Chromatographia*, 1987, **23** 631
205. S B Hawthorne, D J Miller *Abstr. Pap. 194th ACS Nat. Meet. (Am. Chem. Soc.), New Orleans, Aug. 30–Sept. 4, 1987*, p. 119
206. F P Schmitz, E Klesper *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1987, **10** 519
207. M A Schneiderman, A K Sharma, D C Locke *J. Chromatogr.*, 1987, **409** 343
208. T Takeuchi, T Niwa, D Ishii *Chromatographia*, 1987, **23** 929
209. P Macaudiere, M Caude, R Rosser, et al. *J. Chromatogr.*, 1987, **405** 135
210. C Fujimoto, H Yoshida, K Jinno *J. Chromatogr.*, 1987, **411** 213
211. J J Gunderson, M N Myers, J C Giddings *Anal. Chem.*, 1987, **59** 23
212. M M Sanagi, R M Smith *Anal. Proc.*, 1987, **24** 304
213. B W Wright, S R Frye, D C McMinn, et al. *Anal. Chem.*, 1987, **59** 640
214. F P Schmitz *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1987, **10** 650

215. S R Goaters, N A Zabriskie, J K Simones, et al. *Anal. Chem.*, 1987, **59** 2927
216. P Carraud, D Thiebaut, M Caude, et al. *J. Chromatogr. Sci.*, 1987, **25** 395
217. D Thiebaut, M Caude, R Rosset *Analysis*, 1987, **15** 528
218. T Takeuchi, Y Hashimoto, D Ishii *J. Chromatogr.*, 1987, **402** 328
219. J M Levy, W M Ritchey *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1987, **10** 493
220. B W Wright, C W Wright, R W Gale, et al. *Anal. Chem.*, 1987, **59** 38
221. E D Lee, S H Hsu, J D Hemon *Anal. Chem.*, 1988, **60** 1990
222. K D Barthle, A A Clifford, J P Kithnji, et al. *J. Chem. Soc., Faraday Trans. 1*, 1988, **84** 4487
223. J Kiykatsu, N Sakae *J. Chromatogr.*, 1988, **455** 29
224. B Gemmel, F P Schmitz, E Klesper *J. Chromatogr.*, 1988, **455** 17
225. M E P McNally, J R Wheeler *J. Chromatogr.*, 1988, **447** 53
226. T Takeuchi, T Niwa, D Ishii *Chromatographia*, 1988, **25** 332
227. K Punning, T Somer, A Trummel *Izv. Akad. Nauk Eston, SSR Khim.*, 1988, **37** 72
228. W C Engelhart, A C Cargur *Am. Lab.*, 1988, **20** 30
229. T Funazukuri, S Yokoi, N Wakao *Fuel*, 1988, **67** 10
230. H E Schwartz *J. Chromatogr. Sci.*, 1988, **26** 275
231. R J Eathertion, M A Morrissey, H H Hill *Anal. Chem.*, 1988, **60** 2240
232. S Schmidt, L G Blomberg, E R Campbell *Chromatographia*, 1988, **25** 775
233. M Ashraf-Khorassani, L T Taylor *J. Chromatogr. Sci.*, 1988, **26** 331
234. P Macaudiere, M Caude, R Rosset, et al. *J. Chromatogr.*, 1988, **450** 255
235. R C Wieboldt, R J Rosenthal *Microchim. Acta*, 1988, **2** 203
236. J Balsevich, L R Hogge, A J Berry, et al. *J. Natur. Prod.*, 1988, **51** 1173
237. P A David, M Novotny *J. Chromatogr.*, 1988, **452** 623
238. D' Cl Borra, M D Rousseau *Spectra-2000*, 1988, **16** 44
239. E C Huang, B J Jackson, K E Markides, et al. *Anal. Chem.*, 1988, **60** 2715
240. J R Wheeler, M E McNally *J. Chromatogr.*, 1987, **410** 443
241. R M Campbell, N M Djerdjevic, K E Markides, et al. *Anal. Chem.*, 1988, **60** 356
242. P R Geiser *J. Am. Oil. Chem. Soc.*, 1988, **65** 542
243. A Nomura, J Yamada, K-I Tsunoda *J. Chromatogr.*, 1988, **448** 87
244. S B Hawthorne, D J Miller, M S Krieger *Fresenius Z. Anal. Chem.*, 1988, **330** 211
245. E Klesper *Fresenius Z. Anal. Chem.*, 1988 **330** 200
246. H C-K Chang, K E Markides, J S Bradshaw, et al. *J. Chromatogr. Sci.*, 1988, **26** 280
247. W Steuer, M Schindler, C Schill, et al. *J. Chromatogr.*, 1988, **447** 287
248. J Huau, C Tinet *Spectra-2000*, 1988, **16** 49
249. M L Lee, N Djordjevic, K E Markides *J. Res. Nat. Bur. Stand.*, 1988, **93** 409
250. K Anton, N Pericles, S M Fields, et al. *Chromatographia*, 1988, **26** 224
251. K R Jahn, B W Wenclawiak *Fresenius Z. Anal. Chem.*, 1988, **330** 243
252. P P Schmitz, B Gemmel *Fresenius Z. Anal. Chem.*, 1988, **330** 216
253. P G Sim, C M Elson, M A Quilliam *J. Chromatogr.*, 1988, **445** 239
254. K Sigiyama, M Saito *J. Chromatogr.*, 1988, **442** 121
255. H T Kalinoski, R D Smith *Anal. Chem.*, 1988, **60** 529
256. M W Raynon, K D Bartle, I L Davies, et al. *Anal. Chem.*, 1988, **60** 427
257. S B Hawthorne, M S Krieger, D J Miller *Anal. Chem.*, 1988, **60** 472
258. F O Geiser, S G Yoclovich, S M Lurcott, et al. *J. Chromatogr.*, 1988, **459** 173
259. V N Reinhold, D M Sheeley, J Kuei, et al. *Anal. Chem.*, 1988, **60** 2719
260. M L Kumur, R K Houck, H R Winwood *Spectra-2000*, 1988, **16** 47
261. M E P McNally, J R Wheeler *J. Chromatogr.*, 1988, **435** 63
262. R M Smith, M M Sanagi *Chromatographia*, 1988, **26** 77
263. K R Jahn, B W Wenclawiak *Chromatographia*, 1988, **26** 345
264. D E Martire *J. Chromatogr.*, 1989, **471** 71
265. M W Raynor, J P Kithinji, K D Bartle, et al. *J. Chromatogr.*, 1989, **467** 292
266. M Ashraf-Khorassani, L T Taylor, R A Henry *Anal. Chem.*, 1988, **60** 1529
267. H Richard, M Caude, P Sassiat, et al. *Analysis*, 1988, **16** 131
268. R C Wieboldt, C E Adams, D W Later *Anal. Chem.*, 1988, **60** 2422
269. P J Schoenmakers, L G M Uunk *Chromatographia*, 1987, **24** 51
270. J D Pinkston, G D Owens, E Petit *Anal. Chem.*, 1989, **61** 775
271. M Ashraf-Khorassani, L T Taylor *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1989, **12** 40
272. W M A Niesson, M A G Kraa, E R Verheij, et al. *Rapid Commun., Mass Spectrom.*, 1989, **3** 1
273. J H Phillips, R Rodey *J. Chromatogr.*, 1989 **465** 177
274. S B Hawthorne, M S Krieger, D J Miller *Anal. Chem.*, 1989, **61** 735
275. K Shäfer, W Baumann *Fresenius Z. Anal. Chem.*, 1989, **332** 884
276. M Ashraf-Khorassani, L T Taylor *Anal. Chem.*, 1989, **61** 145
277. W H Griest, C Guzman, M Dekker *J. Chromatogr.*, 1989, **467** 423
278. J L Veuthey, M Caude, R Rosset *Chromatographia*, 1989, **27** 105
279. D Nizery, D Thiebaut, M Caude, et al. *J. Chromatogr.*, 1989, **467** 49
280. S Shah, M Ashraf-Khorassani, L T Taylor *Chromatographia*, 1989, **27** 441
281. M Lohleit, K Bächmann *Fresenius Z. Anal. Chem.*, 1989, **333** 717
282. H Kallio, P Laakso, R Huopalahti, et al. *Anal. Chem.*, 1989, **61** 698
283. H Jeff, M Barrie *Int. Labmate*, 1989, **14** 35
284. M Saito, Y Yamauchi, K Ihomata, et al. *J. Chromatogr. Sci.*, 1989, **27** 79
285. W M A Niessen, R A M Hoeven, M A G Kraa, et al. *J. Chromatogr.*, 1989, **474** 113
286. W T Foreman, C L Shellum, J W Birks, et al. *J. Chromatogr.*, 1989, **465** 23
287. Ph Morin, H Richard *J. Chromatogr.*, 1989, **464** 125
288. J D Pinkston, D J Bowling, T E Delaney *J. Chromatogr.*, 1989, **474** 97
289. T A Berger, J F Deye, M Ashraf-Khorassani, et al. *J. Chromatogr. Sci.*, 1989, **27** 105
290. P A David, M Novotny *J. Chromatogr.*, 1989, **461** 111

291. S V Olesik, L A Pekay, E A Paliwoda *Anal. Chem.*, 1989, **61** 58
292. S B Hawthorne, D J Miller *J. Chromatogr.*, 1989, **468** 115
293. E D Ramsey, J R Perkins, D E Gamer, et al. *J. Chromatogr.*, 1989, **464** 353
294. D E Raynie, K E Markides, M L Lee, et al. *Anal. Chem.*, 1989, **61** 1178
295. A C Rosselli, D S Boyer, R K Houck *J. Chromatogr.*, 1989, **465** 11
296. C Borra, F Andreolini, M Novotny *Anal. Chem.*, 1989, **61** 1208
297. S M Fields, H-J Grether, K Grolimund *J. Chromatogr.*, 1989, **472** 175
298. M Bohm, F Umland, B W Wenclawiak *J. Chromatogr.*, 1989, **465** 17
299. B J Fuhr, L R Holloway, C Reichert *Abstr. Pap. 194th ACS Nat. Meet. (Am. Chem. Soc.), New Orleans, Aug. 30—Sept. 4, 1987*, Washington, 1987, p. 491
300. M Ashraf-Khorassani, L T Taylor *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9—13, 1987*, Pittsburg, 1987, p. 819
301. K Jinno, C Fujimoto *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9—13, 1987*, Pittsburg, 1987, p. 799
302. J R Weeler, M E McNally *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9—13, 1987*, Pittsburg, 1987, p. 1050
303. B O Brown, A J Kishbaugh, M E Paulaitis *Fluid Phase Equil.*, 1987, **36** 247
304. S R Zipsky, M L Duffy *L. C. and G. C.*, 1986, **4** 898
305. J L Hensley, H M McNair *J. Liq. Chromatogr.*, 1986, **9** 1955
306. C L Pariente, P R Griffiths *Modern Supercritical Fluid Chromatography* (Edited by C M White), Alfred Huthig, Heidelberg, 1988, p. 81
307. S M Fields, K Grolimund *J. Chromatogr.*, 1989, **472** 197
308. F I Onuska, K A Terry *J. High Resolut. Chromatogr.*, 1989, **12** 357
309. D E Raynie, S M Fields, M M Djordevic, et al. *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1989, **12** 51
310. H E Schwartz, P J Barthel, S E Moring *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1987, **10** 668
311. I L Fulton, R D Smith *J. Phys. Chem.*, 1988, **92** 2903
312. J L Woodruff, S V Olesik *Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., New Orleans, Feb. 22—26, 1988*, Pittsburg, 1988, p. 1158
313. S V Olesik, Kih Huy Soon *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Specrtrosc., Atlantic City, March 9—13, 1987*, Pittsburg, 1987, p. 1048
314. I P Blitz, I L Fulton, R D Smith *J. Phys. Chem.*, 1988, **92** 2708
315. A L Lobachev, I A Platonov, I V Lobacheva, et al. *X Vsesoyuznaya Konferentsiya po Gazovoi Khromatografii. Tezisy Dokladov, Kazan'* (The Xth All-Union Conference on Gas Chromatography. Abstracts of Reports, Kazan), 1991, p. 104
316. M W Ogden, H M NcNair *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1985, **8** 816
317. B J Tarbet, J S Bradshaw, D F Jonson, et al. *J. Chromatogr.*, 1989, **473** 103
318. C R Yonker, R D Smith *Anal. Chem.*, 1989, **61** 1348
319. C R Yonker, R D Smith *J. Chromatogr.*, 1988, **459** 183
320. M I Selim, J R Strubinger *Fresenius Z. Anal. Chem.*, 1988, **330** 246
321. J R Strubinger, M I Selim *J. Chromatogr. Sci.*, 1988, **26** 579
322. C L Woolley, K E Markides, M L Lee, et al. *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9—13, 1987*, Pittsburg, 1987, p. 459
323. M L Lee, S M Fields, J C Kuei, et al. *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9—13, 1987*, Pittsburg, 1987, p. 818
324. J L Hensley, K A Turner, H M McNair *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 10—14, 1986*, Pittsburg, 1986, p. 749
325. D R Gere, R K Houck, F Pacholec, et al. *Fresenius Z. Anal. Chem.*, 1988, **330** 222
326. D Leyendecker, D Leyendecker *GIT*, 1988, **32** 790
327. D E Knowles, B E Richer, M B Wygant, et al. *J. Assoc. Offic. Anal. Chem.*, 1988, **71** 451
328. F Pacholec, C M White, D S Boyer, et al. *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, March 9—13, 1987*, Pittsburg, 1987, p. 813
329. B W Wright, R D Smith *Modern Supercritical Fluid Chromatography* (Edited by C W White), Alfred Huthig, Heidelberg, 1988, p. 189
330. R D Smith, J I Fulton, R C Petersen, et al. *Anal. Chem.*, 1986, **58** 2057
331. T A Berger, C Toney *J. Chromatogr.*, 1989, **465** 157
332. A E Bruno, E Gassmann, N Pericles, et al. *Anal. Chem.*, 1989, **61** 876
333. S D Zaugg, S J Deluca, G U Holzer, et al. *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1987, **10** 100
334. A E Rafael'son, F I Romanov, A I Smirnova, et al. *Nauch Apparatura*, 1988, **3** 3
335. K J Woorheer, S D Zaugg, S J Deluca, et al. *Modern Supercritical Fluid Chromatography* (Edited by C M White), Alfred Huthig, Heidelberg, 1988, p. 211
336. A J Berry, D E Gamer, S Y Hugher, et al. *Kemia-Kemi*, 1988, **15** 1015
337. D A Laude, S L Pentoney, P R Griffiths, et al. *Anal. Chem.*, 1987, **59** 2283
338. D E Games, A J Berry, I C Mylchreest, et al. *Anal. Proc.*, 1987, **24** 371
339. K E Markides, E D Lee, R Bolick, et al. *Anal. Chem.*, 1986, **58** 740
340. Ph Morin, M Caude, H Richard, et al. *Chromatographia*, 1986, **21** 529
341. S Shaf, M Ashraf-Khorassani, L T Taylor *Chromatographia*, 1988, **25** 631
342. C H Lochmuller, L P Mink *J. Chromatogr.*, 1987, **409** 55
343. R J Skelton, K E Markides, P B Farnsworth, et al. *ICP Inf. Newslett.*, 1988, **14** 38
344. S I Abornev, V N Sidel'nikov *Nauchnoe Priborostrostroenie. Fizika Analiticheskikh Priborov* (Scientific Instrument Making. The Physics of Analytical Instruments), Nauka, Leningrad, 1989, p. 56
345. A C Michael, R M Wightman *Anal. Chem.*, 1989, **61** 270
346. H H Hill, S Morrissey, M Morrissey *Modern Supercritical Fluid Chromatography* (Edited by C M White), Alfred Huthig, Heidelberg, 1988, p. 95
347. S Rokushika, H Hatano, H H Hill *Anal. Chem.*, 1987, **59** 8
348. L A Allen, T E Glass, H C Dorn *Anal. Chem.*, 1988, **60** 390
349. D J Bornhop, S Schmidt, N L Porter *J. Chromatogr.*, 1988, **459** 193
350. R C Simpson, J R Gant, P R Brown *J. Chromatogr.*, 1986, **371** 109

351. B W Wright, H T Kalinoski, R D Smith *Anal. Chem.*, 1985, **57** 2823
352. K Jinno, M Saito, T Hondo, et al. *J. Chromatogr.*, 1985, **332** 107
353. C R Yonker, R D Smith *J. Phys. Chem.*, 1988, **92** 1664
354. J Long, R Wang, Y Fan *J. Chem. Ind. Eng.*, 1988, 190
355. T L Chester, D P Innis *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1985, **8** 561
356. T J Bruno *J. Res. Inst. Stand. Technol.*, 1989, **94** 105
357. T Funasukuri, S Hachisu, N Wakao *Anal. Chem.*, 1989, **61** 118
358. A Kopner, A Hamm, J Ellert, et al. *Chem. Eng. Sci.*, 1987, **42** 2213
359. A Wilsch *Diss. Dokt. Naturwiss Abt. Chem. Ruhr-Univ.*, Bochum, 1985, 180 pp
360. C R Yonker, R D Smith *J. Chromatogr.*, 1986, **351** 211
361. D E Martire *J. Chromatogr.*, 1989, **461** 165
362. D E Martire *J. Liq. Chromatogr.*, 1988, **11** 1779
363. D E Martire *J. Liq. Chromatogr.*, 1987, **10** 1569
364. D E Martire *J. Chromatogr.*, 1988, **452** 17

Translated from *Uspekhi Khimii*, **61** 523–547 (1992) U.D.C. 54-128.4:547.1:543.53

Vinyl cations

V D Nefedov, E N Sinotova, V P Lebedev
St Petersburg State University

ABSTRACT. Methods of obtaining vinyl cations, which are derivatives of the ethenyl cation $H_2C=C^+H$ and have the high reactivity of intermediate species, are examined. Particular attention is given to the nuclear chemical method of obtaining free vinyl cations. Data on the reaction of vinyl cations (including free cations) with different classes of compounds containing *n*, π, and σ reaction sites have been correlated.

The bibliography includes 138 references.

Contents

I. Introduction 283
II. Methods of generating vinyl cations 283
III. Reaction of vinyl cations with nucleophilic reagents 287
IV. Reactions of free vinyl cations 291
V. Conclusion 294

I. Introduction

Vinyl cations (VCs) are carbocations that form a class of reactive intermediate species whose parent is the ethenyl (or vinyl) cation $H_2C=C^+H$.[1–7]

Vinyl cations are formed in electrophilic addition reactions to alkynes and allenes, and also by heterolysis of the (C=)C–X bond of vinyl compounds.

The electrophilic addition of water to acetylenes and allenes has been known since the 1870's.[5] At first, however, VCs were not regarded as independent species since it was thought that the presence in them of a charge in combination with an unsaturated bond on the central carbon atom made such intermediates extremely unstable. The idea that the reaction occurs via the formation of VCs was apparently first put forward to explain the formation of an alkyl acetate in the hydration of alkoxyacetylenes in an acidic medium.[5a]

The idea that VCs were unstable was based on the extremely low rates of solvolysis of vinyl halides even under conditions that permit the formation of primary alkyl cations. Nevertheless, the first direct evidence for the existence of VCs was actually obtained in the solvolysis of 1-arylvinyl bromides.[8]

The discovery and practical research application of vinyl compounds containing groups that could readily be eliminated—anions of fluoroalkylsulphonic acid, such as triflate (trifluoromethanesulphonate) anion and nonaflate (nonafluorobutanesulphonate) anion—constituted a stage of fundamental importance in the chemistry of VCs. Since the rate of solvolysis of these esters is higher than that of vinyl halides by a factor of 10^6-10^8, it was thus possible to obtain simple alkylvinyl cations and cyclic VCs with small strained rings.[7,9,10]

Recently, after preparing vinyl compounds containing a ferrocene group on the double bond, which has a strong stabilising effect, it was possible to observe directly the formation of VCs by means of ^1H NMR spectroscopy.[11–13]

A number of reviews attesting to the considerable interest in the problem of VCs have appeared.[1–7,14] In these reviews the methods of generating VCs, their stability, rearrangements, and the mechanisms of reactions involving VCs are widely discussed. On the other hand, these studies, which were excellent at the time, no longer reflect the current state of knowledge concerning the chemistry of VCs.

An attempt has been made in the present review to correlate the existing data, including the most recent information about the methods of obtaining VCs (principally photochemical and nuclear chemical methods) and the reactions of VCs, including those occurring in a free state.

II. Methods of generating vinyl cations

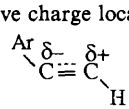
1. Electrophilic addition to alkynes and allenes

a) Alkynes

A study of the mechanism of electrophilic addition to alkynes initiated by Lewis acids showed that initially an ion pair consisting of the anion of the acid and a VC is formed, having a linear or almost linear structure. At the same time the most stable of the possible cations is predominantly formed.[1–7,15–21] The possibility of internal migration in the ion pair and steric separation of the ions predetermine the diversity of products of the alkylation,[16,17] halogenation,[22–24] hydrohalogenation,[1–7] and acylation[25–34] of alkynes.

It was established from a detailed study of the mechanism of hydration of alkynes that the overall rate of this reaction is determined by the rate of the stages involving protonation of the triple bond. This is suggested, in particular, by the substantial kinetic isotope effect that occurs in the hydrolysis of different acetylenic compounds: $k_{H_2O}/k_{D_2O} = 1.7-4.0$.[1–7,35,36]

The results of recent studies of the hydration of substituted alkynes point to the possibility of a considerable acceleration of the addition of a proton to aromatic alkyne molecules under photoexcitation conditions.[37] It is assumed in this case that in its lowest singlet state S_1^* an alkyne molecule acquires a bent structure in which the carbon atoms of the triple bond have an intermediate sp^2-sp character. The bond becomes partially polarised, with the negative charge localised on the β-carbon atom:

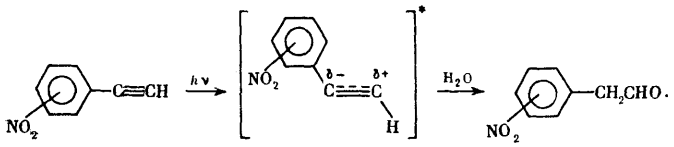


Consequently it is the β-carbon atom that undergoes attack by the proton to form a VC. The activation energy of addition of the proton in this case is much lower than the energy of activation for protonation of alkynes in the ground state. The resulting electronically excited cation rapidly reacts with a water molecule, giving a ketone as the product of photohydration:

$$ArC\equiv CH \xrightarrow{h\nu} [ArC\equiv CH]^{+} \underset{k_{-H}}{\overset{k_H}{\rightleftharpoons}} ArC^{+}=CH_2 \xrightarrow{H_2O} ArCOCH_3 .$$

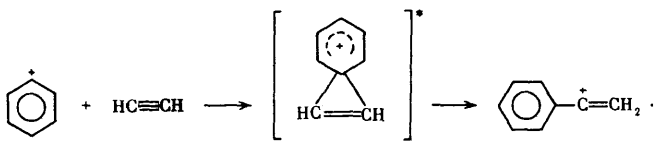
The occurrence of a kinetic isotope effect (k_{H_2O}/k_{D_2O}) indicates that protonation of the acetylene is the rate-limiting stage of photohydration.

In the photohydration of nitrophenylacetylene, an aldehyde rather than a ketone is formed, i.e. protonation does not follow Markownikoff's rule:



This occurs because the nitrophenylacetylene molecule, as a result of the absorption of light (λ = 254 nm), is converted to the T_1 triplet state, in which the distribution of charges on the carbon atoms of the triple bond is the reverse of that in aromatic alkyne molecules in the S_1^* state.[37]

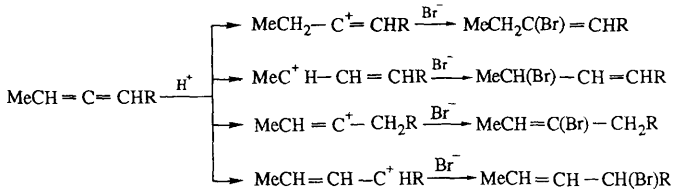
It appears that the alkylation of alkynes in the gas phase also occurs via the formation of VCs. According to the results of Fornarini and Speranza,[38] attack on an acetylene molecule by a free phenyl cation obtained by the nuclear chemical method (see below), yields first an excited bridged phenylvinyl cation, which rapidly isomerises to the more stable 1-phenylvinyl cation:



In a recent study of the kinetics of hydration of acetylene in an acidic medium, results indicating the possible formation of an unsubstituted ethenyl cation in solution were obtained.[39]

b) Allenes

In the addition of electrophilic species to allenes each of the three carbon atoms joined by a cumulated bond can serve as a nucleophilic site. When electrophiles add to the terminal carbon atoms of the cumulated bond, a VC is formed, while attack on the central carbon atoms gives an allylic ion. The direction of attack of electrophiles to allenes is mainly determined by the ability of the substituents to stabilise these ions.[40–44] Thus, in the electrophilic addition of hydrogen bromide to 1,3-dialkylallenes, all possible regioisomers are formed:[45–46]



R= Me, Et, Pr, C_5H_{11}.

In the majority of cases studied the yield of allyl bromides is considerably greater than that of vinyl bromides.

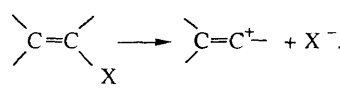
In the photohydration of arylallenes a proton attacks the central atom of the allene group. However, this is due to the presence of a negative charge on the central carbon atom in the allene group of arylallene in an excited state rather than to the effect of the aryl group on the stability.[37]

c) Anchimeric assistance of multiple bonds

Solvolysis of homoallenyl or homopropargyl esters by an S_Ni mechanism is accompanied by the formation of compounds that contain three- or four-membered rings. In the solvolysis of cyclic acetylenic or allenic esters bicyclic compounds are formed.[47–50] According to existing theories,[47–50] as a result of intramolecular attack on a nucleophilic group with a triple or allenic bond by the carbocation centre of the primary cation, cyclic VCs are formed, which participate in the reaction to give the observed cyclic products. In particular, in the solvolysis of homoallenic or homopropargyl esters the formation of a common intermediate, possibly a bicyclobutonium ion, is postulated.[50–52] Stabilisation of cyclic VCs with small rings is achieved through overlap of the vacant orbital of the carbocation centre with the electrons of the C(2)–C(3) σ-bond.[50]

2. Heterolysis of the (C=)C–X bond

Heterolysis of the (C=)C–X bond in vinyl compounds is regarded as an alternative method of obtaining VCs:



This process occurs in the solvolysis of vinyl compounds by an S_Ni mechanism and by the photolysis of vinyl derivatives. Heterolysis of a special type takes place when electron impact and nuclear chemical methods are used.

Reduction of the activation barrier for heterolytic dissociation and formation of intermediate complexes is assisted by those electronic and steric factors that govern the stability of the cations (VCs) and the groups being eliminated. Amongst these are, primarily: different electronegativities of the atoms of the bond to be cleaved; electron-donating effects of the substituents (+*I*, +*C*, anhimeric assistance) that allow delocalisation of the positive charge of the carbocation centre; electron-withdrawing properties of the substituents of the group being eliminated, through which the basicity of X^- is reduced.

The effect of polar properties of the medium which govern the solvation of the ions should be added to those factors already given which assist a reduction in energy of activation of heterolysis of the (C=)C–X bond.

a) Solvolysis of vinyl compounds

As in the case of aliphatic compounds, the rate-limiting stage in S_N1 nucleophilic substitution at an unsaturated carbon atom is cleavage of the (C=)C–X bond.

An increase in stability of the VC and the group being eliminated leads to an increase in the rate of unimolecular substitution in vinyl compounds. The values of log k correlated with the σ^+ constants of the substituents on the double bond in virtually all of the reported cases for this reaction. In terms of its absolute magnitude, the reaction parameter ρ^+ has quite a high negative value, and for arylvinyl derivatives it varies from -6.6 to -2.0 (for aliphatic systems it varies from -7.7 to 0).[53] This phenomenon demonstrates, on the one hand, that a strongly polarised intermediate (vinyl cation) is formed at the intermediate stage of the reaction, and on the other hand, that special stabilisation is required for VCs, which are less stable than their saturated analogues.

Stabilisation of VCs is considerably assisted by groups that have donor properties, including ferrocenyl, aryl, cyclopropyl, vinyl, and allyl. The greatest effect for the stabilisation of VCs occurs when such a group is introduced into an α-position conjugated with the carbocation centre. Quantum-chemical calculations show that an increase in stability of α-arylvinyl cations results from overlap of the HOMO of the π-electron system of the aromatic ring with the vacant 2p orbital of the carbocation centre. In this case a shift in electron density from the ring to the carbocation centre is recorded, which gives rise to positive charges on the carbon atoms at the *ortho* and *para* positions of the aryl group.[54–58]

There has been comparatively little study of ethynylvinyl systems as π-electron systems. An ethynyl group, when it is conjugated with carbocation centre, can destabilise a VC through its electron-withdrawing inductive effect ($-I$ effect). At the same time this group can participate in resonance delocalisation of the positively charged ion, which overall stabilises the cation. According to calculations, ethynyl and methyl groups have comparable stabilising effects.[55] It is assumed that in the 1-ethynylvinyl cation, these effects due to the presence of a triple bond balance each other out. In a study of the solvolysis of ethynylvinyl systems it was established that the response to the question as to whether the electron-withdrawing effect or resonance stabilisation of charge predominates depends on the nature of the substituent on the α-carbon atom of the triple bond.[59–61]

Alkylvinyl halides usually do not undergo an S_N1 type of solvolysis; the solvolysis of brosylates and tosylates takes place very slowly.[1–7] For this reason a study of the effect of alkyl substituents on the rate of reaction has only been possible with the use of the trifluoromethanesulphonate or nonafluorobutanesulphonate ions, which have sufficiently high stability as a result of significant charge delocalisation through the $-I$ effect of the fluorine atoms. The low reactivity of alkylvinyl compounds indicates that stabilisation of VCs by alkyl groups (hyperconjugation effect) is not sufficiently effective. Thus, a study of the effect of alkyl groups at the double bond on the rate of S_N1 solvolysis of alkylvinyl triflates showed that replacement of a methyl group by an ethyl group causes a slight increase in the rate of reaction, which is of a similar magnitude when R = iso-Pr and when R = t-Bu.[62]

Solvolysis of vinyl compounds which are mono- and di-substituted at the β-position but unsubstituted at the α-position, occurs at a low rate and usually gives rearrangement products even when aryl or cyclopropyl groups are used as substituents. At the present time it is thought that the most probable mechanism for solvolysis of compounds of this type is a mechanism involving successive elimination and addition and not involving the formation of a VC.[1–7]

The steric effects of the β-substituents are exhibited most clearly in the solvolysis of α,β-disubstituted vinyl compounds, although it is not always possible to distinguish them from the inductive effect. In a VC the carbocation carbon atom is sp-hybridised and the σ-bonds to it have a linear configuration. In the initial vinyl compound, the carbon atom attached to the substituent and the leaving group (α-atom) is sp^2-hybridised. Hence an increase in the size of the substituent on this atom must give rise to considerable steric repulsion between the substituents on the α- and β-atoms of the vinyl group. This undoubtedly assists the formation of a VC; the rate of solvolysis of the vinyl compound should also increase. In fact, the rate of solvolysis of (*E*)-1-anisyl-2-alkylvinyl bromides increases in the series

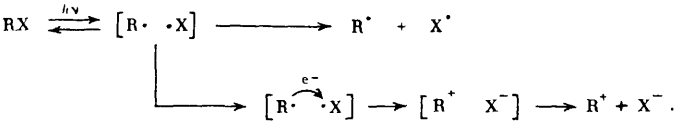
$$H < MeM < p\text{-}MeOC_6H_4 < t\text{-}Bu$$

approximately by a factor of 10^3. At the same time the rate of solvolysis of the (*Z*)-isomers remains virtually unchanged.[63]

As has already been mentioned, one of the factors in the stabilisation of VCs is anchimeric assistance of substituents due to the presence in the initial molecule of a centre of nucleophilicity that is not conjugated with the reaction site. When β-mercapto groups are present in vinyl compounds, acceleration of solvolysis occurs. It may be assumed from the formation of a considerable number of cyclic products (thiophenes) that S_N1 solvolysis of β-arylmercapto-vinyl derivatives takes place as a result of anchimeric assistance from the sulphur atom to form an intermediate thiirenium ion, which has greater stability than a linear VC.[1–7]

b) Photochemical methods for obtaining vinyl cations

The photolysis of vinyl compounds can result in the formation of VCs. According to Kropp and McNeely,[64,65] the formation of VCs is due to electron transfer in the primary radical pair formed on excitation of a vinyl halide molecule:



It is evident that heterolytic cleavage of the bond between the atoms requires a greater consumption of energy than the homolytic cleavage that accompanies the formation of a radical pair. Therefore, ionic products are generally formed with lower yields.[66–68]

A considerable increase in yield of the products of the reactions between photogenerated VCs and nucleophiles can be achieved through oxidation of vinyl radicals by reacting the latter with Cu(II) salts.[69]

Cu(II) salts are capable of almost completely suppressing the formation of products of the photolysis of vinyl halides by a radical mechanism. It is assumed[69] that oxidation with Cu(II) salts is most likely to occur via the formation of an intermediate complex between a vinyl radical and Cu(II), which is supported by the formation of vinyl ethers with a nonrearranged skeleton during photolysis.

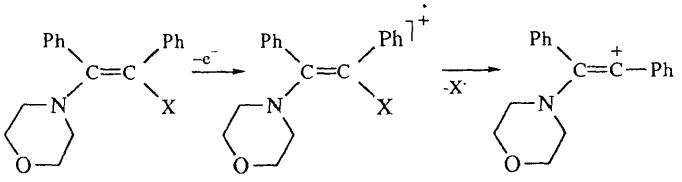
An undoubted advantage of the photochemical method of generating VCs is the possibility of obtaining cations, including primary cations,[65] in a greater variety of nucleophilic media and under milder conditions (absence of strong acids, lower

temperatures) than in the case of solvolysis. However, the reactivity of the cations obtained by this method is higher than that of the cations formed as a result of solvolysis, which may be due to a difference in their energy states. The results of four studies,[14,70–72] according to which the extent of degenerate rearrangements of photogenerated triarylvinyl cations is substantially lower than in species of this type obtained by solvolysis, may be cited as an example. One of the most likely explanations for this phenomenon is that photoexcited VCs evidently have a greater reactivity and the rate of their reaction with nucleophiles is substantially higher than the rate of their isomerisation.

c) Electron impact method

Electron impact, which involves the formation of cations as a result of the fragmentation of the initial vinyl compound on exposure to an electron beam, has found extensive application in research into the thermodynamic properties of simple VCs and in the study of molecular ion reactions.[73–79]

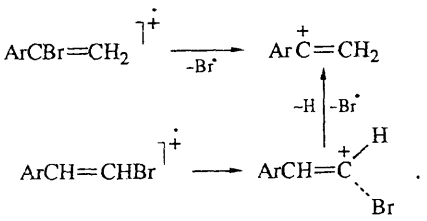
Vinyl cations with a relatively complex structure were obtained by fragmentation of 2-morpholino-*cis*-stilbenyl halide on exposure to a beam of accelerated electrons:[6]



X = Br, Cl.

From a comparison of the relative yields of the VCs in this case it was possible to conclude that atomic chlorine is eliminated with greater difficulty than atomic bromine.

A study of the dissociative ionisation of α- and β-aryl-substituted vinyl bromides showed that monomolecular loss of a Br· radical by the radical cation of the β-bromo derivative is accompanied in the transition state by a rapid 1,2-shift of hydride ion via the double bond to form the more stable secondary 1-arylvinyl cation:[56]

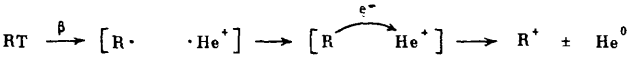


A study of the structures of the species obtained by impact activation with the use of labelled ^{13}C bromine derivatives made it possible to conclude that primary cations are not formed by electron impact.[56]

d) Nuclear chemical method of obtaining vinyl cations

The nuclear chemical method (NCM) occupies a special place amongst those methods used to generate carbocations.[80–83]

On β-decay of a covalently bonded tritium atom that forms part of a hydrocarbon and its conversion to helium, positively charged RHe^+ molecular ions are formed in different energy states and in which the charge is localised on the helium atom. The large difference in ionisation potential between the helium atom and radical R· (approximately 14 eV) causes the positive charge to migrate to the organic fragment. At the same time the neutral helium atom and charged R^+ fragment separate. At the final stage spatial separation of these species occurs, resulting in the formation of free R+ carbocations:



It has been established experimentally that as a result of the β-decay of tritium that is contained in hydrocarbons, singly charged R^+ ions are formed with a yield of the order of 70–80%†, most of which occur in the ground state or in energy levels close to it.[80,81]

During β-decay of tritium there is a marked (twofold) relative change in charge on the nucleus of the daughter He atom—the highest for nuclei undergoing β-decay. However, additional ionisation of the daughter atom as a result of perturbation of the electron shell does not occur, since as a result of the doubling of charge on the nucleus, the electrostatic interaction between the electron and nucleus increases accordingly. This leads to a sharp decrease in yield of species with a charge greater than +1. It should also be stressed that there are no daughter ions having higher charges, because of the impossibility of a cascade of vacancies (the Auger effect) occurring in this case. The latter favourably distinguishes the β-decay of tritium from the decay of radionuclides of other elements such as halogens, whose decay in the form of halogen derivatives of hydrocarbons can also lead to the formation of carbocations.[80,81]

The carbocation nature of the R^+ species obtained by NCM has been demonstrated by numerous experiments, in which their reactions with various nucleophiles were studied (aromatic compounds, ethers and esters, alcohols, etc.).[80–83]

The nature of the processes that occur in molecular systems during β-decay of tritium governs a number of unique features of NCM.

1. During β-decay of tritium that is contained in hydrocarbons, carbocations of a given structure are formed with a strictly determined initial localisation of charge, including that which does not correspond to the most stable state of the ion. The structure of the carbocations is determined by the structure of the initial hydrocarbon and the position in it of the decaying tritium atom

2. The carbocations being generated occur in a free state, i.e. they do not have a counterion or equilibrium solvent cage. The released β-particle (nuclear electron), which provides electrical neutrality to the system as a whole, cannot be regarded as a counterion since it is separated by a distance such that its Coulomb interaction with the carbocation is negligible.

3. With the use of NCM it is possible to obtain carbocations and study their reactions in media of all compositions in the gas, liquid, and solid states. The rate of formation of carbocations in the system is determined by the number of molecules of the tritiated compound (the ion source) and the number of tritium atoms in a molecule of the compound, and it does not depend on external conditions

† The remaining percentage is made up by a large number of ionic and neutral fragments of a different nature. Since the individual contribution of each does not exceed 2–3% and they have a very variable nature, the yields of their reaction products are small.

(temperature, pressure, state of aggregation), since the method is based on radioactive decay processes:

$$dN_{R+}/dt = kq\lambda N_{RT},$$

where dN_{R+}/dt is the rate of formation of carbocations; k is the number of tritium atoms in the molecule (ion source); $q = 0.7-0.8$, a coefficient representing the proportion of effective conversions leading to the formation of a carbocation during tritium decay; λ is the decay constant of tritium, equal to 1.8×10^{-9} s^{-1}; N_{RT} is the number of molecules of the tritiated compound in the system.

4. Reactions in free cation–molecule systems are in best agreement with models used in quantum-chemical calculations of the reaction route (see Section IV).

5. This method presents excellent opportunities for obtaining various reactive species (carbocations, their silicon and germanium analogues, nitronium and nitrenium ions, etc., and halogen ions formed during decay of tritium contained in HHal) in order to study their reactions.

Tritiated hydrocarbons serve as sources of carbocations. In a special case these may be hydrocarbons containing a single tritium atom. However, it is then impossible to monitor the behaviour of cations since the concentration of the reaction products of these ions with given substrates is extremely small. Thus, with an initial activity of the carbocation source of 4×10^7 Bq, about 10^{13} ions are formed over 10–30 days, which corresponds to about 10^{-10} mol of their reaction products. The only method used for determining such small quantities of products is a radiochemical method that is based on the use of hydrocarbons containing at least two tritium atoms as an ion source. The decay of one of these atoms results in the formation of a cation, while the other atom, remaining in the product molecule, can be used for identification of this product chromatographically with detection of its radioactivity‡. We should stress that in contrast to mass spectrometry and ion cyclotron resonance, the radiochemical method can be used to record neutral compounds and, what is very important, distinguish their isomeric forms.

Recently the possibility of using β-decay to obtain reactive species including the case where one radioactive atom forms part of the initial molecule and gives a stable isotope of a neighbouring element, for example, $^{14}CO_2 \xrightarrow{\beta} {}^{14}NO_2^+$, was demonstrated. The yield of products of the reactions that occur with the participation of NO_2^+ can be determined by high-performance liquid chromatographic (HPLC) methods.[84]

NCM was successfully used to generate a number of aliphatic and aromatic C_1-C_{10} carbocations and for studying their reactions with various types of nucleophilic reagents.[80–83,85,86] Subsequently, vinyl[87,88] and ethynyl[89] cations were obtained by the same method. To date the ethenyl cation[88] and 1- and 2-phenylvinyl cations[87] have been obtained. Doubly tritiated ethylene THC=CHT and styrene PhTC=CHT have been used as sources of VCs. β-Decay of tritium in the alkene leads to the formation of free VCs as a result of heterolysis of the C–He bond in the primary molecular ion:

$$RTC{=}CHT \xrightarrow{\beta} R\overset{+}{C}{=}CHT \text{ (or } RTC{=}\overset{+}{C}H)$$

R = H, Ph.

‡ The probability of simultaneous decay of two tritium atoms is negligible, being dependent on the square of the decay constant of tritium.

The ethenyl cation has low thermodynamic stability. Therefore previously it was only possible to detect its formation and reactions through the use of electron impact in the gas phase at low pressures.[77–79] With the application of NCM it was possible to study the reactions of this ion with benzene and methanol in the liquid phase,[88,90] hydrogen and methanol in the gas phase,[91] and with a number of arenes in the gas and liquid phases.[92]

As a result of the nonequivalence of the positions of the tritium atoms in the side chain of the styrene-T_2 molecule, the cations formed through processes initiated by β-decay have different structures and the positive charge on them is localised at different positions. Since decay of each of the tritium atoms is equally probable, the initial number of isomeric 1- and 2-phenylvinyl cations must be the same.

According to quantum-chemical calculations, the heat of formation of 2-$C_8H_7^+$ is higher than that of 1-$C_8H_7^+$.[60,62] Consequently, the 2-$C_8H_7^+$ ion is more reactive. Moreover, its isomerisation to 1-$C_8H_7^+$ by a hydride 1,2-shift is to be expected. The possibility of this isomerisation was examined in the case where generation of 1- and 2-phenylvinyl cations was achieved by dissociative ionisation of the corresponding bromides through electron impact.[56] However, it was shown by MNDO calculations that the isomeric forms of a phenylvinyl cation are separated by a potential barrier of 80 kJ mol^{-1}. As according to theory the vast majority of cations obtained by NCM occur in ground energy states, it is clear that isomerisation of the 2-$C_8H_7^+$ ion to 1-$C_8H_7^+$ must be a difficult process. Hence the difference between the yields of products obtained by reaction of each of the cations with given nucleophilic reagents may be solely dependent on their different reactivities (see Section IV).

III. Reaction of vinyl cations with nucleophilic reagents

According to their definition, VCs constitute a type of carbocation. The carbon atom of the carbocation centre of a VC is formally trivalent and has a vacant orbital§. Therefore VCs, like aliphatic cations, can attack those parts of molecules with increased electron density, namely, atoms with an unshared electron pair (*n*-donors), multiple bonds (π-donors), and σ-bonds. Moreover, VCs can exhibit the properties of Brønsted acids, having the ability to transfer a proton to a specific nucleophile.

1. Reactions of vinyl cations with *n*-donors

The main products of an S_N1 reaction involving the solvolysis of vinyl compounds in oxygen-containing solvents are vinyl ethers and ketones. A number of authors explain the formation of these products by the fact that intermediate oxonium ions are formed during reaction (by analogy with aliphatic ions) as a result of the addition of the VC to the oxygen atom of the solvent. The route of the subsequent decomposition of the oxonium ions depends on the composition of the medium and on steric factors.[94–101]

For the solvolysis of vinyl compounds in alcohols or acids the most typical reaction is formation of vinyl ethers as products of the deprotonation of oxonium ions. The alternative possibility for

§ When considering the structure of the parent cation of this class — the ethenyl cation — nonempirical calculations[93] have shown that it probably possesses a bridged structure, which is estimated to be 12 kJ mol^{-1} more stable than a linear structure.

decomposition of oxonium ions with elimination of R groups and formation of an alcohol (ketone) virtually never occurs. Such selectivity in the course of the reactions of VCs with HOR molecules is evidently due to the impossibility of forming a stable intermediate involving an R group in a nucleophilic medium. This is caused, firstly, by the considerable steric hindrance which arises during the formation of a complex between an eliminated R group and the solvent (or buffer base) compared to similar complexes involving a proton. Secondly, according to the principle of hard and soft acids and bases (HSAB), interaction of the protonised hydrogen atom of an oxonium ion with the oxygen or nitrogen atoms of a nucleophile (solvent, buffer base) is energetically more favourable.

In the solvolysis of 1-anisyl-2-methylpropene-1-yl bromide or tosylate in trifluoroethanol (TFE), the sole product formed is an ether, which is consistent with the idea that an oxonium ion is formed, transferring a proton to a solvent molecule:

$$AnCX{=}CMe_2 \longrightarrow An\overset{+}{C}{=}CMe_2 \xrightarrow{TFE} AnC(OCH_2CF_3){=}CMe_2$$

An–anisil, X = OTs, Br.

The solvolysis of vinyl compounds on treatment with acids sometimes results in the formation of ketones. For example, in the acetolysis of 1-anisyl-2-methylpropen-1-yl bromide in the presence of sodium acetate as a buffer base, a ketone was identified amongst the reaction products:[94,95]

$$AnCBr{=}CMe_2 \longrightarrow An\overset{+}{C}{=}CMe_2 \xrightarrow[-H^+]{HOAc} \longrightarrow AnC(OAc){=}CMe_2 \xrightarrow{HOAc} AnCOCHMe_2.$$

However, it was established that formation of the ketone is not due to decomposition of the oxonium ion through separation of the R group but results from a side reaction in which an initially formed ether is converted to the ketone on treatment with the acid.

In a study of the solvolysis of halogen derivatives of *p*-methoxystyrenes in 80% aqueous ethanol, it was established that when there are no substituents at the β-position, a ketone is the sole product, whereas both a ketone and an ether are formed from the β,β-dimethyl derivative.[95] The authors specially noted the fact that the reaction conditions excluded the possible occurrence of a side reaction involving hydrolysis of the resulting ether and its conversion to a ketone.

The effect of a buffer base on the reactions of VCs was studied by Grob and Nussbaumer.[102] The ratio of the yields of ether to ketone as solvolysis products of the *cis*- and *trans*-isomers of 1-anisyl-propen-1-yl bromide in 80% ethanol increases with an increase in concentration of triethylamine:

$$(E)\text{- or } (Z)\text{-}AnC(Br){=}CHCH_3 \xrightarrow[H_2O]{EtOH} AnCOC_2H_5 + \\ + AnC(OEt){=}CHCH_3. \quad (1)$$

The buffer bases are used to suppress processes competing with the S_N1-type monomolecular nucleophilic substitution which result in the formation of similar products. An $Ad_E{-}E$ process that takes place with an electrophilic addition–elimination mechanism may be examined in this connection. At the first stage protonation of the vinyl compound and formation of a trisubstituted carbocation occur. The ion is then attacked by the nucleophile, resulting in the elimination of HX and the formation of a substitution product. The introduction of a buffer base can suppress the development of an $Ad_E{-}E$ mechanism since the base reacts with the proton.

However, the effect of the buffer bases is evidently more complex, since solvolysis of the vinyl compounds can occur by an electrophilic addition–elimination mechanism even when a buffer is present in the system.[103] It is to be expected that buffer bases not only create favourable conditions for S_N1 solvolysis but are also capable of reacting with the primary products of the reactions between VCs and HOR molecules, namely, oxonium ions. This explains the increase in yield of enol ethers and the decrease in yield of ketone in reaction (1), with an increase in concentration of triethylamine.[103]

The reaction of VCs with anions leads directly to the formation of neutral products. These processes occur most frequently in the electrophilic addition to acetylenes or allenes.

In the electrophilic addition to substituted acetylenes the direction of attack of the anion on the double bond of the VC at the first stage depends to a considerable extent on the size of the substituents at the α- and β-positions of the cation. This occurs because steric strain in the developing vinyl system increases as a result of the relative steric effect of the substituents.[104–107]

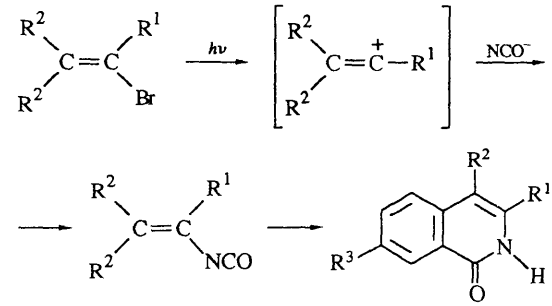
The reaction of VCs with anions during solvolysis has been examined in a number of studies.[6,108,109] In solvolytic systems reactions of VCs may be regarded solely as competing processes for the interaction of cations with the eliminated X^- group and solvent and/or with an added conjugate base $(OR')^-$ and solvent:

$$RX \longrightarrow X^- + R^+ \begin{cases} \xrightarrow{(OR')^-} ROR' \\ \xrightarrow{HOR'} ROR' + H^+. \end{cases}$$

From a study of the effect of additions of a common ion on the rate of solvolysis it was possible to derive a series of reactivity of certain anions that act as *n*-donors towards the 1,2-dianisyl-2-phenylvinyl cation:

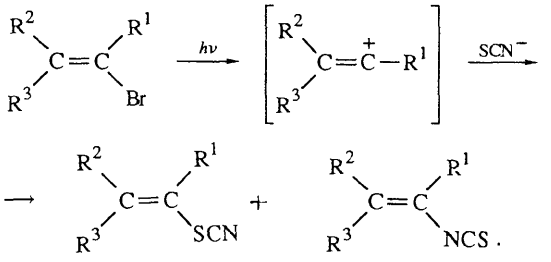
$$Br^- > Cl^- > AcO^- > CH_3SO_2O^- > AcOH.$$

Studies were conducted on the reactions of triarylvinyl cations obtained by photolysis of the corresponding bromides with ambident nucleophiles such as cyanate and thiocyanate anions.[70] The main products of the reaction between the cations and cyanate ion proved to be isoquinolones:



$R^1 = An$; $R^2 = Ph$, *p*-An; $R^3 = H$(when $R^2 = Ph$), OMe(when $R^2 = p$-An).

The reaction with thiocyanate anion occurs by two routes, which is caused by the presence of the two reaction sites on the anion—the sulphur atom and the nitrogen atom:



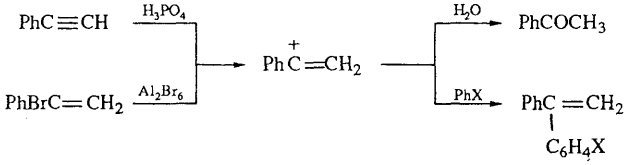
It should be noted that the VC mainly attacks the sulphur atom of the thiocyanate anion. This is due to the fact that the sulphur atom is a softer reaction site than the nitrogen atom and, according to the HSAB principle, attack by a soft reactant such as triarylvinyl cation is energetically more favourable on the sulphur atom.

2. Reactions of vinyl cations with π-electron systems

a) Aromatic compounds

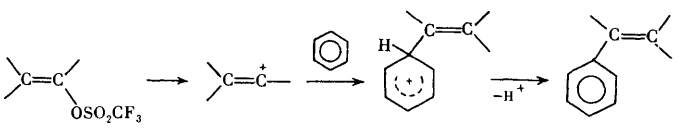
Although they are of undoubted practical interest, the reactions of VCs with π-electron systems have received very little study. This is primarily related to the question of using vinyl and acetylenic compounds as vinylating agents in electrophilic substitution reactions in aromatic systems.

In a study of the reaction between toluene and α-bromostyrene or phenylacetylene in the presence of Al_2Br_6 or H_3PO_4 it was found[110] that products derived from the replacement of a hydrogen atom at the *ortho* and *para* positions of the benzene ring of toluene and also acetophenone are mainly formed in this reaction. Vinylation of anisole with phenylacetylene in H_3PO_4 also results in the formation of the *ortho* and *para* derivatives. These results are consistent with the proposed formation of an intermediate of a 1-phenylvinyl cation:



Trisubstituted vinyl bromides in the presence of silver tetrafluoroborate as a catalyst were used as the vinylating agent in substitution reactions in a series of aromatic compounds, making it possible to obtain vinyl-substituted arenes in high yield.[69]

When alkylsulphonates are used it is possible to carry out the alkylation in the absence of Friedel–Crafts catalysts.[111] Vinyl triflates were very promising in this respect. The results are consistent with the assumption that the reaction takes place by a mechanism whose first stage is elimination of the $CF_3SO_2O^-$ anion from vinyl triflate to give a VC. The subsequent reaction with arene results in the formation of a phenonium ion (σ-complex), which is converted to the substitution product after elimination of a proton:



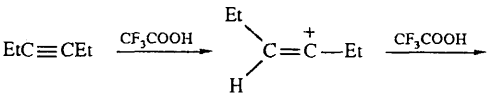
The σ^+ constants of Brown are the most suitable for a determination of the effect of a substituent on the rate of vinylation with vinyl triflates. The value of $\rho = -2.57$ obtained for the reaction parameter indicates that a positive charge develops on the reaction site.

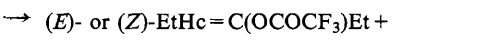
On the other hand, the absence of a kinetic isotope effect in this reaction suggests that vinylation of arenes by vinyl triflates occurs by an electrophilic substitution mechanism. The ratio of the rate constants of reactions involving normal and perdeuterated benzenes ($k_H/k_D = 0.98$) is consistent with the ratios $k_H/k_D = 0.90$ for nitration and $k_H/k_D = 1.13$ for benzylation.

The absolute value of the reaction parameter ρ for alkylation of vinyl triflates is one of the lowest in a series of electrophilic substitution reactions of aromatic compounds.[111] This is due to the high reactivity of the alkylating agent—a vinyl cation—and hence indicates its lack of selectivity towards different monosubstituted arenes containing both electron-donating and electron-withdrawing substituents.

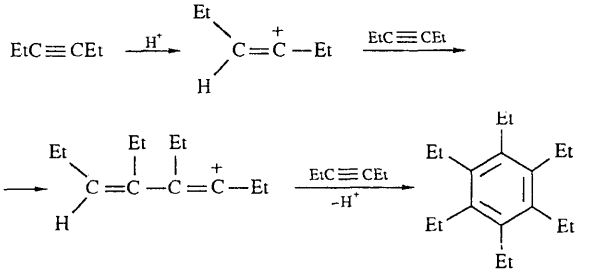
b) Alkenes and alkynes

In the reaction between hex-3-yne and trifluoroacetic acid, isomeric vinyl trifluoroacetates are formed in almost equal quantities and are stable under the reaction conditions:[112]





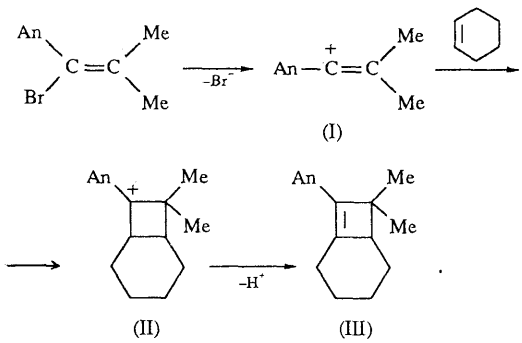
These products are formed as a result of the nonstereospecific addition of trifluoroacetic acid to the linear hexene-3-yl cation. On increasing the concentration of hex-3-yne, hexaethylbenzene is formed. This product most probably occurs as a result of the reaction of the hexen-3-yl cation with an alkyne molecule, which leads to the formation of a homoallylic ion[31–34] and then to trimerisation:



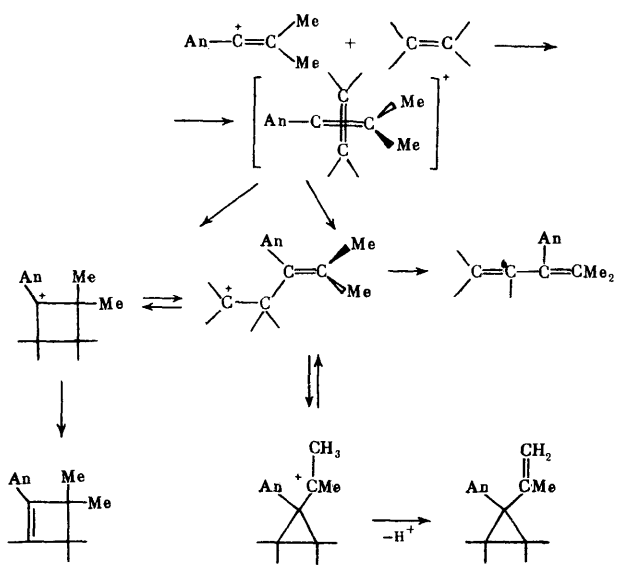
The mechanism of cycloaddition of VCs to olefins was studied in detail by Hanack, et al.[113–117]

On treatment of 1-anisyl-2-methylpropen-1-yl bromide with silver tetrafluoroborate in cyclohexene, compound (III) was obtained in 60% yield. It is evidently formed through the involvement of cation

(II), which occurs as a result of the concerted or stepwise cycloaddition of VC (I) to cyclohexene:



In the reaction between VCs and certain olefins, cyclopropane derivatives were isolated together with cyclobutene derivatives:[116,117]



The formation of cyclobutenes is apparently due to the presence of silver ions in the reaction medium. Silver very readily forms complexes with unsaturated organic compounds and may serve as a catalyst for the process that leads to the formation of cyclobutene derivatives. If VCs are obtained by solvolysis of triflates in the absence of silver ions, cyclopropane derivatives are mainly formed, as a result of [2 + 1] cycloaddition. When silver salts are introduced, the formation of cyclobutenes occurs again. The results obtained suggest that cycloaddition of VCs to olefins occurs by a successive addition mechanism.

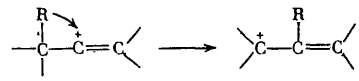
3. Reactions of vinyl cations with the electrons of σ-bonds

Reactions of this type include the conversions of VCs in which the carbocation centre of the cation makes its vacant orbital available to the pair of electrons participating in the formation of a σ-bond between atoms, such as C–H or C–C. There is only a limited number of such reactions, but of these the rearrangement of VCs and the deprotonation of VCs with the formation of acetylenes may be singled out.

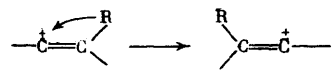
a) Rearrangements of vinyl cations

Rearrangement of VCs takes place as a result of 1,2-shifts of groups of atoms:

1) transfer of groups to a double bond with the formation of allylic cations:



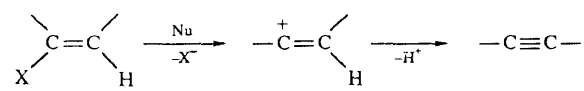
2) displacement of groups between carbon atoms forming a double bond, with the result that one VC is isomerised to another



Comprehensive information on the rearrangements of VCS and essential examples can be obtained from a monograph[4] and two reviews;[6,14] therefore they are not included in this review.

b) Deprotonation of vinyl cations

In the solvolysis of β-unsaturated vinyl compounds, in many cases acetylenes are formed together with ketones and/or ethers:



From a study of the mechanism of elimination reactions in a series of vinyl compounds undergoing solvolysis it was possible to establish that the ratio of the yield of products of an S_N1 reaction to that of products of $E1$ deprotonation depends to a considerable extent on the structure of the VC, the nature of the solvent in which solvolysis is occurring, and the basicity of the reaction medium.

As was mentioned in the examination of solvolytic methods for generating VCs, a decrease in steric strain in the initial vinyl compound through the formation of a VC with an *sp*-hybridised carbocation centre assists heterolysis of the (C=)C–X bond. In this case the yield of alkynes must increase with increased size of the substituents; elimination of a proton from the cation reduces the steric strain to an even greater extent. On the other hand attack by a nucleophile on the carbocation centre has the reverse effect.[8,63,98,118,119]

In addition to steric factors, the basicity of the reaction medium has a considerable effect on the ratio of substitution to elimination products. This can be illustrated in the case of the hydrolysis of *p*-aminobromostyrene in ethanol at different pH values.[120] With an increase in pH from 3.8 to 13.1 the yield of *p*-aminophenylacetylene increases from 16 to 85%, which on the whole is consistent with the HSAB principle. The carbocation centre of the cation is classed as a soft reaction site, whereas a hydrogen atom which has a partial positive charge is a hard reaction site. Since interactions between centres of the same type are energetically more favourable, the use of hard strongly basic nucleophiles favours the removal of a proton from the vinyl cation, which is reflected in an increased yield of alkynes.

IV. Reactions of free vinyl cations

As was mentioned in our description of the nuclear chemical method of generating carbocations, these cations occur in the free state, i.e. they do not have a counterion or equilibrium solvent cage and their reactions are classed as ion–molecule reactions (IMRs).

The rate of the reactions between ions and molecules is extremely high; in the majority of known cases the rate constants of IMRs are $10^{-12}-10^{-8}$ cm^3 mol^{-1} s^{-1}, which are many orders higher than the constants for reactions between neutral molecules. The low of zero values of the energy of activation and the high collision cross-sections account for this. As a consequence the cross-sections of IMRs (10^{-14} cm^2) match the cross-sections for collisions between ions and species of the medium.[80–84]

In the interaction between a thermolysed molecule and ion, an associated state, or "long-lived complex", develops, in which a statistical exchange of energy between different vibrational degrees of freedom occurs. In this case excitation of the internal degrees of freedom of the reacting species occurs and the complex is converted to a vibrationally excited state. Further conversion of the "long-lived complex" depends on the nature of the distribution of its internal energy and the degree of complexity of its transformation to the corresponding activated complex and then to the reaction products.

In the gas phase species have a long mean free path and in the intervals between collisions they may be regarded as free. At low densities when there is no interaction between the species, the distribution of the latter is random and the activation barrier for unimolecular decomposition or isomerisation of the activated complex in the gas phase may be surmounted through the energy of its collisions with species of the medium.

A completely different pattern occurs in the reaction between free cations and molecules in condensed phases (liquid phase and solid vitreous phase, which occurs as a result of a marked cooling of the liquid below the freezing point)¶.

A short mean free path is typical of the species in a condensed phase. Each molecule of liquid is surrounded by a given number of its immediate neighbours, but thermal movement results in disruption of the order arising on interaction between the species themselves.

Let us examine which processes occur in a liquid with the "instantaneous" formation in it of a carbocation as a result of the β-decay of tritium forming part of a hydrocarbon molecule.

A carbocation is formed at the concluding stage of nuclear chemical processes on cleavage of the C^+-He bond in the initial RHe^+ ion. Cleavage of this bond occurs over a period of $10^{-14}-10^{-13}$ s, which is of the same order of magnitude of time for atomic vibrations in a molecule.[80–84] It is evident that over approximately the same period of time the initial structure of the ion is transformed to an equilibrium state through vibrational relaxation.

The ion inherits the solvent cage of the mother molecule, which is not in equilibrium with the ion. In order for this cage to be reorganised, the following must change:[121]

a) the average radius of the cage, if it is assumed to be spherical;

b) the coordination number;

c) the symmetry of the quasi-crystalline structure of the cage, i.e. its shape;

d) the position of molecules with a permanent dipole;

e) the magnitude of the induced dipole moment and the induction energy, which change as a result of a charge developing;

f) the energy of the dispersion interaction, related to the polarisability of the ion.

The rate of these changes accompanying the formation of a carbocation is variable, $10^{-15}-10^{-10}$ s being required to accomplish them. The most rapid are the electronic forms of polarisation (10^{-15} s) and dispersion interactions (10^{-13} s). Orientational polarisation occurs more slowly (10^{-11} s) and the reorganisation of complexes of molecules fixed by hydrogen bonding is even slower (10^{-10} s). Hence, as a result of the very rapid redistribution of charges when a carbocation is suddenly formed, inductive polarisation of the medium by the field of the charge mainly occurs without any change in the spatial distribution of the species. In this sense a carbocation obtained by the nuclear chemical method can be regarded as being in a free state and the formation of the ion as a special Franck–Condon transition. It is clear that in condensed phases the excess energy of a "long-lived complex" is dispersed extremely rapidly by collisions with the surrounding species of the medium. The existence of an ion-dipole interaction between the complex and molecules of the medium increases the probability of such a transfer of energy to an even greater extent. For these reasons the reactions of a "long-lived complex" in solution are determined almost exclusively by the lowest vibrational energy level of this complex.

One of the most fruitful concepts that relates the electronic structure of molecules and ions to their behaviour in chemical reactions has been the frontier orbital theory of Fukui.[122] According to this approach, the frontier orbitals of reacting species play a decisive role in chemical interactions. It was shown by the PMO method that the interaction of the HOMO of one of the reactants (electron donor) with the LUMO of the other reactant (acceptor) makes a predominant contribution to the attractive energy.[123–125] In this case a reaction which results in the formation of a bond between atoms with the maximum charge densities in their frontier orbitals (reaction sites) becomes the most probable. This does not exclude a different coordination of the reactants with respect to each other and a reaction occurring by an alternative route involving other atoms and other reaction sites.[126]

It should be noted that the use of quantum-chemical methods of determining reactivity is most justified for free species, such as in gas-phase reactions (the "isolated molecule" approximation).

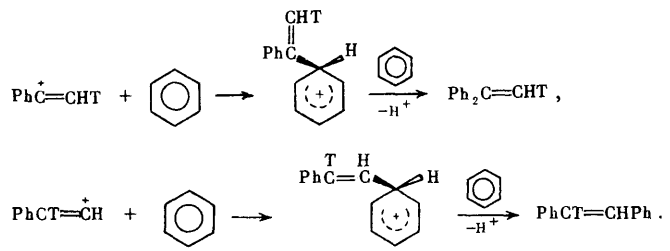
Since low or zero energies of activation and high rates are typical of ion-molecule reactions, the interaction between free cations and molecules in condensed phases may be regarded to the first approximation as the interaction of two free species which also results in the formation of a vibrationally excited "long-lived complex" or a polarised capture complex. Assuming a rapid transfer of energy to molecules of the surrounding medium, this phenomenon makes it sufficiently valid to use different quantum-chemical models, including PMO theory, for predicting the reactivity of free cations generated by the nuclear chemical method.

1. Reaction of free vinyl cations with aromatic and oxygen-containing compounds

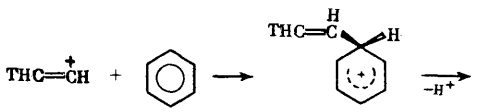
The reactions of free ethenyl and phenylvinyl cations obtained as a result of decomposition of the tritium atoms in doubly tritiated ethylene and styrene (see Section II.4) have been investigated in several studies.[85,87,88,90–92,126,127] Ethenyl cations were generated in benzene and methanol in the liquid state. Phenylvinyl cations were

¶ At the present time the state of a supercooled liquid in which the structure of the initial liquid is preserved is usually regarded as a solid vitreous state.

obtained in the presence of benzene and oxygen-containing compounds with the general formula ROR′ (R, R′ = H, Et) in the gas, liquid, and solid states. It was established in this case that the state of aggregation of the reaction system affects the route of the reactions between free vinyl cations and nucleophiles. The main products of the reaction between free phenylvinyl cations and benzene were 1,1-diphenylethylene, *trans*-stilbene, and isomers of phenylstyrene (see Section IV.2):



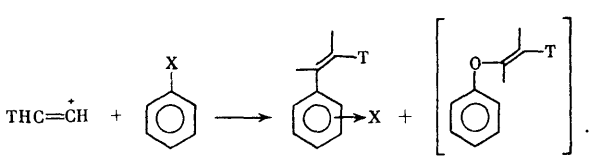
Attack on a benzene molecule by an ethenyl cation results in the formation of styrene:



The formation of diphenylethylene, stilbene, and styrene is consistent with the idea that arenonium ions (σ-complexes) are formed at an intermediate stage of the reaction.

Recently the reactivity and selectivity of free ethenyl cations towards substituted arenes such as toluene, anisole, fluoro-, chloro-, and bromo-benzene in the liquid and gas phases were studied by the method of competing reactions.[92]

In liquid-phase systems the predominant route was exothermic attack by an ethenyl cation on the π-electron system of an aromatic compound. As a result of this attack, an excited arenonium ion (σ-complex) is formed, being deactivated by collisions with molecules of the surrounding medium and undergoing deprotonation to form substituted styrenes. Anisole acts as an ambidentate nucleophile in reactions with an ethenyl cation since, in addition to the phenyl group, the unshared electron pair of the oxygen atom of the methoxy group also undergoes electrophilic attack, resulting in the formation of an oxonium ion. It is converted to phenyl vinyl ether as a result of reaction with another molecule of substrate. However, the efficiency of this process is very low. In reactions with halobenzenes the ethenyl cation exclusively attacks the phenyl group:



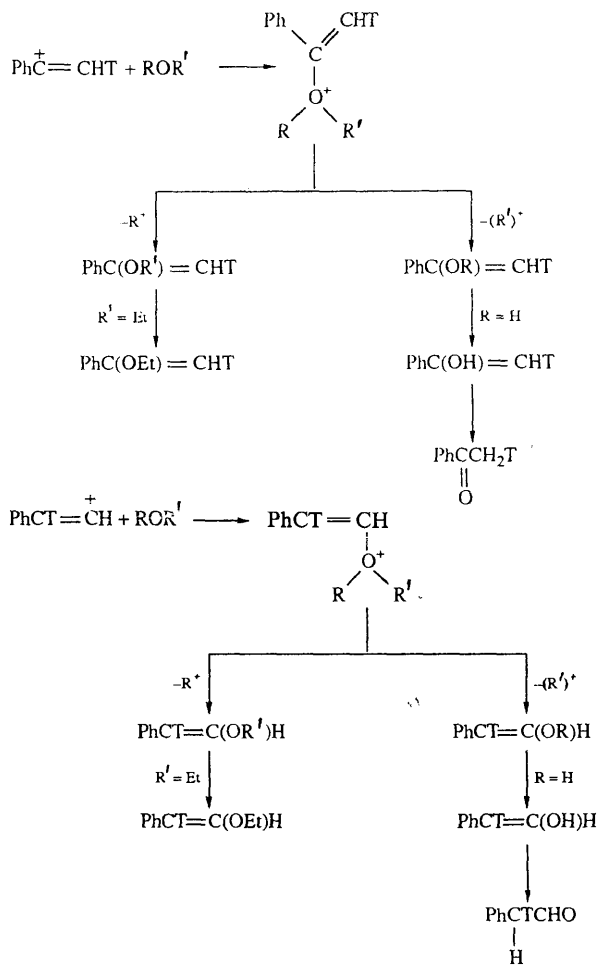
X = Me, OMe, F, Cl, Br X = OMe

The nucleophilic reagents that have been studied can be arranged in the following series of reactivity towards the ethenyl cation in the liquid phase: PhOMe > PhCl > PhMe.

The results obtained from studies on gas-phase reactions of free ethenyl cations with arenes are consistent with the hypothesis that isomeric conversions of their primary reaction products—arenonium or onium ions—take place. In this case the latter occur in an excited state for a considerable time as a result of the difficulty or impossibility of their deactivation through collisions.[80–81,128] Therefore, in contrast to liquid-phase reactions, the isomeric composition of substituted styrenes in gas-phase reactions approximates to the thermodynamically stable composition with a predominance of *meta* isomers. Similar results were obtained in a radiochemical study of ion-molecule reactions of free methyl and phenyl cations with certain alkylbenzenes.

Oxonium ions are known to act as adducts in electrophilic addition reactions of aliphatic carbocations to molecules with the general formula ROR′ (R, R′ = H, Alk).[80,81] The results of four studies[92,124,125,129] are also consistent with the idea that these intermediates are formed as a result of attack by free ethenyl and phenylvinyl cations on the unshared electron pair of the oxygen atom of an ROR′ molecule.

From a quantitative determination of the yields of products formed in the liquid phase it was possible to conclude that the oxonium ions decompose preferentially with the detachment of an alkyl group Et^+ (or Me^+). Thus, in the case of 1- and 2-phenylvinyl cations the yields of acetophenone or phenylethanol were approximately ten times higher than the yields of 1- or 2-ethoxystyrenes respectively:[129]



Formation of an ion by an S_N1 mechanism is accompanied by a substantial reorganisation of the surrounding medium with a change in the orientation of the molecules of the medium and their relative configuration. The cation is in thermodynamic equilibrium with the medium.

In contrast to this, when cations are generated by NCM in condensed phases, the molecules of the medium hardly change their spatial configuration at all relative to the ion formed because of the high rates of nuclear chemical processes. Since for IMRs extremely high reaction cross-sections are typical and virtually every collision of the reacting species results in reaction, the excited intermediate complex between an ion and molecule (an oxonium ion in this case) appears to be isolated from the surrounding medium. As a result, the transfer of excitation energy from the complex to the medium is difficult. Therefore, the complex mainly decomposes by a unimolecular mechanism with formation of the thermodynamically most stable species (an alkyl cation), while elimination of a proton is forbidden. To a certain extent this resembles the reaction of carbocations in the gas phase, such as the reaction of free methyl cations with alcohols and ethers.[80-81] The presence of ethers amongst the products of reactions between free phenylvinyl cations and ethanol in the liquid phase is an indication of the contribution of a bimolecular mechanism for decomposition of the oxonium ion through the transfer of a proton to a substrate molecule. This is due to the occurrence of hydrogen bonding in alcohols.

In competing reactions of free phenylvinyl cations with ethanol and water in equimolar quantities, the ratio of yields of ether to ketone was approximately 0.1 : 1, which indicated the higher reactivity of ethanol relative to water.[129] This is consistent with results on the solvolysis of anisylvinyl halides in 80% aqueous ethanol,[130] which is also supported by a study of reactions involving free triarylvinyl cations produced by flash photolysis.[131] In the latter study it was established that the nucleophilicity of alcohols decreases in the series: MeOH > EtOH > iso-PrOH > (H_2O) > t-BuOH. The ratio of rate constants of reactions between the 2,2-diphenyl-1-anisylvinyl cation and methanol and t-butanol is 12 : 1, while in the case of reactions of the trianisylvinyl cation it is 21 : 1. This variation in reactivity is evidently due to an increase in steric hindrance in the intermediate complex. The low reactivity of water is probably due to the fact that its molecules and the molecules of the solvent — acetonitrile — in which flash photolysis was conducted from clusters via hydrogen bonds, and this makes water less nucleophilic. However, the question as to whether this series of reactivity of alcohols and water is retained when the composition of solution is changed was not discussed by Kobayashi, et al.[131]

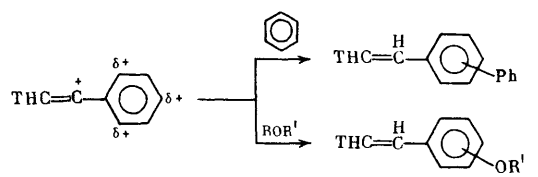
Free VCs of the type $R^1R^2C{=}C^+R^3$ ($R^1{-}R^3$ = Ph, An, Me) which are obtained by flash photolysis of the corresponding bromides in acetonitrile have a characteristic band (λ = 355 nm) in their absorption spectrum and a lifetime of 1 – 20 μs.[132] The rate constants of reactions between nucleophilic reagents (*N*-methyl and *N*-vinyl-2-pyrrolidone styrene, *n*-butyl vinyl ether, α-methylstyrene, methyl methacrylate, tetrahydrofuran, ethers, and aliphatic alcohols) and cations are $10^5 - 10^8$ litre mol^{-1} s^{-1}. The composition of the products has not been studied. The highest reactivity of the 1-(*p*-anisyl)-2,2-dimethylvinyl cation has been attributed to the high positive charge on its carbocation centre and low steric hindrance (in the series of VCs studied).

2. Participation of aryl groups in reactions of free substituted vinyl cations

As was demonstrated by quantum-chemical calculations of the electron densities on the atoms of phenylvinyl cations, the 1-phenylvinyl cation is stabilised through overlap of the vacant 2*p* orbital of the carbocation centre and the HOMO of the phenyl group, occurring as a result of the Ph group rotating through 90°. This causes the carbon atoms at the *ortho* and *para* positions of the phenyl group to be activated. The $2p_y$ orbitals of these atoms participate in the formation of the LUMO of the cation, which results in a positive charge developing at these positions.

The 1-phenylvinyl cation can be regarded as a multicentre electrophile. The 2-phenylvinyl cation is a single-centre electrophile as its LUMO is formed almost completely from $2p_y$ atomic orbitals of the carbocation centre, on which the main positive charge is localised.[55,57,58]

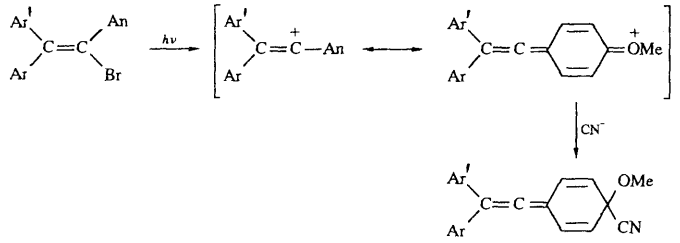
By regarding the interaction between carbocations obtained by NCM and molecules as an interaction between free species whatever their state of aggregation might be, the formation of "long-lived complexes" involving each reaction site may be assumed.[58,87,126-128] This can explain the replacement of a hydrogen atom at the *ortho* and *para* positions of the phenyl group of phenylvinyl cations and the formation of their reaction products with benzene — *o*- and *p*-phenylstyrenes — as well as the formation of hydroxy- and ethoxystyrenes when they react with ROR′ compounds (R, R′ = H, Et):



In a condensed state, in contrast to gas-phase reactions, interaction between phenylvinyl cations and benzene does not lead to the formation of *o*-phenylstyrene. Furthermore, the reaction sites at the *ortho* position of the phenyl group in 1-$C_8H_7^+$ in the addition of this cation to ROR′ molecules had no recorded effect on the process. This is presumably due to the fact that in a condensed state the conversion of *ortho*-oriented complexes to reaction products encounters a number of difficulties caused by electronic repulsion of the vinyl residue in the sterically strained molecule of the *ortho* isomer and the need to disrupt the conjugation between the vacant orbital of the carbocation centre and the HOMO of the phenyl group of 1-$C_8H_7^+$. In the gas phase these barriers are readily surmounted, since the resulting complexes occur in a vibrationally excited state.[58,87,126-128]

A study of the flash photolysis of arylvinyl bromides has supported the idea that α-aryl groups participate in reactions of the resulting VCs.[131-133] Thus, because of the delocalisation of positive charge and the development of additional reaction sites, the addition of cyanide or alkoxide ions becomes possible not only to the carbocation centre of the 1-(*p*-anisyl)-2,2-diarylvinyl cation but also to the α-anisyl substituent, which is accompanied by *ipso*-substitution

of the methoxy group. The intermediate of *ipso*-substitution—diarylmethoxycyanovinylidenecyclohexadiene—was identified by ^{1}H NMR[133–135] and isolated from the reaction mixture.[136,137]



In the photolysis of 1-(*p*-anisyl)-2,2-diarylvinyl bromide in solutions of MeOH, EtOH, and PrOH in the presence of NEt_3, pyridine and $NaHCO_3$, *ipso*-substitution does not take place.[134] Diphenylvinylidenecyclohexadienone acetal—a product of *ipso*-substitution—is stable in neutral and weakly acidic media, while in an acidic medium it decomposes to form a 2,2-diphenyl-1-alkoxyphenylvinyl cation, which made it possible to study the reaction of the latter with methanol, water, anisole, and bromide and thiocyanate ions.[138]

3. Free-cationic polymerisation

One of the most important reactions of carbocations with olefins is cationic polymerisation. The process is initiated by the addition of an ion to an olefin molecule, as a result of which a new carbocation is formed that is also capable of attacking an olefin molecule.

This question has not been studied in relation to VCs except in the specific case of the free-cationic polymerisation of styrene in bulk and also in its solutions in cyclohexane and methylcyclohexane by phenylvinyl cations generated by NCM.[124] The polymers obtained had a high molecular weight—10^6 in the polymerisation of pure styrene and 10^5 in 10% solutions of these solvents. They had a unimodal molecular weight distribution. The latter circumstance provides evidence that polymerisation is initiated by species of the same nature, namely, phenylvinyl cations. On lowering the temperature to −78 °C the molecular weight of the polymer increased, which also pointed to the cationic nature of the processes occurring. However, the possibility of radical cations which may be formed as a result of radiolysis of components of the solution participating in these processes cannot yet be excluded categorically.

V. Conclusion

Vinyl cations, which were discovered more than 25 years ago, have become the subject of intense experimental and theoretical study, and they have currently gained general recognition.

Vinyl cations, as has been convincingly demonstrated in a considerable number of studies, are in many respects similar to the well-studied alkyl and aryl cations. They may be obtained by methods that are similar to those used for generating saturated cations, such as by electrophilic addition to the triple bond of acetylenes and the cumulene bond of allenes, including intramolecular attack on the double bonds of the carbocation centre formed as a result of solvolysis. The method based on heterolysis, in particular solvolysis of the (C=)C−X bond in vinyl compounds, has been used the most extensively.

Unique opportunities are presented by the nuclear chemical method of generating VCs in a free stage. This is related to the application of the β-decay of tritium that is covalently bound in vinyl compounds (a free state is taken to mean a state that is characterised by the absence of a counterion and an equilibrium solvent cage).

According to quantum-chemical calculations that have been confirmed experimentally, VCs mainly have a structure with a linear or quasi-linear configuration of the σ-bonds at the carbocation carbon atom. Cycloalkenyl cations with small rings (C_3−C_6) in which this linear structure does not occur have been theoretically predicted and obtained.

Studies on the rearrangements of VCs using labelled atoms clearly attest to the possibility of bridged VC structures being formed, especially as a result of the migration of aryl groups.

The results collected to date demonstrate that VCs act as typical electrophilic reagents. Because of the presence of a vacant 2*p* orbital, VCs participate in reactions with *n* and π-donors and they are capable of attacking the σ-electrons of C−C or C−H bonds.

The role of the individual groups of substituents in VCs and their saturated analogues appear to be similar in many respects. However, VCs have greater reactivity as intermediates than aliphatic cations. The reactions in which VCs participate take place with lower selectivity. The main characteristics of VCs are governed by the presence of a rigid double bond, which to a considerable extent affects the stereochemistry of many reactions involving VCs.

References

1. G Modena, U Tonellato *Adv. Phys. Org. Chem.*, 1971, **9** 184
2. P J Stang *Prog. Phys. Org. Chem.*, 1973, **10** 205
3. M Hanack *Acc. Chem. Res.*, 1976, **10** 364
4. P J Stang *Acc. Chem. Res.*, 1978, **11** 107
5. P J Stang, Z Rappoport, M Hanack, L B Subramanian *Vinyl Cations*, Academic Press, New York, 1979, p. 684

5a. T L Jacobs, S Searles *J. Am. Chem. Soc.*, 1944, **66** 686

6. M Hanack *Acc. Chem. Res.*, 1970, **3** 209
7. Z Rappoport *React. Intermed.*, 1983, **3** 427
8. C A Grob, G Cseh *Helv. Chim. Acta*, 1964, **47** 194
9. P J Stang, R H Summerville *J. Am. Chem. Soc.*, 1969, **91** 4600
10. L R Subramanian, M Hanack *Chem. Ber.*, 1972, **105** 1465
11. T S Abram, W E Watts *J. Chem. Soc., Perkin Trans. 1*, 1977, 1522
12. L I Zakharkin, V V Kobak *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1919
13. E W Koch, H U Siehl, M Hanack *Tetrahedron Lett.*, 1985, **26** 1493
14. A A Shchegolev, M I Kanishchev *Usp. Khim.*, 1981, **50**(6) 1046 [English translation in *Russ. Chem. Rev.*, 1981(6)]
15. D Kaufman, R Kupper, T Neal *J. Org. Chem.*, 1979, **44** 3076
16. F Marcuzzi, G Melloni, M V Zucca *Gazz. Chim. Ital.*, 1987, **117** 219
17. G Melloni, G Modena, U Tonellato *Acc. Chem. Res.*, 1981, **14** 227
18. H Martens, F Janssens, G Hoornaert *Tetrahedron*, 1975, **31** 177
19. B E McCarry, R L Markezich, W S Johnson *J. Am. Chem. Soc.*, 1973, **95** 4416
20. W S Johnson, T M Yarwell, R F Myer, et al. *Tetrahedron Lett.*, 1978, 2549

21. J Pornet, D Damour, L Miginiac *J. Organomet. Chem.*, 1987, **319** 333
22. K Yates, G H Schmid, T W Regulski, et al. *J. Am. Chem. Soc.*, 1973, **95** 160
23. G Modena, F Rivetti, U Tonellato *J. Org. Chem.*, 1978, **43** 1521
24. M F Ruasse, J E Dubois *J. Org. Chem.*, 1977, **42** 2686
25. Sh O Badanyan, G G Melikyan, G R Mkhitaryan, et al. *Arm. Khim. Zh.*, 1981, **34** 926
26. A V Shastin, E S Balenkova, Yu N Luzikov, et al. *Zh. Org. Khim.*, 1985, **21** 1598
27. I D Gridnev, E S Balenkova, Yu N Luzikov, et al. *Zh. Org. Khim.*, 1988, **24** 1605
28. S V Borodaev, E V Naumova, S M Luk'yanov *Zh. Org. Khim.*, 1986, **22** 1789
29. S V Borodaev, S V Zubkova, S M Luk'yanov *Zh. Org. Khim.*, 1988, **24** 2330
30. D Maniou, M Maniou, G Dinulescu, et al. *Rev. Roum. Chim.*, 1984, **29** 193
31. D Maniou, M Maniou, G Dinulescu, et al. *Rev. Roum. Chim.*, 1984, **29** 201
32. D Maniou, M Maniou, G Dinulescu, et al. *Rev. Roum. Chim.*, 1984, **29** 671
33. D Maniou, M Maniou, G Dinulescu, et al. *Rev. Roum. Chim.*, 1984, **29** 857
34. D Maniou, M Maniou, G Dinulescu, et al. *Rev. Roum. Chim.*, 1985, **30** 223
35. A D Allen, G Angelini, G Paradisi, et al. *Tetrahedron Lett.*, 1989, **30** 1315
36. A D Allen, Y Chiang, A J Kresge, et al. *J. Org. Chem.*, 1982, **47** 775
37. P Wan, K Yates *Rev. Chem. Intermed.*, 1984, **5** 157
38. S Fornarini, M Speranza *J. Chem. Soc., Chem. Commun.*, 1985, 1692
39. V Lucchini, G Modena *J. Am. Chem. Soc.*, 1990, **112** 6291
40. K Grisbaum *Angew. Chem., Int. Ed. Engl.*, 1969, **8** 993
41. F Amar, D R Dalton, G Eisman, et al. *Tetrahedron Lett.*, 1974, 3037
42. T L Jacobs, R N Johnson *J. Am. Chem. Soc.*, 1960, **82** 6397
43. C U Pittman *J. Chem. Soc., Chem. Commun.*, 1969, 122
44. W Smadja *Chem. Rev.*, 1983, **83** 263
45. A V Fedorova *Zh. Obshch. Khim.*, 1963, **33** 3508
46. A V Fedorova, A A Petrov *Zh. Obshch. Khim.*, 1962, **32** 1740
47. M Hanack, A E F Wachtler *Chem. Ber.*, 1987, **180** 727
48. M Hanack, G J Collins, H Stutz, et al. *J. Am. Chem. Soc.*, 1981, **103** 2356
49. M Hanack, G J Collins, H Stutz, et al. *J. Org. Chem.*, 1983, **48** 5260
50. M Hanack, G Auchter *J. Am. Chem. Soc.*, 1985, **107** 5238
51. M Santelli, M Bertrand *Tetrahedron*, 1974, **30** 227
52. Y Apeloig, J B Collins, D Cremer, et al. *J. Org. Chem.*, 1980, **45** 3496
53. P J Stang *Acc. Chem. Res.*, 1978, **11** 107
54. Y Apeloig, P V R Schleyer, J A Pople *J. Am. Chem. Soc.*, 1977, **99** 5901
55. Y Apeloig, P V R Schleyer, J A Pople *J. Org. Chem.*, 1977, **42** 3004
56. Y Apeloig, W Franke, Z Rappoport, et al. *J. Am. Chem. Soc.*, 1981, **103** 2770
57. H Mayr, R Schneider, D Wilhelm, et al. *J. Org. Chem.*, 1981, **46** 5336
58. V P Lebedev, A Yu Shibaev *Zh. Org. Khim.*, 1986, **22** 918
59. J B Hassendenteufel, M Hanack *Tetrahedron Lett.*, 1980, 503
60. M Schiavelli, D M Jung, A K Vaden, et al. *J. Org. Chem.*, 1981, **46** 92
61. H Taniguchi, S Kobayashi, T Nishi, et al. *J. Chem. Soc., Chem. Commun.*, 1980, 103
62. R H Summerville, G A Senkler, P V R Schleyer, et al. *J. Am. Chem. Soc.*, 1974, **96** 1110
63. Z Rappoport, N Pross, Y Apeloig *Tetrahedron Lett.*, 1973, 2015
64. P J Kropp, S A McNeely *J. Am. Chem. Soc.*, 1983, **105** 6907
65. S A McNeely, P J Kropp *J. Am. Chem. Soc.*, 1976, **98** 4319
66. T Suzuki, T Sonoda, S Kobayashi, et al. *J. Chem. Soc., Chem. Commun.*, 1976, 180
67. T Kitamura, S Kobayashi, H Taniguchi *Tetrahedron Lett.*, 1979, 1619
68. W Schnabel, I Naito, T Kitamura, et al. *Tetrahedron*, 1980, **36** 3229
69. T Kitamura, S Kobayashi, H Taniguchi *J. Am. Chem. Soc.*, 1986, **108** 2641
70. T Kitamura, S Kobayashi, H Taniguchi *Chem. Lett.*, 1984, 1526
71. T Kitamura, S Kobayashi, H Taniguchi *J. Org. Chem.*, 1984, **49** 3167
72. T Kitamura, S Kobayashi, H Taniguchi, et al. *J. Org. Chem.*, 1982, **47** 5003
73. F P Lossing *Can. J. Chem.*, 1971, **49** 357
74. F P Lossing, G P Semeluk *Can. J. Chem.*, 1970, **48** 955
75. F P Lossing *Can. J. Chem.*, 1972, **50** 3973
76. D H Aue, W H Davidson, M T Bowers *J. Am. Chem. Soc.*, 1976, **98** 6700
77. G G Freeman, P W Harland, M J McEwan *Mon. Not. R. Astron. Soc.*, 1979, **187** 441
78. F P Lossing, J L Holmes *J. Am. Chem. Soc.*, 1984, **106** 6917
79. S N Senzer, K P Lim, F M Lampe *J. Phys. Chem.*, 1984, **88** 5314
80. V D Nefedov, E N Sinotova, M A Toropova *Khimicheskie Posledstviya Radioaktivnogo Raspada* (Chemical Results of Radioactive Decay), Energoizdat, Moscow, 1981, p. 104
81. V D Nefedov, E N Sinotova, M A Toropova *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk.*, 1980, (3) 35
82. M Speranza *Gazz. Chim. Ital.*, 1983, **113** 37
83. F Cacace *Adv. Chem. Sci.*, 1981, **97** 33
84. V D Nefedov, M A Toropova, T P Simonova, et al. *Zh. Org. Khim.*, 1989, **25** 136
85. M Attina, F Cacace, R Cipollini, et al. *J. Am. Chem. Soc.*, 1985, **107** 4824
86. G Angelini, Y Keheyan, G Lilla, et al. *Gazz. Chim. Ital.*, 1989, **119** 107
87. V D Nefedov, E N Sinotova, V P Lebedev, et al. *Radiokhimiya*, 1985, **27** 144
88. S Fornarini, M Speranza *Tetrahedron Lett.*, 1984, **25** 869
89. G Angelini, M Hanack, J Vermehren, et al. *J. Am. Chem. Soc.*, 1988, **110** 1298
90. S Fornarini, M Speranza *J. Am. Chem. Soc.*, 1985, **107** 5358
91. S Fornarini, M Speranza *J. Phys. Chem.*, 1987, **91** 2154
92. S Fornarini, M Speranza *J. Am. Chem. Soc.*, 1989, **111** 7402
93. L A Curtiss, J A Pople *J. Chem. Phys.*, 1988, **88** 7405
94. Z Rappoport, J Kaspi, Y Apeloig *J. Am. Chem. Soc.*, 1974, **96** 2612
95. Z Rappoport, A Gal *J. Chem. Soc., Perkin Trans. 2*, 1973, 301

96. Z Rappoport, J Kaspi *J. Am. Chem. Soc.*, 1974, **96** 4518
97. Z Rappoport, Y Apeloig *J. Am. Chem. Soc.*, 1975, **97** 836
98. Z Rappoport, A Gal *J. Org. Chem.*, 1972, **37** 1174
99. Z Rappoport, Y Apeloig, J Greenblatt *J. Am. Chem. Soc.*, 1980, **102** 3837
100. Z Rappoport, N Pross *J. Org. Chem.*, 1980, **45** 4309
101. Z Rappoport, J Kaspi, D Tsidoni *J. Org. Chem.*, 1984, **49** 80
102. C A Grob, R Nussbaumer *Helv. Chim. Acta*, 1971, **54** 2528
103. L Eckes, M Hanack *Chem. Ber.*, 1978, **111** 1253
104. F Marcuzzi, G Melloni *J. Am. Chem. Soc.*, 1976, **98** 3295
105. F Marcuzzi, G Melloni *Gazz. Chim. Ital.*, 1975, **105** 495
106. R Maroni, G Melloni, G Modena *J. Chem. Soc., Perkin Trans. 2*, 1974, 353
107. F Marcuzzi, G Melloni *J. Chem. Soc., Perkin Trans. 2*, 1976, 1517
108. Z Rappoport, Y Apeloig *J. Am. Chem. Soc.*, 1975, **97** 821
109. Z Rappoport, M Atidia *J. Chem. Soc., Perkin Trans. 2*, 1972, 2316
110. R M Roberts, M B Abdel-Basset *J. Org. Chem.*, 1976, **41** 1697
111. P J Stang, A G Anderson *J. Am. Chem. Soc.*, 1978, **100** 1520
112. P E Peterson *Acc. Chem. Res.*, 1971, **4** 407
113. G Hammen, M Hanack *Angew. Chem.*, 1979, **91** 649
114. M Hanack *Tetrahedron Lett.*, 1981, **22** 553
115. M Hanack *Pure Appl. Chem.*, 1984, **56** 1819
116. K P Bofinger, M Hanack *Chem. Ber.*, 1985, **118** 2993
117. M Hanck, I Harder *Chem. Ber.*, 1985, **118** 2974
118. Z Rappoport, P Schulman, M Thuval *J. Am. Chem. Soc.*, 1978, **100** 7041
119. K Yates, J Perie *J. Org. Chem.*, 1974, **39** 1902
120. C A Grob, H R Pfaendler *Helv. Chim. Acta*, 1971, **34** 2060
121. S G Entelis, R P Tiger *Kinetika Reaktsii v Zhidkoi Faze. Kolichestvennyi Uchet Vliyaniya Sredy* (Reaction Kinetics in the Liquid Phase. A Quantitative Determination of the Effect of the Medium), Khimiya, Moscow, 1973, p. 416
122. K Fukui *Angew. Chem.*, 1982, **94** 852
123. G Klopman *J. Mol. Struct., Suppl. Theochem.*, 1983, **103** 121
124. G Klopman (Editor) *Reactivity and Reaction Pathways* (Translated into Russian), Mir, Moscow, 1977, p. 384
125. V F Traven' *Elektronnaya Struktura i Svoistva Organicheskikh Molekul* (Electronic Structure and Properties of Organic Molecules), Khimiya, Moscow, 1989, p. 384
126. V P Lebedev, Candidate's Thesis in Chemical Sciences, Leningrad State University, Leningrad, 1986, p. 152
127. V D Nefedov, E N Sinotova, V P Lebedev, et al. *Zh. Org. Khim.*, 1988, **24** 90
128. V A Koptyug *Arenonievye Iony: Stroenie i Reaktionnaya Sposobnost'* (Arenonium Ions: Structure and Reactivity), Nauka, Novosibirsk, 1983, p. 270
129. V D Nefedov, E N Sinotova, V P Lebedev, et al. *Radiokhimiya*, 1987, **29** 73
130. F C Schadt, T W Bentley, P V R Schleyer *J. Am. Chem. Soc.*, 1976, **98** 7667
131. S Kobayashi, T Kitamura, H Taniguchi, et al. *Chem. Lett.*, 1983, 1117
132. S Kobayashi, Q Q Zhu, W Schnabel *Z. Naturforsch., B*, 1988, **43** 825
133. T Kitamura, M Murakami, S Kobayashi, et al. *Tetrahedron Lett.*, 1986, **27** 3885
134. T Kitamura, T Kabashima, S Kobayashi, et al. *Chem. Lett.*, 1988, 1951
135. T Kitamura, T Nakamura, T Kobashima, et al. *J. Chem. Soc., Chem. Commun.*, 1989, 1154
136. T Kitamura, T Kabashima, S Kobayashi, et al. *Tetrahedron Lett.*, 1988, **29** 6141
137. T Kitamura, R Furuki, H Taniguchi, et al. *Tetrahedron Lett.*, 1990, **31** 703
138. T Kitamura, T Nakamura, T Kobashima, et al. *J. Am. Chem. Soc.*, 1990, **112** 6149

Translated from *Uspekhii Khimii* **61** 548–563 (1992) U.D.C. 547.196.6:541.6

N-Functionalised carbodiimides

M V Vovk, L I Samarai
The Institute of Organic Chemistry of the Academy of Sciences of the Ukrainian SSR, Kiev

ABSTRACT. A systematic review is presented on the synthesis and the physical and chemical properties of *N*-acyl, *N*-sulphonyl-, *N*-phosphoryl- and *N*-alkenyl-carbodiimides.

The bibliography contains 90 references.

Contents

I. Introduction 297
II. Synthesis of *N*-functionalised carbodiimides 297
III. Physical and chemical properties 301

I. Introduction

Organic carbodiimides are important members of the heterocumulene class of compound. Being highly reactive, they are key starting materials in organic synthesis and, in addition to this, possess of a whole range of properties which have been usefully applied. Since the discovery of the first carbodiimides by Weit in 1874,[1] the chemistry of this class of compound has developed extensively, and data primarily on alkyl and aryl carbodiimides has been surveyed systematically in a number of reviews.[2–5] It is also possible to isolate carbodiimides with functional groups on nitrogen (e.g. RC(O), RSO_2, $R_2P(O)$, $R_2C{=}CR$, R_3Si, etc.), which possess unusual properties quite distinct from unfunctionalised carbodiimides. Most of the work relating to such *N*-functionalised derivatives has been reported during the last 20–25 years and, with the exception of the data relating to *N*-silylcarbodiimides,[6] the information contained therein has not been reviewed.

Up to now, most of the research in this field has been devoted to *N*-acyl-, *N*-sulphonyl-, *N*-phosphoryl- and *N*-alkenyl-carbodiimides. Their syntheses and properties have been examined systematically in the present review.

II. Synthesis of *N*-functionalised carbodiimides

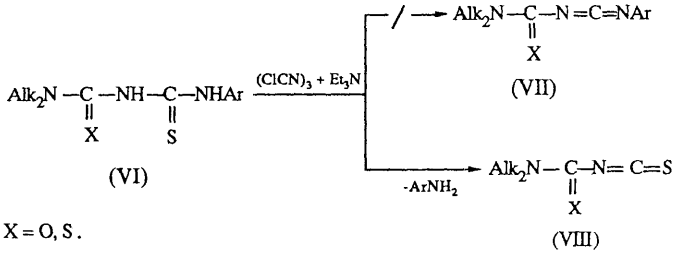
1. *N*-acyl(thioacyl, imidoyl) carbodiimides

Most of the carbodiimides in this category have been prepared by the same methods as used for the synthesis of unsubstituted alkyl and aryl carbodiimides.[4] The commonest route involves dehydrosulphuration of the corresponding thiourea:[7–13]

$$\mathrm{AcylNH{-}C(=S){-}NHR} \xrightarrow[-H_2S]{} \mathrm{AcylN{=}C{=}NR}\ ,\qquad \text{(I)–(V)}$$

R = Alk, Ar.

As seen in Table 1, the yield of carbodiimides (I–V) varies significantly, depending on the nature of the thiourea, the dehydrosulphurating agent, and the reaction conditions. The reaction can be conducted on heating in benzene, acetone or methylene chloride if HgO, PbO or NaOCl is used as the reagent. However, such conditions are unsuitable for preparing *N*-carbamoyl-, *N*-thiocarbamoyl- and *N*-imidoyl-carbodiimides (III–V) which tend to dimerise at elevated temperature. For these carbodiimides, the preferred dehydrosulphurating reagent is cyanuric chloride in the presence of triethylamine, with which reaction can be carried out conveniently at 0 °C; the formation of by-product is minimal and does not complicate the isolation procedure. However, it is not possible to apply this method to the preparation of *N*-(thio)carbamoyl-*N'*-arylcarbodiimides (VII) since the starting (thio)biurets react by cleavage of amine to give the corresponding isothiocyanate (VIII).[9]



X = O, S.

Table 1. *N*-Acyl-, *N*-thioacyl-, and *N*-imidoyl-carbodiimides, AcylN=C=NR (I–V).

Compound	Acyl	Dehydrosulphurating agent	Yield, %	Refs.
(I)	AlkC(O)	HgO	60—90	[7]
		NaClO	см*	[7]
(II)	AlkOC(O)	HgO	37—45	[8]
		$COCl_2 + Et_3N$	см*	[8]
(III)	$Alk_2NC(O)$	$(ClCN)_3 + Et_3N$	53—91	[9]
(IV)	$Ar_2NC(S)$	$(ClCN)_3 + Et_3N$	72—88	[10]
(V)	ArC(=NAr)	$(ClCN)_3 + Et_3N$	72—82	[11, 12]
		$Ph_3P + Et_3N + I_2$	86—95	[13]

*There are no data on the yield.

Mercuric benzamide, diethyl azodicarboxylate–triphenylphosphine and azodibenzoyl–triphenylphosphine[14] have also been used as mild dehydrosulphurating agents for the preparation of *N*-acylcarbodiimides.

A simple route has been devised for the preparation of *N*-ethoxycarbonyl-*N'*-alkylcarbodiimides (IX) as hetero-analogues of *N*-ethoxycarbonylisothiocyanates,[15] which are widely used in the synthesis of heterocyclic compounds. The method is based on the reaction of ethoxycarbonyliminophosgene (X) with sterically hindered primary amines.[16]

$$\underset{\text{(X)}}{EtOC(O)N{=}CCl_2} + AlkNH_2 \xrightarrow[-2HCl]{} \underset{\text{(IX)}}{EtOC(O)N{=}C{=}NAlk},$$

Alk = Pr^i, Bu^i, Bu^t, cyclo-C_6H_{11}.

A similar method has been used for the synthesis of *N,N'*-carbonyldicarbodiimides (XI) as hetero-analogues of *N,N'*-carbonyldiisocyanate.[17]

$$Cl_2C{=}N{-}\underset{\underset{O}{\|}}{C}{-}N{=}CCl_2 + 4AlkNH_2 \xrightarrow[-4HCl]{} AlkN{=}C{=}N{-}\underset{\underset{O}{\|}}{C}{-}N{=}C{=}NAlk.$$

(XI)

Recently, it has been shown that *N*-acylcarbodiimides (XII) and *N*-imidoylcarbodiimides (XIII) can be conveniently prepared by the reaction of trichloromethyl dichlorodiazadienes (XIV) or the isomeric pentachloroethylcarbodiimides (XV) with alcohols and amines, respectively.[18]

$$\underset{\text{(XIV)}}{CCl_3CCl{=}N{-}CCl{=}NR} \xrightarrow[-HCl,\ -MeCl]{MeOH} \underset{\text{(XII)}}{CCl_3\overset{\overset{O}{\|}}{C}{-}N{=}C{=}NR}$$

or

$$\underset{\text{(XV)}}{CCl_3CCl_2N{=}C{=}NR} \xrightarrow[-2HCl]{ArNH_2} \underset{\text{(XIII)}}{CCl_3\overset{\overset{NAr}{\|}}{C}{-}N{=}C{=}NR}$$

R = Pr^i, Ph, 2,4,6-$Me_3C_6H_2$.

A number of *N*-acylcarbodiimides have been obtained by the acylation of monosubstituted cyanamides—the method used by Fromm et al. in 1922 for the preparation of the first member of this class to be characterised, namely (XVII).[19] This was obtained by treatment of the cyanamide (XVI) with benzoyl chloride.

$$\underset{\text{(XVI)}}{N{\equiv}C{-}NHCH_2CH_2OH} \xrightarrow{2PhC(O)Cl} \underset{\text{(XVII)}}{PhC(O)N{=}C{=}NCH_2CH_2OC(O)Ph}.$$

In a subsequent development of the method,[20,21] it was proposed that reaction involves initial formation of an acylcyanamide, isomerisation of which yields the desired carbodiimide. This is not unlike the synthesis of *N*-silylcarbodiimides (XIX), which proceeds via *N*-silylation of the corresponding *N*-acylcyanamide (XVIII).[22,23]

$$\underset{\text{(XVIII)}}{RC(O)NH{-}C{\equiv}N} + Me_3SiCl \longrightarrow [RC(O)N(SiMe_3){-}C{\equiv}N] \longrightarrow \underset{\text{(XIX)}}{RC(O)N{=}C{=}NSiMe_3}$$

R = MeO, EtO.

N-Acyl-*N'*-silyl(stannyl)carbodiimides (XX) are obtained in high yield by acylation of the corresponding silyl(stannyl)carbodiimides (XXI) with carboxylic acid anhydrides or halides,[24,25] or with phenyl isocyanate:[26]

$$\underset{\text{(XXI)}}{R_3MN{=}C{=}NMR_3} + R'COX \xrightarrow{20\ ^\circ C} \underset{\text{(XX)}}{R'C(O)N{=}C{=}NMR_3},$$

R_3M = Me_3Si, Bu_3Sn; R' = Me, CF_3, Ph; X = Cl, MeC(O)O.

Catalytic decarboxylation of isocyanates,[27] which has been widely applied to the synthesis of diarylcarbodiimides, cannot be used for the synthesis of *N*-acylcarbodiimides because of their low thermal stability. However, there is a reference to the *in situ* formation of bis(trichloroacetyl)carbodiimides (XXII) by this route.[28]

$$2CCl_3C(O)N{=}C{=}O \xrightarrow[-CO_2]{} \underset{\text{(XXII)}}{CCl_3C(O)N{=}C{=}NC(O)CCl_3}$$

N-Carbamoylcarbodiimides (XXV) have been prepared by the interaction of isothioureas (XXIII) or chloroformamidines (XXIV) with Ag(I)-cyanate.[9] The isomerisation of the intermediate isocyanatoformamidines (XXVI), takes place by a four-centred mechanism. A similar process was identified earlier during the reversible isomerisation of acylisothiocyanates to thioacylisocyanates.[29]

$$\underset{\text{(XXIII)}}{RN{=}C(SCH_2Ph){-}NMe_2} \xrightarrow{AgOCN} \left[RN{=}C(NMe_2){-}N{=}C{=}O\right] \longrightarrow$$

$$\underset{\text{(XXIV)}}{RN{=}C(Cl){-}NMe_2} \xrightarrow{AgOCN} \left[RN{=}C(NMe_2){-}N{=}C{=}O\right] \longrightarrow$$

(XXVI)

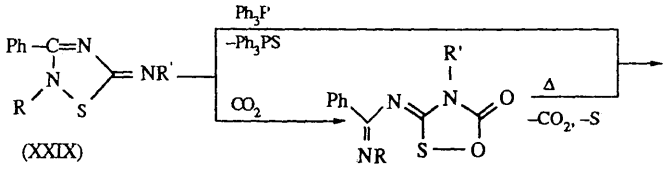
$$\longrightarrow \left[Me_2\overset{+}{N}{=}C(NR){-}C(=O){-}N^-\right] \longrightarrow \underset{\text{(XXV)}}{Me_2NC(O){-}N{=}C{=}NR},$$

R = Bu^t.

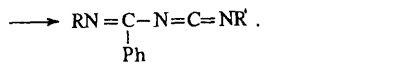
Zimmerman and Olofson devised a novel route to carbodiimides (XXVII) based on the ring opening of 1,2,4-oxadiazolium salts (XXVIII) on treatment with triethylamine.[30]

$$\underset{\text{(XXVIII)}}{Ph{-}C(=N{-}O{-}){=}N{-}} \xrightarrow{Alk_2O^+BF_4^-} Ph{-}C(=N{-}O^+(Alk)){=}N{-}\ BF_4^- \xrightarrow{Et_3N} \underset{\text{(XXVII)}}{PhC(O){-}N{=}C{=}NAlk}.$$

Other five-membered heterocyclic compounds, e.g. 1,2,4-thiadiazolines, may be converted to *N*-imidoylcarbodiimides, e.g. (XXX), by reaction with triphenylphosphine[13] or carbon dioxide.[31]

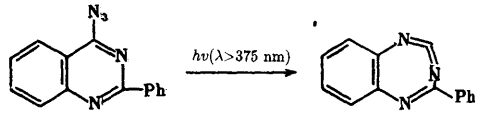


(XXIX)



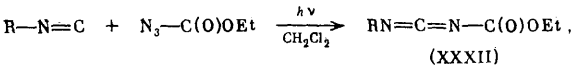
(XXX)

The cyclic imidoylcarbodiimide (XXXI) has been detected spectroscopically as a product derived by photochemical decomposition of 4-azido-2-phenylquinazoline in an argon matrix at 10 K.[32]

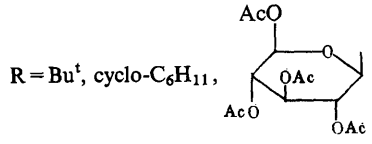


(XXXI)

However, photochemical decomposition of ethyl azidoformate in the presence of isonitriles leads to the corresponding *N*-carbalkoxycarbodiimides (XXXII) in high yield.[33]

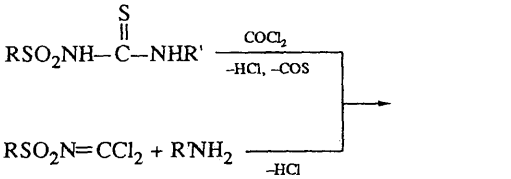


(XXXII)



2. *N*-Sulphonylcarbodiimides

The first representative of this class of compound were prepared by heating the corresponding *N*-sulphonylthiourea with phosgene in toluene or chlorobenzene.[34–39] Reaction proceeds by the initial formation of the corresponding *N*-sulphonylchloroformamidine (XXXIII), dehydrochlorination of which yields the desired carbodiimides (XXXIV).[40–42] The chloroformamidines are also formed as intermediates in the preparation of (XXXIV) from *N*-sulphonyliminophosgenes and primary amines.[43–47]

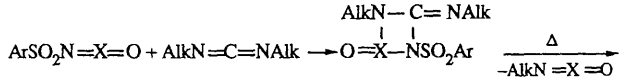


(XXXIII)

(XXXIV)

R, R' = Alk, Ar.

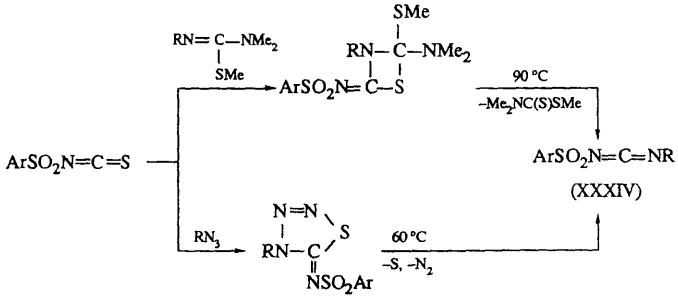
The synthesis of *N*-sulphonylcarbodiimides by metathesis with other types *N*-sulphonylheterocumulene is also worthy of note. Normally, reactions of this type involve initial formation of a [2+2]-cycloadduct, which subsequently decomposes on increasing the temperature. Thus, *N*-sulphonylcarbodiimides (XXXIV) are obtained in high yield by the interaction of *N*-arylsulphonylisocyanates[48–50] or *N*-sulphonylthionylimines[51] with *N,N'*-dialkylcarbodiimides.



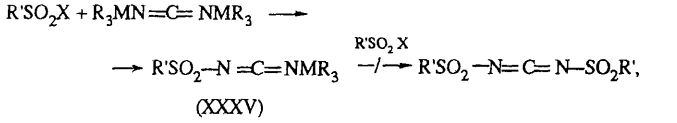
(XXXIV)

X = C, S.

In a similar way, *N*-sulphonylcarbodiimides can be obtained by reaction of *N*-sulphonylisothiocyanates with isothioureas[52] or azides.[53,54]



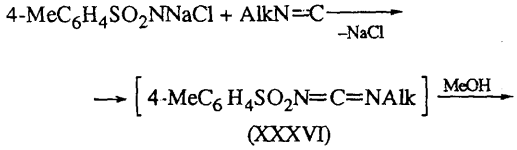
N-Sulphonylcarbodiimides of type (XXXV) have been prepared by sulphonylation of elementoorganic [Group 4] carbodiimides with sulphonyl chlorides.[55,56] However, it is not possible to obtain symmetrical *N,N'*-disulphonylcarbodiimides by reaction of (XXXV) with a second molecule of RSO_2X, presumably because the electron-accepting *N*-sulphonyl group in (XXXV) deactivates the M–N bond.



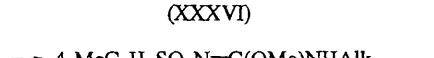
(XXXV)

X = Cl, NCO; R_3M = Me_3Si, Bu_3Sn, Et_3Ge.

There is also the possibility of preparing *N*-sulphonylcarbodiimides (XXXVI) by the scheme: N + CN→NCN, e.g. from Chloroamine T and alkyl isonitriles.[58] However, the desired carbodiimides have only been identified by subsequent adduct formation, e.g. with methanol.



(XXXVI)



3. *N*-Phosphorylcarbodiimides

By comparison with *N*-acyl- and *N*-sulphonyl-carbodiimides, *N*-phosphoryl analogues are less stable because of their tendency to disproportionate and polymerise spontaneously.

It has been reported that a number of *N*-phosphorylcarbodiimides (XXXVII) may be prepared by elimination of H_2S from the corresponding thiourea with HgO or $COCl_2$ in the presence of molecular sieves.[59]

$$R_2P(O)NH-\overset{\overset{S}{\|}}{C}-NHR' \xrightarrow{HgO \text{ or } COCl_2} R_2P(O)N=C=NR'.$$

(XXXVII)

The same reaction with the thiophosphorylated thiourea (XXXVIII) is more complex, being associated with the formation of an *N*-thiophosphorylisothiocyanate and an *N*-thiophosphoryl-guanidine.[60]

$$(EtO)_2\overset{\overset{S}{\|}}{P}NH-\overset{\overset{S}{\|}}{C}-NHPh \xrightarrow{HgO}$$

(XXXVIII)

$$\longrightarrow (EtO)_2\overset{\overset{S}{\|}}{P}N=C=S + (EtO)_2\overset{\overset{S}{\|}}{P}N=C(NHPh)_2.$$

Dehydrochlorination of *N*-phosphorylated chloroformamidines (XXXIX), obtained either from the corresponding *N*-phosphorylated urea or by treatment of *N*-phosphorylated iminophosgenes with primary amines, affords the corresponding *N*-phosphoryl-*N'*-arylcarbodiimides (XL) in high yield.[61]

$$ArNH-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{N}HP(OAlk)_2 \xrightarrow{PCl_5} ArNH-\overset{\overset{Cl}{|}}{C}=\overset{\overset{O}{\|}}{N}P(OAlk)_2 \xleftarrow{ArNH_2} Cl_2C=\overset{\overset{O}{\|}}{N}P(OAlk)_2$$

(XXXIX)

$$\downarrow Et_3N$$

$$ArN=C=\overset{\overset{O}{\|}}{N}P(OAlk)_2.$$

(XL)

The *N*-phosphorylcarbodiimides (XLI) and (XLII) may be prepared conveniently from metalated *N*-phosphorylcyanamides[62] or by treatment of Ag(I)-cyanamide with phosphorus(V) acid chlorides.[63–65]

$$M[Ph_2P(X)NCN] + R_3M'Cl \xrightarrow[-MCl]{} Ph_2P(X)N=C=NM'R_3,$$

(XLI)

$$Ag_2CN_2 + 2Ph_2P(X)Cl \xrightarrow[-2AgCl]{} Ph_2P(X)N=C=NP(X)Ph_2$$

(XLII)

M = Na, Ag; X = O,S; R_3M' = Ph_3Si, Ph_3Sn, Ph_3Pb, Me_3Sn.

By using diphenylhalogenophosphines in the latter reaction, the desired carbodiimide was isolated in the form of a 1:1:1 adduct, $Ph_2P-N=C=N-PPh_2 \cdot AgHal \cdot solvent$.[63]

Replacement of a trimethylsilyl group in the carbodiimides (XLIII) by a phosphoryl, thiophosphoryl or iminophosphoryl group can only be achieved under forcing conditions.[66–68] Thus, *N*-difluorothiophosphoryl-*N'*-trimethylsilylcarbodiimide (XLIV) is obtained in 35% yield by prolonged heating (50 h) of the reactants at 140–150 °C.[66]

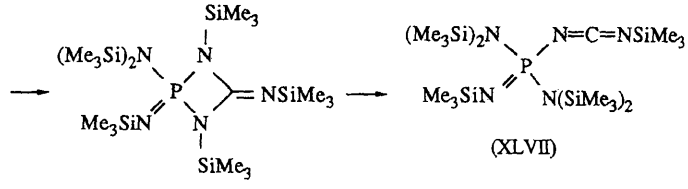
$$Me_3SiN=C=NSiMe_3 + P(S)F_3 \longrightarrow Me_3SiN=C=NP(S)F_2 + Me_3SiF.$$

(XLIII) (XLIV)

On the other hand, reaction of carbodiimides (XLIII) with the aminodiiminophosphorane (XLV) readily affords a [2+2]-cycloadduct (XLVI), which is converted to (XLVII) on standing over a long period.[69]

$$Me_3SiN=C=NSiMe_3 + \begin{matrix}(Me_3Si)_2N \\ \diagdown \\ P=NSiMe_3 \\ \diagup \\ Me_3SiN\end{matrix} \longrightarrow$$

(XLIII) (XLV)



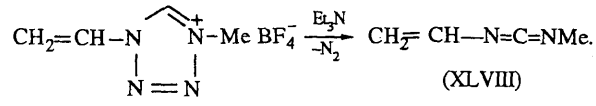
(XLVI)

$$\longrightarrow (Me_3Si)_2N-P(=N-C=NSiMe_3)-N(SiMe_3)_2$$

(XLVII)

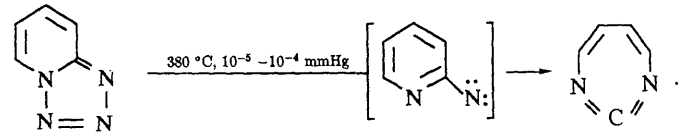
4. *N*-Alkenylcarbodiimides

The highly reactive vinylcarbodiimides were unknown before 1970. The first member of this class of compound—the unstable *N*-methyl-*N'*-vinylcarbodiimides (XLVIII)—was obtained by fragmentation of a tetrazolium salt with triethylamine in sulfolane.[30]



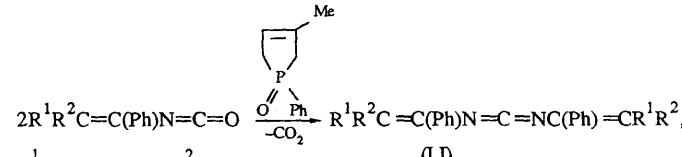
(XLVIII)

According to spectroscopic data, the relatively stable cyclic divinylcarbodiimide (XLIX) is formed by thermal rearrangement of the nitrene (L), obtainable by thermolysis of tetrazolo[1,5-*a*]pyridine at high temperature.[70]



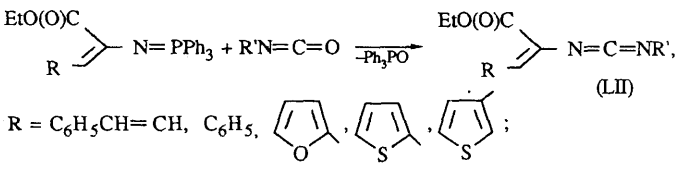
(L) (XLIX)

The stability of *N*-alkenylcarbodiimides increases significantly with substitution in the alkenyl residue. Thus, the stable *N,N'*-bis-(1-alkenyl)carbodiimides (LI) are obtained by catalytic decarboxylation of the corresponding *N*-alkenylisocyanate.[71]



(LI)

The most general and convenient route to *N*-alkenylcarbodiimides (LII) involves aza-Wittig conversion of the corresponding *N*-alkenyliminophosphorane,[72–77] e. g.

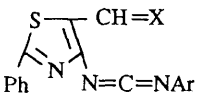


(LII)

R = $C_6H_5CH{=}CH$, C_6H_5, ;

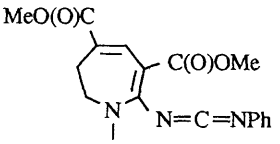
R' = Alk, Ar.

If the carbon–carbon double bond of the *N*-alkenyliminophosphorane is in the form of a pyrrole,[78] pyrazole,[79,80] or pyrimidine[81,82] ring, the corresponding carbodiimides are only formed as intermediates. However, thiazole[79] and azepine[83] derivatives afford stable carbodiimides (LIII) and (LIV).



(LIII)

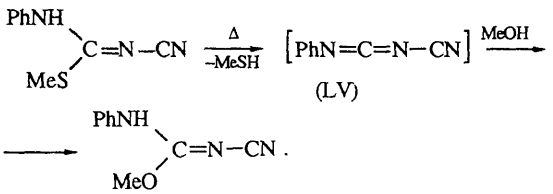
X = O, NAr.



(LIV)

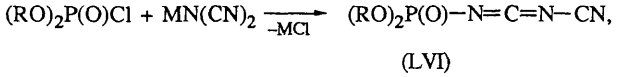
5. Other types of *N*-functionalised carbodiimide

In this category are *N*-cyano- and *N*-amino-carbodiimides which are relatively unstable and, as a rule, are only isolable by derivatisation. Thus, *N*-phenyl-*N'*-cyanocarbodiimide (LV) is formed by thermal elimination of methanethiol from *N*-phenyl-*N'*-cyano-*S*-methylisothiourea.[84]



(LV)

The stability of *N*-cyanocarbodiimides is significantly increased if an *N*-phosphoryl residue is present. Thus, *N*-cyano-*N'*-phosphorylcarbodiimides (LVI) are quite stable.[64,65]



(LVI)

M = Na, K, Ag.

N-Dialkylaminocarbodiimides, $Alk_2N{-}N{=}C{=}NR$, are very unstable, readily dimerising immediately they are formed. A few of these compounds have been mentioned in an earlier review.[85]

III. Physical and chemical properties

1. Physical properties

The majority of *N*-functionalised carbodiimides are crystalline compounds or liquids which may be distilled under a high vacuum. Like unfunctionalised carbodiimides, they are readily soluble in organic solvents, but are less stable on prolonged storage even with the exclusion of atmospheric moisture.

The IR spectra of these carbodiimides are characterised by intense absorption in the region 2130–2170 cm^{-1}, corresponding to the N=C=N function. The nature of the *N*-substituent does not have a significant effect on the position of this absorption band. However, with certain *N*-acylcarbodiimides[17,21] and *N*-sulphonylcarbodiimides,[35] the absorption is shifted into the region 2185–2200 cm^{-1}.

^1H NMR and ^{13}C NMR spectroscopic data are available for *N*-acylcarbodiimides;[17,18,30] ^{31}P NMR data for *N*-phosphorylcarbodiimides,[62,64] and ^1H NMR data for *N*-alkenylcarbodiimides.[35,71,74,75,83]

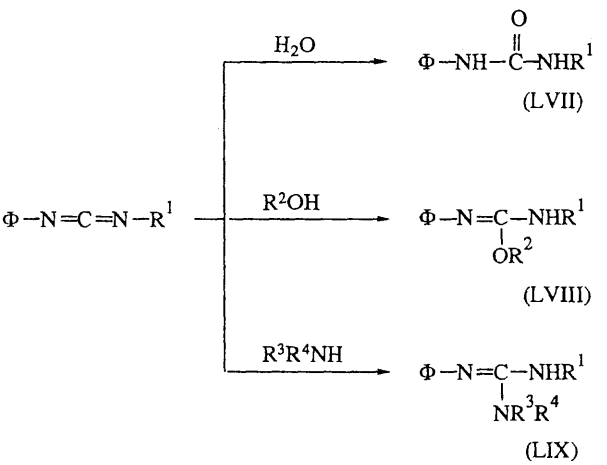
Theoretical calculations have been made on the hypothetical difluorocarbodiimide, F–N=C=N–F, in order to study the geometry of the molecule and its isomerisation.[86]

2. Chemical properties

a) Reactions with nucleophiles

The chemistry of *N*-functionalised carbodiimides is determined to a large extent by the presence of both the heterocumulene bond and the functional group. The electron-accepting acyl, sulphonyl and phosphoryl groups significantly increases the electrophilicity of the heterocumulene bond and facilitate the reactions of these compounds with nucleophiles.

Substituted ureas (LVII),[9,18,40,45,46,52,53,60,62] isoureas (LVIII) [10,12,40,58] and guanidines (LIX) [12,40,42,58] are formed by the reaction of the corresponding *N*-functionalised carbodiimide with water, alcohols (or phenols) and amines, respectively, at room temperature in the absence of a catalyst.



(LVII)

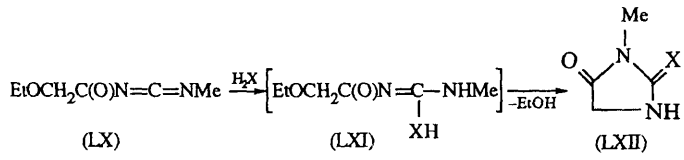
(LVIII)

(LIX)

Φ = $Alk_2NC(S)$, $ArN(=CAr)$, $ArSO_2$, $AlkSO_2$, Alk_2P, $(AlkO)_2P(O)$;

R^1, R^2 = Alk, Ar; R^3 = H, Alk; R^4 = Alk, Ar.

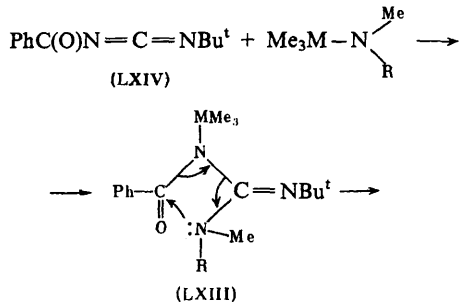
The reaction of carbodiimide (LX) with amines and hydrazines, however, does not stop at adduct formation (LXI); instead, the latter cyclises to give the corresponding hydantoin derivative (LXII) [30] by elimination of ethanol.



(LX) (LXI) (LXII)

X = NAlk, N —NHAlk .

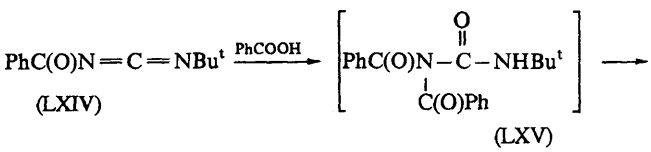
Similarly, the guanidine derivative (LXIII), obtained from carbodiimide (LXIV), fragments with participation of the benzoyl group.[87]



M = Si, Ge; R = Me, Me_3Si.

b) Reactions with electrophiles

The *N*-benzoylcarbodiimide (LXIV) reacts with benzoic acid in conventional manner[4] to give the *N,N*-dibenzoylurea (LXV), which undergoes subsequent cleavage to give the imide (LXVI) and tert-butyl isocyanate.[14]

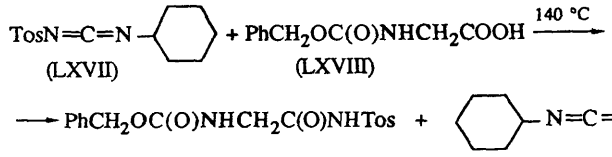


(LXIV) (LXV)

$\longrightarrow [PhC(O)]_2NH + Bu^tN{=}C{=}O$.

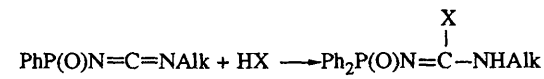
(LXVI)

The *N*-tosylcarbodiimide (LXVII) reacts similarly with *N*-carbobenzoxyglycine (LXVIII).[38]



(LXVII) (LXVIII)

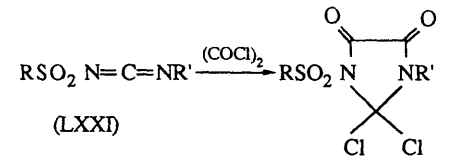
N-Phosphorylated carbodiimides (LXIX) react with inorganic acids by adduct formation across the C=N bond.[88]



(LXIX) (LXX)

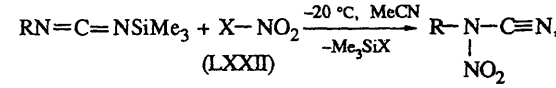
X = Cl, CN .

N-Sulphonylcarbodiimides (LXXI) are slowly acylated with oxalyl chloride, but do not react with phosgene because of the decrease in basicity of the nitrogen atoms of the carbodiimide group.[35,53]



(LXXI)

The reaction of *N*-acyl- or *N*-sulphonyl-carbodiimides with neutral nitrating agents (LXXII) proceeds by cleavage of the Si—N bond rather than by addition across the carbodiimide residue.[22]



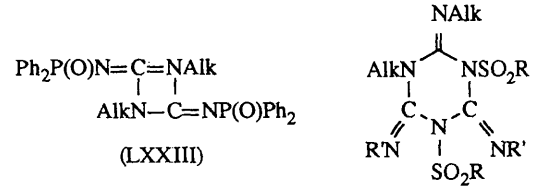
(LXXII)

R = MeOC(O); X—NO_2 = N_2O_5, $(NO_2)_2SiF_6$; R = $MeSO_2$;

X—NO_2 = $(NO_2)_2SiF_6$.

c) Cycloaddition

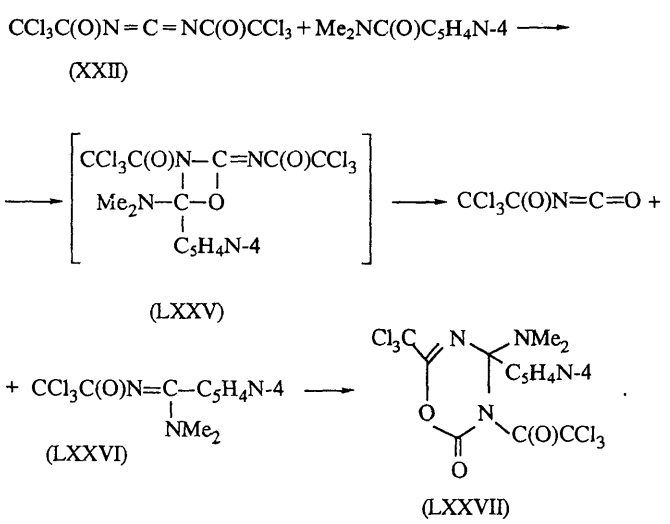
N-Phosphorylated carbodiimides readily dimerise by [2+2]-cycloaddition to give the diazetidines (LXXIII).[88] However, *N*-sulphonylcarbodiimides react with dialkylcarbodiimides to give [2+2+2]-cycloadducts (LXXIV).[49]



(LXXIII) (LXXIV)

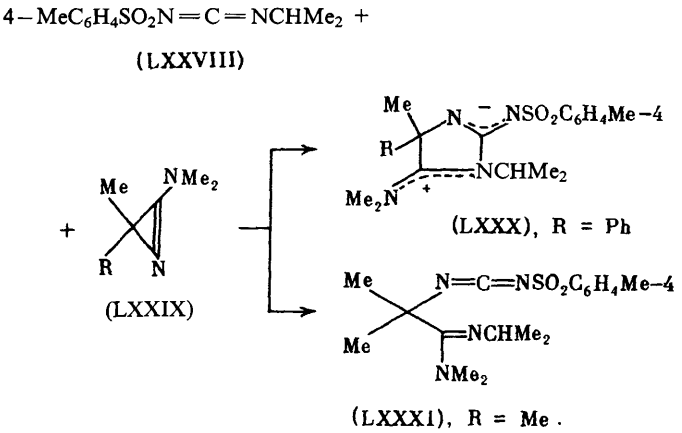
The reaction of bis(trichloroacetyl)carbodiimide (XXII) with *N,N'*-dimethylisonicotinamide leads initially to the adduct (LXXV), which undergoes fragmentation to give trichloroacetyl isocyanate

and the amidine (LXXVI). The latter reacts subsequently to give the oxadiazine (LXXVII).[28]



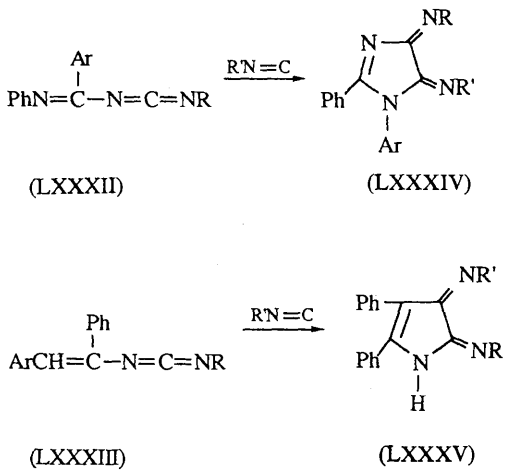
(XXII) (LXXV) (LXXVI) (LXXVII)

The reaction of the *N*-sulphonylcarbodiimide (LXXVIII) with azirine (LXXIX) proceeds by an initial [2+2]-cycloaddition, after which the resulting[2+2]-adduct is converted either to a zwitterionic imidazoline (LXXX) or to a carbodiimide (LXXXI), depending on the nature of the R group on the azirine ring.[89]



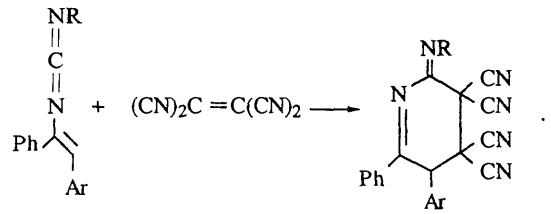
(LXXVIII) (LXXIX) (LXXX), R = Ph (LXXXI), R = Me.

Cycloaddition is particularly favourable with *N*-acyl derivatives, their analogues, and with *N*-alkenyl derivatives which are prone to undergo 1,4-dipole formation. Such compounds are notably of value in the synthesis of various types of heterocycle. Thus, imidoylcarbodiimides (LXXXII) and *N*-alkenylcarbodiimides (LXXXIII) form cycloadducts with isonitriles, namely the respective 4,5-diiminoimidazolines (LXXXIV) and 2,5-diiminopyrrolines (LXXXV).[74]



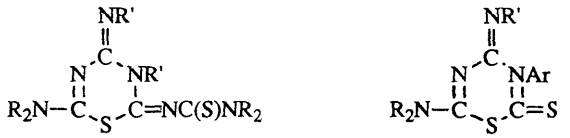
(LXXXII) (LXXXIV) (LXXXIII) (LXXXV)

The interaction of carbodiimides (LXXXIII) with tetracyanoethylene proceeds by [4+2]-cycloaddition to give the tetrahydropyridines (LXXXVI).[72]



(LXXXIII) (LXXXVI)

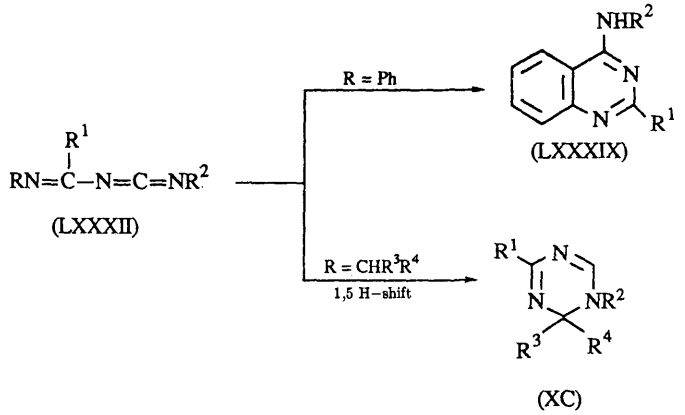
Similarly, dimerisation of *N*-thiocarbamoylcarbodiimides, and reaction of the latter with isothiocyanates, leads to the respective thiadiazines (LXXXVII) and (LXXXVIII).[10]



(LXXXVII) (LXXXVIII)

Recently there has been much interest in the spontaneous intramolecular heterocyclisation of imidoylcarbodiimides (LXXXII).[31] These react with participation of phenyl or alkyl substituent on the

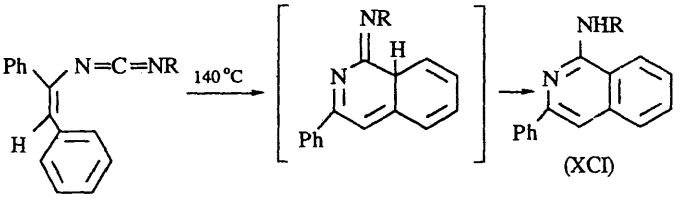
imidoyl nitrogen to give 4-aminoquinazolines (LXXXIX) or dihydro-1,3,5-triazines (XC).



(LXXXII) (LXXXIX) (XC)

R^1 = Ar; R^2, R^3, R^4 = Alk, Ar.

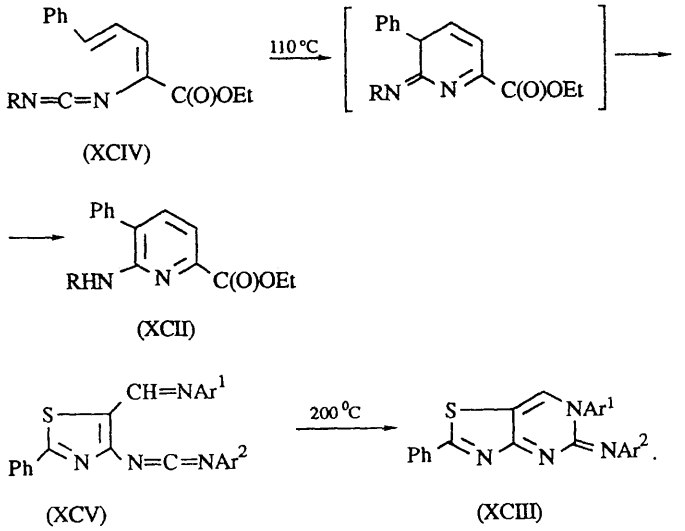
N-Alkenylcarbodiimides (LXXXIII) undergo a similar cyclisation to give substituted quinolines (XCI), but only on heating in xylene.[72]



(LXXXIII) (XCI)

R = Alk, Ar.

The pyridine (XCII) and pyrimidine derivatives (XCIII) have been prepared by a novel route based on the electrocyclisation of carbodiimides (XCIV) and (XCV), respectively.[77,79,82]



(XCIV) (XCII) (XCV) (XCIII)

A recently published review makes reference to a similar type of heterocyclisation based on the intermediate formation of *N*-heteroarylcarbodiimides possessing an alkenyl group on the heterocyclic ring.[90]

From the present review, it is evident that *N*-functionalised carbodiimides possess quite novel properties, as distinct from those of unfunctionalised carbodiimides. The potential for the development of new routes to a variety of acyclic and heterocyclic compounds is clear to see.

References

1. W Weit *Chem. Ber.*, 1874, 7 10
2. B V Bocharov *Usp. Khim.*, 1965, **34**(3) 488 [English translation in *Russ. Chem. Rev.*, 1965(3)]
3. F Kurzer, K Douraghi-Zadeh *Chem. Rev.*, 1967, **67** 107
4. M Mikolajczyk, P Kielbasinski *Tetrahedron*, 1981, **37** 233
5. A Williams, I T Ibrahim *Chem. Rev.*, 1981, **81** 589
6. A S Gordetsov, V P Kozyukov, I A Vostokov, et al. *Usp. Khim.*, 1982, **51**(4) 848 [English translation in *Russ. Chem. Rev.*, 1982(4)]
7. BDR P. 12 405 195; *Chem. Abstr.*, 1967, **67** 73 181
8. R Neidlein, E Heukelbach *Tetrahedron Lett.*, 1965, 149
9. J Goerdeler, S Raddatz *Chem. Ber.*, 1980, **113** 1095
10. J Goerdeler, R Losch *Chem. Ber.*, 1980, **113** 79
11. J Goerdeler, H Lohmann, R Losch, S Raddatz *Tetrahedron Lett.*, 1971, 2765
12. J Goerdeler, H Lohmann *Chem. Ber.*, 1977, **110** 2996
13. J Goerdeler, J Haag, C Lindner, R Losch *Chem. Ber.*, 1974, **107** 502
14. O Mitsunobu, M Tomari, H Morimoto, et al. *Bull. Chem. Soc. Jpn.*, 1972, **45** 3607
15. B George, E P Papadopoulos *J. Heterocyclic Chem.*, 1983, **20** 1127
16. M V Vovk *Zh. Org. Khim.*, 1987, **23** 2023
17. R Bunnerberg, J C Jochims, H Härle *Chem. Ber.*, 1982, **115** 3587
18. V I Gorbatenko, Yu I Matveev, L I Samarai *Zh. Org. Khim.*, 1987, **23** 2385
19. E Fromm, E Honold *Chem. Ber.*, 1922, **55** 902
20. Netherlands P. 6 610 608; *Chem. Abs.*, 1967, **67** 90 554
21. B. P. 1 167 127; *Chem. Abs.*, 1970, **72** 31 480
22. A M Churakov, B N Khasanov, S L Ioffe, I A Tartakovskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 650
23. V I Gorbatenko, N V Mel'nichenko, M N Gortsyuk, L I Samarai *Zh. Org. Khim.*, 1976, **12** 2103
24. W Lidy, W Sundermeyer *Chem. Ber.*, 1976, **109** 1491
25. V F Gerega, Yu I Mushkin, Yu I Baukov, Yu I Dergunov *Zh. Obshch. Khim.*, 1978, **48** 1146
26. V P Kozyukov, S V Sheludyakova, V S Nikimin, et al. *Zh. Obshch. Khim.*, 1978, **48** 1429
27. T W Campbell, J J Monagle, V S Foldi *J. Am. Chem. Soc.*, 1962, **84** 3673
28. B A Arbuzov, N N Zobova, O V Sofronova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 476
29. J Goerdeler, H Schenk *Chem. Ber.*, 1965, **98** 2954
30. D M Zimmerman, R A Olofson *Tetrahedron Lett.*, 1970, 3453
31. J Goerdeler, W Eggers *Chem. Ber.*, 1986, **119** 3737
32. C Wentrup, C Thetaz, E Tagliaferri, et al. *Angew. Chem.*, 1980, **92** 559
33. E Kozlowska-Gramsz, G Descotes *Tetrahedron Lett.*, 1982, 1585
34. H Ulrich, A A R Sayigh *Angew. Chem.*, 1964, **76** 781
35. H Ulrich, B Tucker, A A R Sayigh *Tetrahedron*, 1966, **22** 1565

36. US P. 3 358 159; *Chem. Abs.*, 1968, **69** 35 780
37. US P. 3 422 201; *Chem. Abs.*, 1969, **70** 77 584
38. R K Gupta, C H Stammer *J. Org. Chem.*, 1968, **33** 4368
39. US P. 3 384 643; *Chem. Abs.*, 1968, **69** 59 235
40. T Kodama, K Uehara, K Hisada, S Shiohara *Yuki Gosei Kagaku Kyokai Shi*, 1967, **25** 493; *Chem. Abs.*, 1968, **68** 12 620
41. Japan P. 6 902 702; *Chem. Abs.*, 1969, **71** 30 227
42. V N Sevast'yanov, E A Abrazhanova *Zh. Org. Khim.*, 1981, **17** 91
43. R Neidlein, W Haussmann *Chem. Ber.*, 1966, **99** 1252
44. B.P. 1 022 040; *Chem. Abs.*, 1966, **64** 15 801
45. Netherlands P. 6 413 827; *Chem. Abs.*, 1966, **64** 19 506
46. B Anders, E Kuhle *Angew. Chem.*, 1965, **77** 430
47. R Neidlein, E Heukelbach *Tetrahedron Lett.*, 1965, 2667
48. H Ulrich, B Tucker, A A R Sayigh *J. Am. Chem. Soc.*, **90** 528
49. H Ulrich, B Tucker, F A Stuber, A A R Sayigh *J. Org. Chem.*, 1969, **34** 2250
50. US P. 3 527 800; *Chem. Abs.*, 1970, **73** 98 995
51. T Minami, M Fucuda, M Abe, T Agawa *Bull. Chem. Soc. Jpn.*, 1973, **46** 2156
52. E Schaumann, E Kausch *J. Liebigs Ann. Chem.*, 1978, 1560
53. G L'abbe, E Van Loock, R Albert, et al. *J. Am. Chem. Soc.*, 1974, **96** 3973
54. G L'abbe, G Verhelst, C-C Yu, S Toppet *J. Org. Chem.*, 1975, **40** 1728
55. Yu I Dergunov, V F Gerega, M G Ivanov, Yu I Baukov *Zh. Obshch. Khim.*, 1977, **47** 1071
56. W Bub, H J Krannich, W Sundermeyer *Chem. Ber.*, 1976, **109** 1486
57. Yu I Dergunov, A S Gordetsov, I A Vostokov, V A Gal'perin *Zh. Obshch. Khim.*, 1975, **45** 2234
58. W Aumüller *Angew. Chem.*, 1963, **75** 857
59. G Tomaschewski, B Breitfeld, D Zanke *Tetrahedron Lett.*, 1969, 3191
60. A F Grapov, V N Zontova, N N Mel'nikov *Dokl. Akad. Nauk SSSR*, 1980, **251** 882
61. G I Derkach, N N Liptuga *Zh. Obshch. Khim.*, 1966, **36** 461
62. L Jacer, H Koehler, A J Brusilovec, V V Scopenko *Z. Anorg. Allg. Chem.*, 1988, **564** 85
63. A Weiz, K Utvary *Monatsh. Chem.*, 1968, **99** 2498
64. H Koehler, L Jaeger *Z. Chem.*, 1984, **24** 379
65. H Koehler, M Kretscmann, R Skirl, et al. *Z. Anorg. Allg. Chem.*, 1988, **577** 165
66. O Glemzer, E Niecke *Z. Naturforsch.*, 1968, **23** 741
67. H W Resky, L E Grimm *Chem. Ber.*, 1970, **103** 1664
68. E Niecke, J Stenzel *Z. Naturforsch.*, 1967, **22** 785
69. R Appel, M Holstenberg *J. Organomet. Chem.*, 1976, **116** 13
70. G Wentrup, H-W Winter *J. Am. Chem. Soc.*, 1980, **102** 6159
71. V N Fetyukhin, V V Korbzhitskii, L I Samarai *Zh. Org. Khim.*, 1981, **17** 2452
72. T Saito, M Makame, M Endo, H Yamashita *Chem. Lett.*, 1986, 135
73. L Capuano, B Dahm, P Volker, et al. *Chem. Ber.*, 1988, **121** 271
74. J Barluenga, M Ferrero, F Palacios *Tetrahedron Lett.*, 1988, 4863
75. S Motoki, T Saito, M Makame *Heterocycles*, 1984, **21** 665
76. P Molina, P N Fresneda, F Hurtabo *Synthesis*, 1987, 45
77. P Molina, P N Fresneda, P Alarcon *Tetrahedron Lett.*, 1988, 379
78. H Wamhoff, H Wintersohl, S Stolben, et al. *J. Liebigs Ann. Chem.*, 1990, 901
79. P Molina, A Arques, M V Vinader *J. Org. Chem.*, 1988, **53** 4654
80. P Molina, A Arques, M V Vinader *Synthesis*, 1990, 469
81. H Wamhoff, J Muhr *Synthesis*, 1988, 919
82. P Molina, M J Vilaplaha *Synthesis*, 1990, 474
83. H Wamhoff, G Hendrikx *Chem. Ber.*, 1985, **118** 863
84. C G McCarty, J E Parkinson, D M Wieland *J. Org. Chem.*, 1970, **35** 2067
85. W Reichen *Chem. Rev.*, 1978, 569
86. M S Cordon, H Fischer *J. Am. Chem. Soc.*, 1968, **90** 2471
87. I Matsuda, I Kenji, Y Ishii *J. Organomet. Chem.*, 1974, **69** 353
88. G Tomaschewski, D Zanke *Z. Chem.*, 1974, **14** 234
89. E Schaumann, S Grabby *J. Liebigs Ann. Chem.*, 1981, 290
90. N I Gusar *Usp. Khim.*, 1991, **60**(2) 285 [English translation in *Russ. Chem. Rev.*, 1991(2)]

Translated from *Uspekhi Khimii* 61 564–615 (1992) U.D.C. 547.26'118

Reactions of phosphorus-containing compounds with diazo-compounds and carbenes

B A Khaskin, O D Molodova, N A Torgasheva
All-Union Institute of Chemical Plant Protecting Agents, Moscow

ABSTRACT. The reactions of various phosphorus-containing systems with diazo-compounds and carbenes are presented for the first time in a general form and a systematic account is given of literature data on the reactivities of phosphorus-containing acids, salts, esters, amides, sulphenamides, phosphorus acid sulphenyl halides, phosphorus halides, and derivatives of mono-, di-, and tri-coordinate phosphorus in reactions with diazo-compounds and carbenes.

The differences between the reactivities of diazo-compounds and carbenes in relation to the above groups of organophosphorus compounds are demonstrated.

The bibliography includes 244 references.

Contents

I. Introduction 306
II. Phosphorus-containing acids, salts, esters, amides, sulphenamides, phosphorus acid sulphenyl halides, phosphorus halides, and phosphorus-containing polysulphides in reactions with diazo-compounds and carbenes 306
III. Phosphines and phosphites in reactions with diazo-compounds and carbenes 314
IV. Reactions of diazo-compounds and carbenes with phosphorus-containing systems having multiple bonds 320
V. Derivatives of di- and mono-coordinate phosphorus in reactions with diazo-compounds and carbenes 325

I. Introduction

The advances in the study of the reactivities of phosphorus-containing compounds in relation to diazo-compounds and carbenes are considered in the present review. These studies play an important role both in the synthetic and theoretical chemistry of organophosphorus compounds.

The beginning of studies on the reactions of diazo-compounds with phosphorus-containing systems dates back to the second decade of the present century. Systematic investigation of the reactions of phosphorus-containing compounds with carbenes developed in the last 30 years.

Extensive data have now accumulated on this problem and a number of special reviews have been published in both Russian and foreign literature on individual aspects of the interaction of certain phosphorus-containing compounds with diazo-compounds and carbenes, especially on the dual reactivity of phosphoromonothioic, phosphoromonoselenoic, and phosphoroselenothioic acids,[1] the reactions of phosphorus-containing polysulphides,[2] the 1,3-dipolar cycloaddition reactions,[3–5] and the reactions of α-ketophosphoryl compounds.[6]

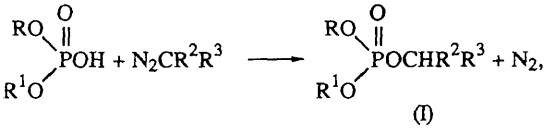
The reactions of different phosphorus-containing systems with diazo-compounds and carbenes are presented in the present review for the first time in a general form and a systematic account is given of literature data on the reactivities of phosphorus-containing acids, salts, esters, amides, sulphenamides, phosphorus acid sulphenyl halides, phosphorus halides, and derivatives of mono-, di-, and tri-coordinate phosphorus in reactions with diazo-compounds and carbenes. Studies concerned with the reactivities of phosphorus-containing diazo-compounds and carbenes are not considered in the review.

II. Phosphorus-containing acids, salts, esters, amides, sulphenamides, phosphorus acid sulphenyl halides, phosphorus halides, and phosphorus-containing polysulphides in reactions with diazo-compounds and carbenes

1. Interaction of phosphoric, phosphonic, phosphinic, and phosphorous acids and their esters with diazo-compounds

The reactions of organophosphorus acids and their esters, containing P–O–H bonds, with diazo-compounds proceed as a rule with evolution of nitrogen and the insertion of a methylene or substituted methylene group in the O–H bond.

Thus in the reactions with diazo-compounds dialkylphosphoric acids form phosphates (I),[7–9] while hypophosphorous acid forms *O*-alkyl esters (II).[10] Even in the presence of a large excess of diazoalkane further reaction does not occur, i.e. there is no insertion in a P–H bond of the ester (II):



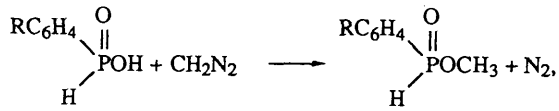
(I)

R = H, Alk(C_1 — C_4), $CH_2C_6H_5$, $(CH_2)_{17}CH_3$;
R^1 = Alk(C_1 — C_4), $(CH_2)_3Br$,
$(CH_2)_{18}CH_3$, $CH_2C_6H_5$; $R^2 = R^3 = C_6H_5$;
$R^3 = C_6H_5$, $R^3 = C(O)C_6H_5$; R^2 = H,
$R^3 = C(O)(CH_2)_{18}CH_3$,

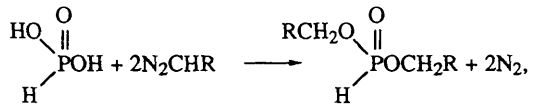
(II)

$R^1 = H, CH_3$.

Arylphosphinic acids[11] and phosphorous acid[12,13] react similarly:

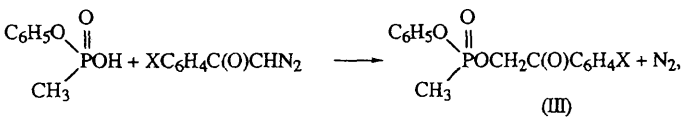


$R = H$, 3-Cl, 3-Br.



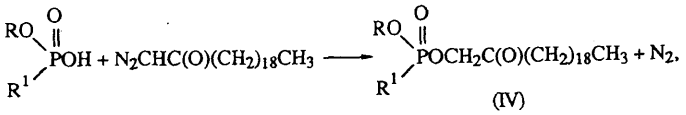
$R = CH_3, C(O)C_2H_5$.

The synthesis of the phosphonates (III) and (IV) by the reaction of phenoxymethylphosphonic acid with aromatic diazoketones and of alkyl(chloroalkyl)phosphonic acid esters with higher alkyl homologues of diazoacetone has been described:[9,14]



(III)

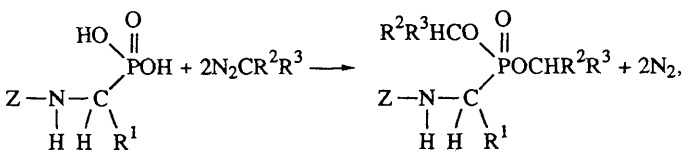
X = H, 4-Cl, 4-CH_3O, 4-NO_2, 4-CH_3, 2-CH_3, 3,5-NO_2,



(IV)

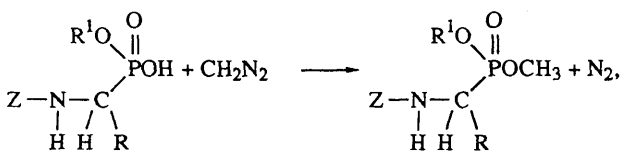
R = H, $(CH_2)_{17}CH_3$, $CH_2C_6H_5$; $R^1 = CH_3$, CH_2CH_2Cl, CH_2Cl.

The phosphonates (V) and (VI) have been obtained from *N*-acylated 1-aminoalkylphosphonic acid or its ester with diazomethane and diphenyldiazomethane:[15–17]



(V)

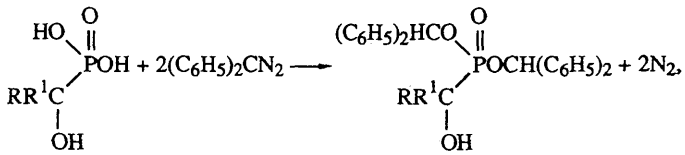
$R^1 = H$, Alk; $R^2 = R^3 = H, C_6H_5$,



(VI)

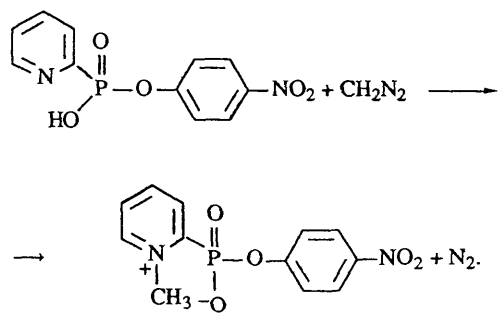
$R = R^1 = H$, Alk, C_6H_5; Z = $CH_3C(O)$, $C_6H_5CH(OH)C(O)$, $CH_3C_6H_4SO_2$, $(CH_3)_3COC(O)$, $C_6H_5CH_2OC(O)$.

The reactions of hydroxyalkylphosphonic acids with diphenyldiazomethane involve the insertion of the diphenylmethylene group only in the acid OH groups:[18]

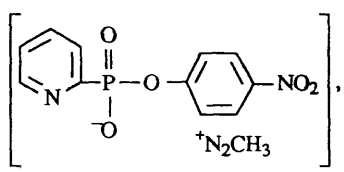


$R = R^1 = Alk, C_6H_5$.

In this connection, it is of interest to note a study[19] where it was shown that the interaction of 4-nitrophenyl-2-pyridylphosphonic acid with diazomethane proceeds selectively with formation of the *N*-methyl derivative:



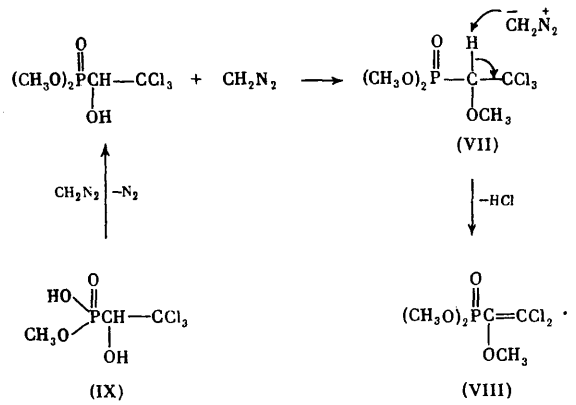
The authors attribute the formation of this product to alkylation by diazomethane at the nitrogen atom via the intermediate formation of the ion pair



where the phosphonate anion is a weaker nucleophile than the pyridinium nitrogen in relation to the methanediazonium cation.

The dimethyl ester of 2,2,2-trichloro-1-hydroxyethylphosphonic acid is methylated by diazomethane at the alcoholic OH group, which has been attributed to the strong electron-accepting influence of the trichloromethyl group, with formation of the dimethyl ester of 2,2,2-trichloro-1-methoxyethylphosphonic acid (VII), the excess diazomethane playing the role of a dehydrochlorinating agent, which leads to the formation of the ester (VIII). The latter has been

obtained also by treating methyl 2,2,2-trichloro-1-hydroxyethylphosphonate (IX) with an excess of diazomethane:[20]

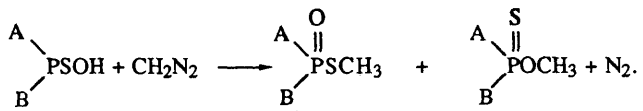


(IX) (VIII)

2. Phosphoromonothioic, phosphoromonoselenoic, and phosphoroselenothioic acids in reactions involving alkylation by diazo-compounds

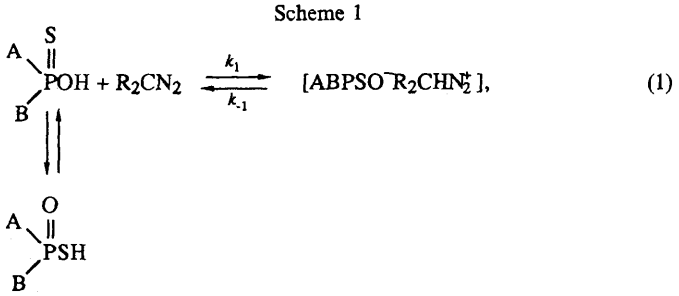
Phosphoromonothioic, phosphoromonoselenoic, and phosphoroselenothioic acids are typical substances involved in triad tautomerism and are therefore convenient objects for the study of the dual reactivities of ambident anions. Their reactions with diazocompounds have been studied by Mastryukova and Kabachnik[21–35] and have been described in detail in a review.[1] Here we shall confine ourselves to the considerations of general information about the results of such investigations.

The study of the reactions of phosphoromonothioic acids with diazomethane showed that alkylation proceeds with the preferential formation of *S*-methyl esters of phosphorothioic acids in 81–95% yield:[22]



The reaction mechanism is presented in Scheme 1 below:[1,21,22]

Scheme 1



$$[ABPSO^-R_2CHN_2^+] \xrightarrow{k_2} [ABPSO^-R_2CH^+] + N_2, \quad (2)$$

$$[ABPSO^-R_2CHN_2^+] \xrightarrow{k_3} ABP(O)SCHR_2 + N_2, \quad (3)$$

$$[ABPSO^-R_2CHN_2^+] \xrightarrow{k_3'} ABP(S)OCHR_2 + N_2, \quad (4)$$

$$[ABPSO^-R_2CH^+] \xrightarrow{k_4} ABP(S)OCHR_2, \quad (5)$$

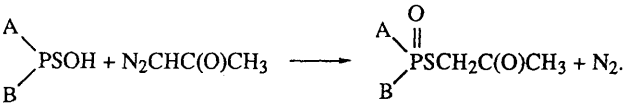
$$[ABPSO^-R_2CH^+] \xrightarrow{k_4'} ABP(O)SCHR_2. \quad (6)$$

In the reversible reaction of phosphorothioic acid with diazomethane [Eqn. (1)], the methanediazonium cation, behaving as the counterion in the ion pair formed, interacts as the attacking electrophile with the ambident anion via a reaction of the S_N2 type [reactions (3) and (4)] or a methyl cation is generated via a reaction of the S_N1 type [reaction (2)], recombining rapidly with the anion [reactions (5) and (6) in Scheme 1].

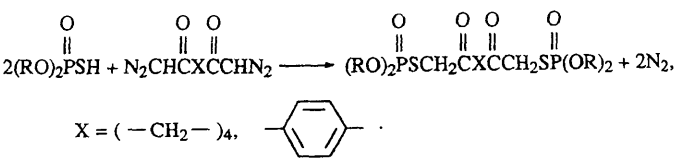
In conformity with the mechanism involving two types of reactions of phosphorothioic acids with diazomethane, it was postulated that the methanediazonium cation attacks only the sulphur atom as the most nucleophilic atom of the triad (S_N2), while the methyl cation attacks the oxygen atom in the same triad (S_N1). Evidently the yields of the *S*- and *O*-methyl derivatives depend on the nucleophilicity of the sulphur end of the triad, which is determined by the electron-accepting properties of the substituents at the phosphorus atom and by the relative rate of decomposition of the diazonium cation within the ion pair, which depends both on the polarity of the solvent and on the stability of the carbonium ion formed.[1,21,22]

The established features of the dual reactivity of phosphorothioic acids were confirmed and subsequently elaborated in reactions of phosphorothioic acids and cyclic phosphorothioic, phosphoroselenoic, and phosphoroselenothioic acids with other diazocompounds.[1,21,23–27]

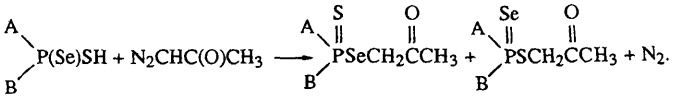
Thus primary diazoketones, in particular diazoacetone, give rise exclusively to the *S*-thiol ester in their reactions with phosphorothioic acids,[30,32] which has been attributed to the high reactivity of the diazonium cation:



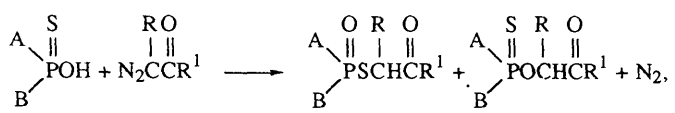
It has been shown recently that, similarly to their reactions with diazoacetone, phosphorothioic acids readily interact with bisdiazoketones: 1,8-bisdiazooctane-2,7-dione and 1,4-bis(diazoacetyl)benzene, affording thiol derivatives of bisphosphorylated products of insertion in the S–H bond of phosphorothioic acids:[39]



Phosphoroselenothioic acids react with diazoacetone to form both Se- and S-isomers, since both ends of the ambident triad are highly nucleophilic:[25]



Diazoacetic ester and a secondary diazoketone (α-phenylbenzoyldiazomethane) react with phosphorothioic acids to form both isomers. The presence of a large amount of the thionic esters (X) was attributed by the authors to some increase in the stability of the corresponding carbonium ions:[30,33]



R =H, $R^1 = OC_2H_5$; $R = R^1 = C_6H_5$.

The results of kinetic studies on the reactivities of five- and six-membered cyclic phosphorothioic acids in reactions with diphenyldiazomethane, obtained by Pudovik and co-workers,[36–38] are consistent with data for the reactions of phosphorothioic acids with diphenyldiazomethane.[26]

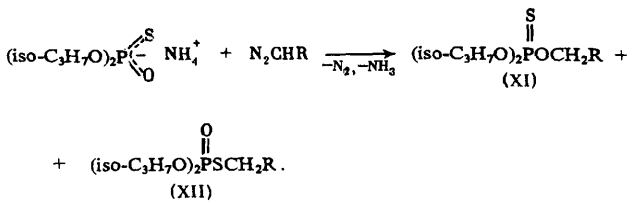
Thus the study of the alkylation of organophosphorus acids with diazo-compounds has made a major contribution to investigations of problems of the dual reactivities of both phosphorothioic and phosphoroselenoic acids themselves and the problem of dual reactivity as a whole.

3. Salts of phosphoromonothioic and phosphorodithioic acids in reactions with diazo-compounds and dihalocarbenes

Among different factors influencing the dual reactivity of ambident anions (polarisation, polarisability, the nature of the attacking agent, and the nature of the bond), the question of the influence of the metal and ammonium cations in ambident phosphorus systems has not so far been considered in the literature.

Khaskin et al.[40] was the first to investigate the dual reactivity of phosphorothioic salts in reactions involving alkylation and acylation by diazomethane, diazoacetone, and diazoacetophenone. It was established that alkali metal salts of phosphorothioic acids and a quaternary ammonium salt of phosphoric acid do not react with diazo-compounds in polar and non-polar solvents.

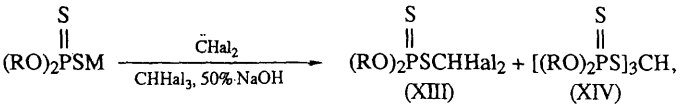
In contrast to this, the ammonium salts of phosphorothioic acids react with diazomethane to form a mixture of thione–thiol esters (XI) and (XII), the yield of the *O*-isomer (XI) increasing with increase in the dielectric constant of the solvent, while the reactions with diazoacetone and diazoacetophenone in both polar and weakly polar solvents afford exclusively the *S*-isomer (XII) with R = $C(O)CH_3$ or $C(O)C_6H_5$, since the formation of an acyl or an arylacyl carbonium ion is unfavourable because of energy factors:[30]



The reaction mechanism under discussion[40] agrees well with the mechanism proposed previously by Mastryukova and Kabachnik for phosphoromonothioic acids (see above).

Dihalocarbenes, generated by the alkaline hydrolysis of haloforms, behave differently in relation to salts of phosphorothioic and phosphorodithioic acids.

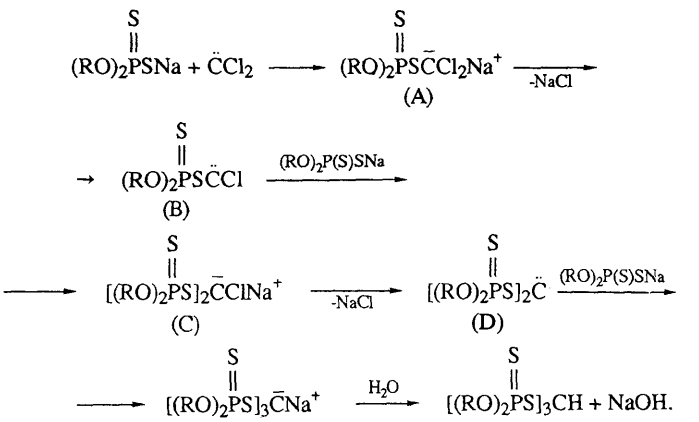
Thus alkali metal salts of phosphorodithioic acids form *O,O*-dialkyl *S*-dihalomethyl phosphorodithioates (XIII) in 20–70% yield as the main product and tris(*O,O*-dialkylthiophosphoryl-thio)methanes (XIV) in 5–20% yields as the side product:[41,42]



M = Na, K; Hal = Cl, Br.

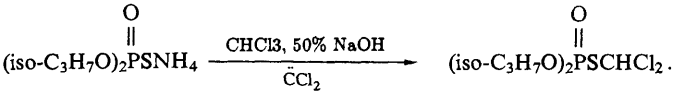
The formation of compound (XIII) is represented as the result of the electrophilic attack by the dihalocarbene in the singlet state, formed at the interface,[43–46] on the sulphur atom in the molecule of phosphorodithioic acid to form an ion pair, which subsequently reacts with water:

Since *O,O*-dialkyl *S*-dihalomethyl phosphorodithioates (XIII) do not react with the initial phosphorodithioic acid salts, the formation of compound (XIV) is represented as the result of the successive generation in the course of the reaction of unstable monothio- and dithio-derivatives of phosphorus-containing carbenes (B) and (D) via the intermediate formation of the ion pairs (A) and (C):



Similar products (XIII) and (XIV) were obtained from *O,O*-dialkylphosphorodithioic acids and bis(dialkoxythiophosphoryl) disulphides also under the conditions of the alkaline hydrolysis of haloforms, where a salt of the phosphorodithioic acid is formed initially.

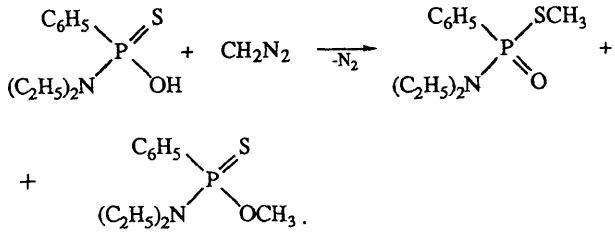
The attempt to extend this reaction to the salts of *O,O*-dialkylphosphorothioic acids and bis(dialkoxyphosphoryl) disulphides was unsuccessful. Only *O,O*-diisopropyl *S*-dichloromethyl phosphate was obtained by this procedure from the ammonium salt of *O,O*-diisopropylphosphorothioic acid in a yield of only about 2% as a consequence of the rapid hydrolysis of the final products:[42]



4. Reactions of the amides of phosphoric, phosphorothioic, phosphonothioic, and phosphinothioic acids and phosphoric acid sulphenamides with diazo-compounds

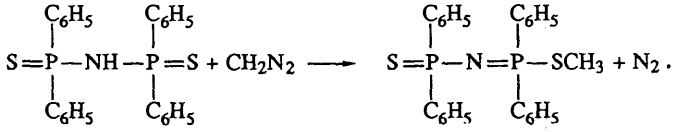
Dual reactivity is also manifested by the amides of phosphorus thio-acids when they are alkylated by diazo-compounds.[47–54]

The reaction of the diethylamide of phenylphosphonothioic acid with diazomethane involves the formation of both the *S*- and *O*-methyl esters of *N*,*N*-diethylphenylphosphonamidothioic acid:[47]

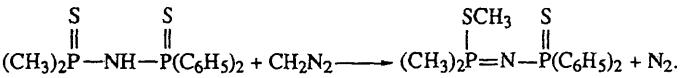


The dimethylamides of cyclohexylphosphonothioic and cyclohexylmorpholinophosphonothioic acids react similarly.[47]

In their study of the methylation of tetraphenyldiphosphinamidothioic acid, Schmidpeter and Groeger[48] established the exclusive formation of the product of alkylation at the sulphur atom — *S*-methyl tetraphenyldiphosphinimidothioate:

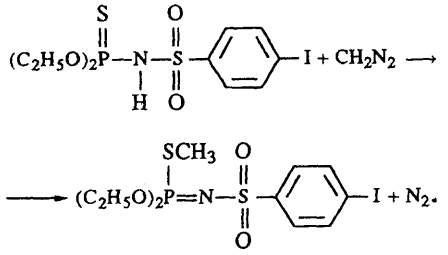


In the case of dimethyldiphenyldiphosphinamidodithioic acid, *S*-methylation with diazomethane takes place at the thiophosphoryl group linked to the methyl substituents:[49]

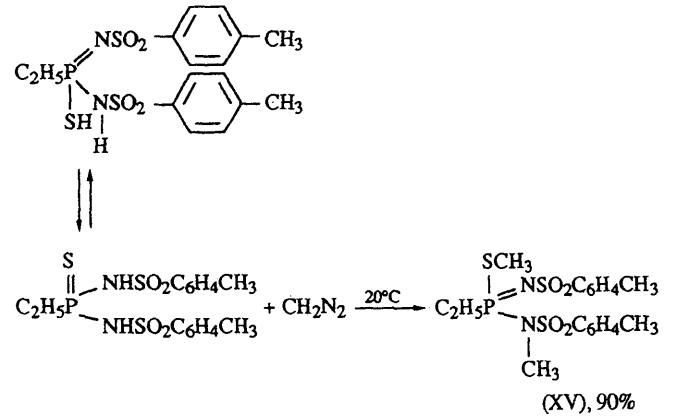


The formation of thiol imidoesters was detected similarly from the shift of the bond vibration band in the IR spectra in the reactions of phosphinothioic acid amides with diazomethane:[50]

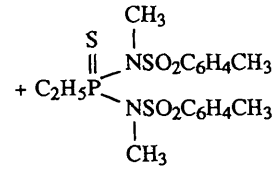
The *S*-methyl ester was also isolated as the main product in the methylation of *O*,*O*-diethyl *N*-(*p*-iodobenzenesulphonyl)phosphoramidothioate:[51]



In contrast to the reactions of phosphorus thio-acid amides presented above, the interaction of ethylphosphonothioic acid bis(*p*-methylbenzenesulphonamide) with diazomethane involves alkylation at both the sulphur and nitrogen atoms. The high yield of the *S*-methyl derivative (XV) together with the insignificant amount of the *N*-methyl derivative (XVI) are associated with the fact that the phosphonothioic acid diamide exists predominantly in the tautomeric imidothiol form:[52]

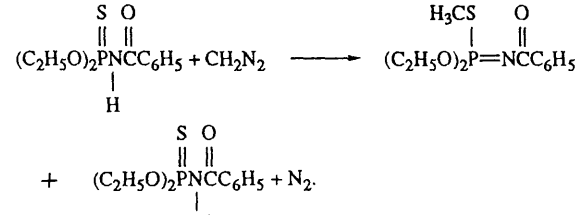


(XV), 90%

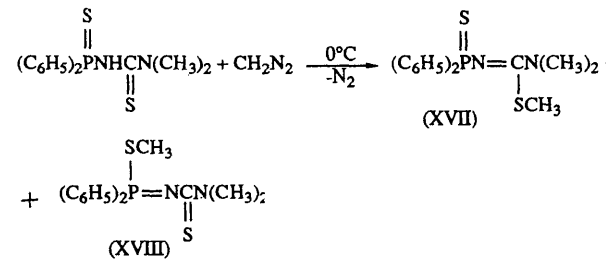


(XVI), 4%.

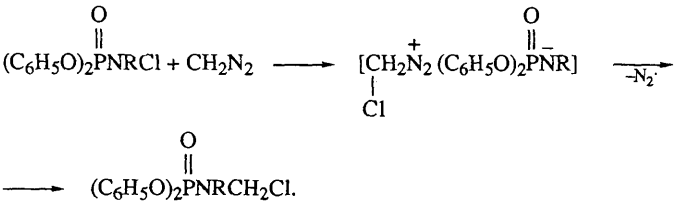
The reaction of *O*,*O*-diethyl *N*-benzoylphosphoramidothioate with diazomethane gives rise to yields of the *S*- and *N*-methyl derivatives in proportions of 5 : 1:[53]



The methylation with diazomethane of the *N*-dimethylthioureide of diphenylphosphinothioic acid takes place to the extent of 74% at the thiocarbonyl group with formation of *S*-methyl diphenylphosphinoisothioureidothioate (XVII) and to the extent of 26% at the thiophosphoryl group with formation of *S*-methyl diphenylphosphino(*N*-dimethylthiocarbamoylimido)thioate (XVIII):[54]

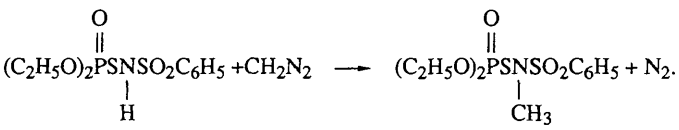


In contrast to the phosphorus thio-acid amides, the amides and sulphenamides of phosphoric acid are not methylated by diazomethane at the oxygen atom of the phosphoryl group. Thus *N*-chloromethylphosphoramidate was obtained from *N*-chlorophosphoramidate, its formation being represented as a result of the formal insertion of the methylene group in the N–Cl bond:[55]



R = Alk, $CH_2C_6H_5$.

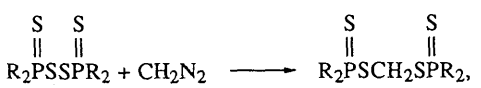
We are aware of only one study of the reactivity of the sulphenamides of phosphorus acids, described in the literature, in which it was shown that the aryl-substituted sulphenamide of diethylphosphoric acid affords the product of the methylation at the nitrogen atom on interaction with diazomethane:[56]



5. Interaction of phosphorus-containing polysulphides, sulphenyl halides of phosphorus acids, and phosphorus halides with diazo-compounds and carbenes

The interaction of phosphorus-containing polysulphides with diazo-compounds and carbenes has been studied only in recent years.[57–69] The review published previously[2] is supplemented here with new experimental data on the reactivities of phosphorus-containing polysulphides and sulphenyl halides of phosphorus acids.

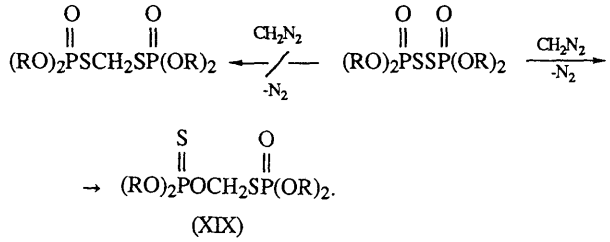
Thus symmetrical bis(dialkoxythiophosphoryl) and bis(diarylthiophosphoryl) disulphides react with diazomethane to form the products of the insertion of methylene in the S–S bond of the disulphides:[57,58]



R = AlkO, Ar.

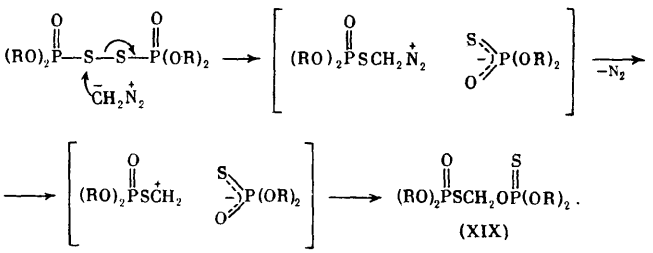
Similar products resulting from the insertion in the S–S bond are formed from aromatic disulphides by reaction with the Simmons-Smith reagent (ICH_2ZnI) and with carboxylic diazoacid esters.[70,71]

It is of interest that, in contrast to bis(dialkoxythiophosphoryl) and bis(diarylthiophosphoryl) disulphides, bis(dialkoxyphosphoryl) disulphides never form products of the insertion of the methylene group in the S–S bond on reaction with an excess of diazomethane in ethereal solution under various conditions (radiation with light from a mercury lamp, in daylight, or in the dark); this reaction leads to the formation, as a result of the phosphoryl–thiophosphoryl rearrangement, of products with an asymmetric structure, namely dialkoxythiophosphoryloxy(dialkoxyphosphorylthio)methanes (XIX):[59,60]

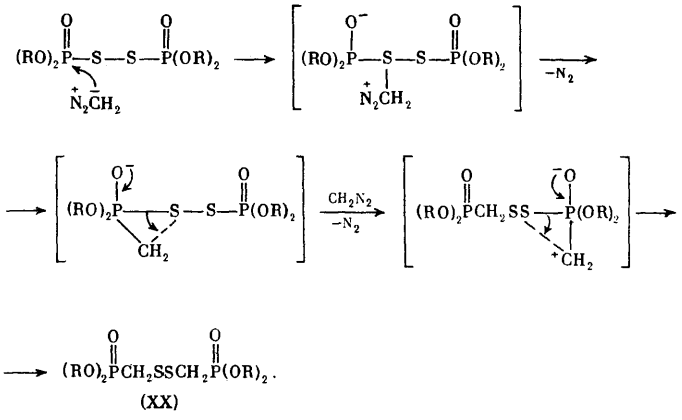


It has been suggested that, at least in the absence of illumination, bis(dialkoxyphosphoryl) disulphides interact with the undissociated diazomethane molecule. In the dark, the reaction is not restricted to the phosphoryl–thiophosphoryl rearrangement but is accompanied by the formation of the product of the insertion of two methylene groups in both P–S bonds of the disulphide with retention of the S–S bond and of the symmetry of the structure of compound (XX).[60] The formation of the products of the phosphoryl–thiophosphoryl rearrangement [compound (XIX)] and of insertion in the P–S bond [compound (XX)] is illustrated by Schemes 2 and 3 respectively:[59,60]

Scheme 2

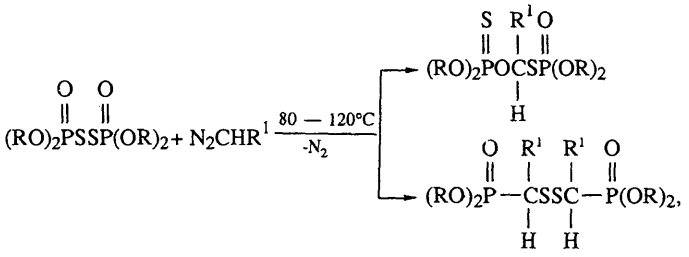


Scheme 3



The reactions of bis(dialkoxyphosphoryl) disulphides with diazoacetic ester and diazoacetone proceed similarly, with formation of the products of the phosphoryl–thiophosphoryl rearrangement

and of insertion in the P–S bond, under conditions which do not promote the formation of the corresponding carbenes:[60,61]

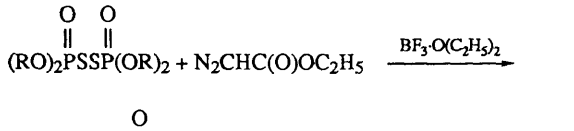


$R^1 = C(O)OC_2H_5$, $C(O)CH_3$.

The two competing reactions proceed at different rates, so that, depending on the reaction conditions, there is a possibility of the formation of one of the reaction products separately or of their mixtures in different proportions.

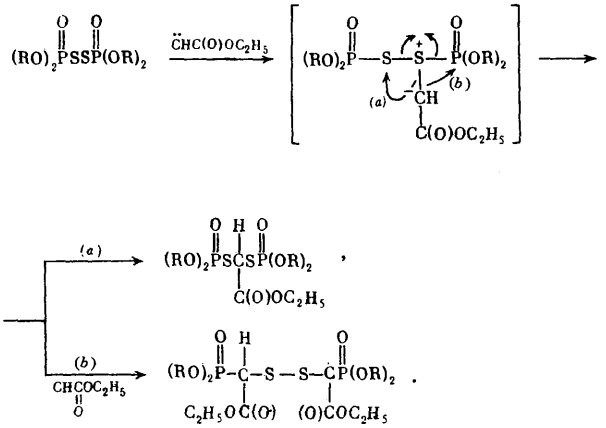
The reaction leads to different results under the conditions of the catalytic generation of ethoxycarbonylcarbene.

Thus the reaction of bis(dialkoxyphosphoryl) disulphides with diazoacetic ester in the presence of catalytic amounts of boron trifluoride etherate results in the formation, even at −20–8 °C, of bis(dialkoxyphosphoryl)ethoxycarbonylmethanes — the products of the insertion of ethoxycarbonylcarbene in the S–S bond:[62]



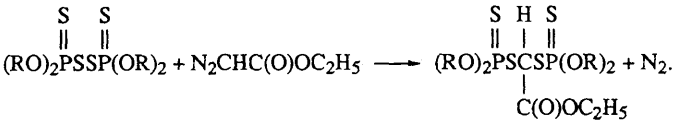
Under the conditions of the catalytic generation of ethoxycarbonylcarbene in the presence of copper powder at 80 °C in benzene or at 80–120 °C without a solvent, the reaction involving insertion in both P–S bonds competes with that leading to the formation of the products of the insertion of ethoxycarbonylcarbene in the S–S bond of the disulphide (Scheme 4):[62]

Scheme 4



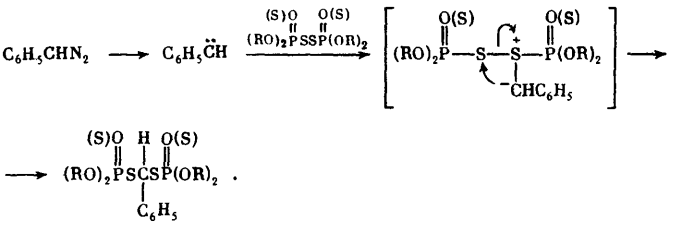
In contrast to diazoacetic ester, diazoacetone reacts with bis(dialkoxyphosphoryl) disulphides at 55–60 °C in the presence of metallic copper to form only the products of the insertion of acetylmethylene in the P–S bonds.[61]

The interaction of bis(dialkoxythiophosphoryl) disulphides with diazoacetic ester both via a non-catalytic reaction (80 °C, benzene) and under the conditions of the thermocatalytic decomposition of diazoacetic ester (Cu, 80 °C) proceeds selectively with formation of bis(dialkoxythiophosphorylthio)ethoxycarbonylmethanes only:[58]

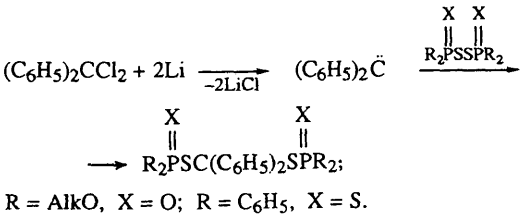


The reaction of bis(dialkoxythiophosphoryl) disulphides with diazoacetone under the conditions involving the generation of acetylcarbene (Cu, 55–60 °C) takes place with formation of the products of insertion in both S–S and P–S bonds,[61] while the reaction with benzoylcarbene afforded only the products of insertion in the S–S bond alone.[63]

It is of interest that the interaction of phenyldiazomethane with bis(dialkoxyphosphoryl) and bis(dialkoxythiophosphoryl) disulphides occurs even at room temperature and involves only the insertion of phenylmethylene in the S–S bond of the disulphide. The authors suggest that the reaction has a carbene mechanism and proceeds via an intermediate sulphonium ylid, whose conversion into the reaction products can occur as a concerted process as a result of a 1,2-sigmatropic rearrangement:[63]



In contrast to phenyldiazomethane, diphenyldiazomethane does not react with phosphorus-containing disulphides either on heating to 90 °C or under the conditions of the photolytic generation of diphenylcarbene. The interaction of bis(dialkoxyphosphoryl) and diphenylthiophosphoryl disulphides with diphenylcarbene, generated by treating dichlorodiphenylmethane with metallic lithium at 20 °C, was achieved. It afforded the products of the insertion of diphenylcarbene in the S–S bond of the disulphide:[63]



R = AlkO, X = O; R = C_6H_5, X = S.

Methylphenylcarbene, obtained from dichloro(methylphenyl)-ethane and metallic lithium, reacts with bis(diethoxythiophosphoryl) disulphide similarly to diphenylcarbene.[63]

The reaction of phosphorus-containing trisulphides and tetrasulphides with diazomethane affords the products of the phosphoryl–thiophosphoryl rearrangement:[64]

$$(RO)_2PS_nP(OR)_2 \xrightarrow[-N_2]{CH_2N_2} (RO)_2POCH_2S_{n-1}P(OR)_2 + (RO)_2POCH_2S_{n-2}CH_2OP(OR)_2;$$

$n = 3,4.$

In the reaction with diazoacetic ester, the rearrangement does not occur, but the products of the insertion of the ethoxycarbonylmethylene group in one of the P–S bonds of the polysulphide are formed in a high yield:[65]

$$(RO)_2PS_nP(OR)_2 + N_2CHC(O)OC_2H_5 \longrightarrow (RO)_2PCH(C(O)OC_2H_5)S_nP(OR)_2 + N_2;$$

$n = 3, 4.$

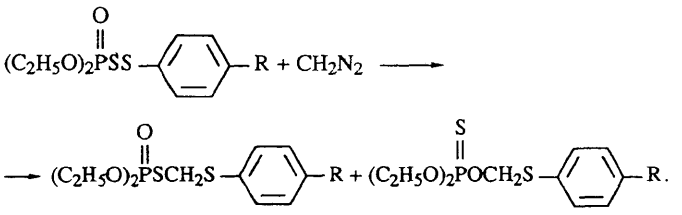
In the presence of an excess of diazoacetic ester, two ethoxycarbonylmethylene groups are inserted in the P–S bonds of polysulphides with partial desulphurisation:[65]

$$(RO)_2PS_nP(OR)_2 + N_2CHC(O)OC_2H_5 \longrightarrow \rightarrow [(RO)_2PC(H)(C(O)OC_2H_5)S]_2 + N_2 + (n-2)S;$$

$n = 3, 4.$

Reactions analogous to those described above have also been considered in relation to thiophosphoryl-substituted trisulphides and tetrasulphides.[66] The products of the insertion of the ethylene group both in one and in two disulphide bonds closest to the phosphorus atom were obtained.

In the case of phosphorus-containing disulphides with an asymmetric structure, namely aryl diethoxyphosphoryl disulphides, the insertion of the methylene group in the S–S bond has been reported, while the products of the phosphoryl-thiophosphoryl rearrangement have been obtained in an insignificant yield:[72–74]



The authors of the above studies suggest that the phosphoryl–thiophosphoryl rearrangement involves interaction with an undissociated molecule of the diazo-compound, while the insertion in the S–S bond is a reaction of the carbene type. As regards the insertion in the P–S bond, the reaction can apparently have both carbene and non-carbene mechanisms.

Thus the reactions of phosphorus-containing polysulphides with diazo-compounds make it possible to obtain organophosphorus compounds which are otherwise difficult to synthesise or were previously unknown, and lead to interesting possibilities for the investigation of carbene reactions in the chemistry of organophosphorus compounds.

Dithio- and monothio-phosphoryl groups

$$-(RO_2)PS(O)-$$

in phosphorus-containing polysulphides behave in many reactions as a pseudo-halogen.[75,76] This is confirmed by the analogous behaviour of thiophosphorylsulphenyl halides and disulphides in reactions with diazo-compounds and carbenes.

The first reports concerning the reactivity of sulphenyl halides derived from phosphorus acids in relation to diazoalkanes appeared in the 1960s. The interaction of diethoxy(thio)phosphorylsulphenyl chlorides with diazomethane and diazoethane has been described.[77,78] α-Chloro-substituted esters of phosphoromonothioic and phosphorodithioic acids were obtained:

$$(C_2H_5O)_2P(X)SCl + N_2CHR^1 \longrightarrow (C_2H_5O)_2P(X)SCH(Cl)R^1 + N_2;$$

$X = O, R = H; X = S, R = CH_3.$

Later, other investigators[79–81] studied the interaction of dialkoxy(thio)phosphorylsulphenyl halides with various diazo-compounds: diazomethane, aryl- and diaryl-diazoalkanes, diazoacetic ester, and mono- and bis-diazoketones. It was shown that the reactions of dialkoxy(thio)phosphorylsulphenyl halides with the above diazo-compounds proceed similarly to those described above, with formation of the products of the insertion of the methylene or substituted methylene group in the S–halogen bond in the sulphenyl halides:

$$(RO)_2PS(O)Hal + N_2CR^1R^2 \longrightarrow (RO)_2PS(O)CR^1R^2Hal + N_2;$$

$Hal = Cl; R^1 = H, R^2 = C(O)OC_2H_5, C_6H_5, C(O)(CH_2)_4C(O)CHN_2,$

$C(O)CH_3, C(O)C_6H_5; R^1 = R^2 = C_6H_5; Hal = Br; R = Alk; R^1 = H;$

$R^2 = C(O)OC_2H_5, C_6H_5; R^1 = R^2 = H, C_6H_5.$

However, in the reaction of dialkoxyphosphorylsulphenyl bromides with diazoacetone and diazoacetic ester, a mixture of phosphorothiolic and phosphorothionic acid esters is formed, i.e., together with the insertion of the acetyl- and ethoxycarbonylmethylene group in the S–Br bond of the sulphenyl

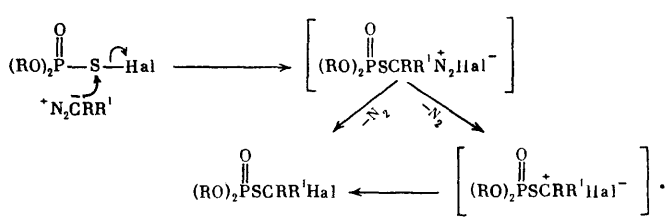
bromide, the products of the phosphoryl–thiophosphoryl rearrangement are formed:

$$(RO)_2P(O)SBr + N_2CHR^1 \longrightarrow (RO)_2P(O)SCHR^1Br + (RO)_2P(S)OCHR^1Br + N_2;$$

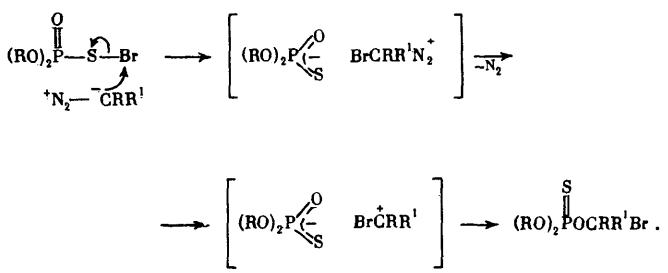
$R^1 = C(O)CH_3, C(O)OC_2H_5$.

The experimental conditions ($t = -50$ to -20 °C, absence of the catalyst or UV irradiation) enabled the authors of the above studies to reject the carbene reaction mechanism and to regard the interaction of dialkoxy(thio)phosphorylsulphenyl halides with an undissociated molecule of a diazo-compound via the intermediate formation of the diazonium cation as a result of nucleophilic attack either on the sulphur atom (Scheme 5) or on the halogen atom (Scheme 6):

Scheme 5



Scheme 6



The exclusive formation of the products of the insertion of the substituted methylene group in the S–halogen bond in the sulphenyl halides is evidence in support of Scheme 5. However, Scheme 6, involving nucleophilic attack on the bromine atom, operates in the reaction of diazoacetone and diazoacetic ester with dialkoxyphosphorylsulphenyl bromides.

As can be seen from the foregoing, the interaction of phosphoryl- and thiophosphoryl-sulphenyl halides with diazo-compounds involves mainly the insertion of the methylene or a substituted methylene group in the S–halogen bond. It is therefore of interest to examine the reactivities of phosphorus halides in relation to diazo-compounds, since this entails the insertion of the methylene group in the P–halogen bond.

Thus Yakubovich and Ginzburg[82] showed in 1952 that, under certain conditions ($t = -60$ °C), the interaction of phosphorus trichloride or tribromide with diazoalkanes proceeds smoothly with formation of haloalkyldihalophosphines:

$$PHal_3 + RCHN_2 \longrightarrow HalCHRPHal + N_2;$$

Hal = Cl, Br; R = H, CH_3.

Phosphorus pentachloride reacts with diazomethane to form tris(chloromethyl)dichlorophosphine, which is converted subsequently into tris(chloromethyl)phosphine oxide in the presence of traces of moisture:[82]

$$PCl_5 + 3CH_2N_2 \longrightarrow (ClCH_2)_3PCl_2 \xrightarrow{H_2O} (ClCH_2)_3P{=}O.$$

Phenylphosphorus tetrachloride behaves similarly:[83]

$$C_6H_5PCl_4 + 3CH_2N_2 \xrightarrow[-40°C]{} [C_6H_5P(CH_2Cl)_2Cl_2] \xrightarrow{H_2O}$$

$$\rightarrow C_6H_5P(O)(CH_2Cl)_2.$$

Phosphorus oxide chloride and phosphorus oxide bromide do not react with diazoalkanes even under the conditions involving the generation of the corresponding carbenes.[82]

III. Phosphines and phosphites in reactions with diazo-compounds and carbenes

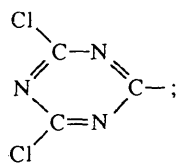
1. Reactions of acyclic trialkyl- and triaryl-phosphines and tertiary cyclic phosphines and their oxides with diazo-compounds

The reactions of trivalent phosphorus derivatives with diazo-compounds were first achieved by Staudinger and co-workers in 1919–1922 for acyclic tertiary phosphines.[84] Later, other workers greatly expanded the range of applications of this reaction.[85–91]

It has been shown in relation to acyclic tertiary phosphines that trialkyl- and triaryl-phosphines react with different acyclic diazo-compounds to form phosphazines:

$$R^1R^2R^3P + N_2CR^4R^5 \longrightarrow R^1R^2R^3P{=}N{-}N{=}CR^4R^5,$$

$R^1 = R^2 = R^3 = C_6H_5, C_2H_5, C_6H_5C_6H_4$; R^4 = H, C_6H_5, $C_6H_5C(O)$, $CH_3C(O)$, $CH_3C(O)O$, $C_2H_5OC(O)$, $CH_3OC(O)$, C_6H_5SO,

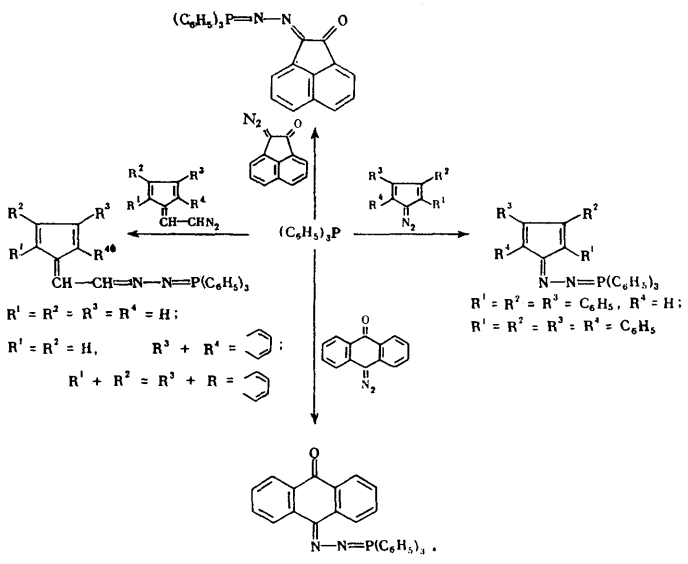


$R^5 = C_6H_5, C_2H_5OC(O), C_6H_5C(O), CH_3C(O), CH_3OC(O)$,

$C_6H_5CH{=}CHC(O)$, $C_6H_5S(O)O$.

The reactions of triphenylphosphine with cyclic diazo-compounds, namely diazoacenaphthene,[92] diazoanthrone,[93] diazoethylidene derivatives of cyclopentadiene, indene, and fluorene,[94] and

diazocyclopentadiene and its phenyl derivatives,[95,96] proceed similarly to form cyclic phosphazenes:



A kinetic study[97,98] confirmed the second order and irreversibility of the reactions of triphenylphosphines and aromatic ring-substituted triphenylphosphines with diazoalkanes and 9-diazofluorene.

It is of interest that the nature of the final product of the reactions of acyclic phosphines with diazo-compounds is influenced by the nature of the substituents at the phosphorus atom. In the presence of a mobile hydrogen atom in the phosphine molecule, phosphazines are not formed. Thus dibutoxyphosphine reacts with diphenyldiazomethane to form a mixture of the isomeric adducts (XXI) and (XXII), while the reactions with diazoacetone and diazoacetic esters afford only one adduct—the hydrazone (XXI):[99]

$$(C_4H_9O)_2PH + N_2CRR^1 \longrightarrow \underset{\text{(XXI)}}{(C_4H_9O)_2PNHN{=}CRR^1} + \underset{\text{(XXII)}}{(C_4H_9O)_2PN{=}NCHRR^1};$$

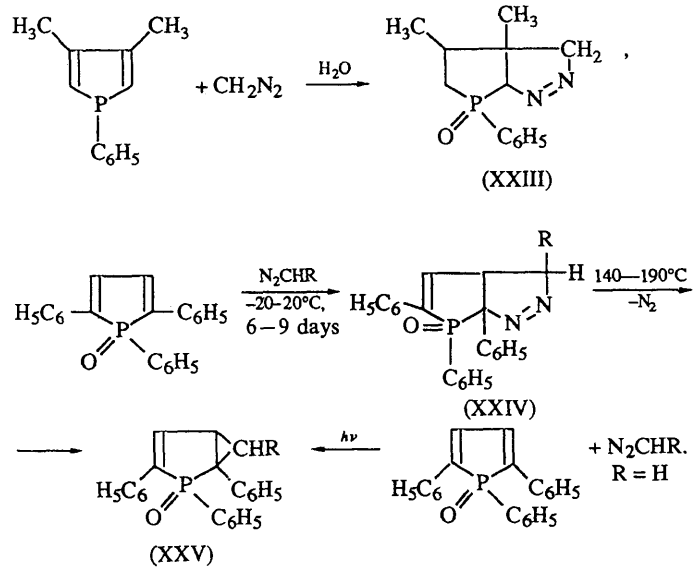
$$R = R^1 = C_6H_5;\ R = H,\ R^1 = C(O)CH_3,\ C(O)OC_2H_5.$$

In contrast to the reactions of acyclic phosphines, the reaction of an acyclic tertiary phosphine, having a mobile hydrogen atom in the α-position, with diazomethane takes place via the phosphoryl group to form a phosphorane:[100]

$$(C_6H_5)_2P(O)CH(SO_2C_6H_5)_2 + CH_2N_2 \longrightarrow (C_6H_5)_2P(OCH_3){=}C(SO_2C_6H_5)_2 + N_2.$$

The reactions of unsaturated tertiary cyclic phosphines and their oxides proceed quite differently.

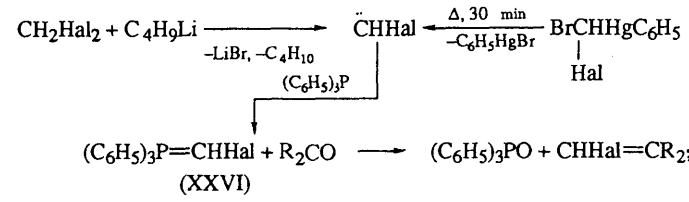
Thus the reactions of 3,4-dimethyl-1-phenylphosphole with diazomethane in the presence of water[101] and of 1,2,5-triphenylphosphole oxide with diazomethane and diazoacetic acid esters[102] proceed as 1,3-dipolar cycloaddition to one of the multiple bonds of the ring with formation of the pyrazoline derivatives (XXIII) and (XXIV) respectively. The cyclopropane derivatives (XXV) were obtained by the thermal decomposition of compound (XXIV). They are formed as a result of the photochemical reaction of 1,2,5-triphenylphosphole oxide with diazomethane:



2. Reactions of trialkyl- and triaryl-phosphines with carbenes

The reactivity of phosphines in relation to carbenes has been studied in fair detail and it has been found that trialkyl- and triarylphosphines are mild carbene trapping agents and that this reaction serves as one of the methods for the synthesis of phosphorus ylids which are used in synthetic organic chemistry for the synthesis of olefins by the Wittig reaction.[93,103–116]

Halomethylenephosphoranes (XXVI) are formed in the reaction of triphenylphosphine with chlorocarbene, generated from methylene chloride by treatment with butyllithium[103–105] or by the thermolysis of phenyl(bromohalomethyl)mercury:[106]



Hal = Cl, Br.

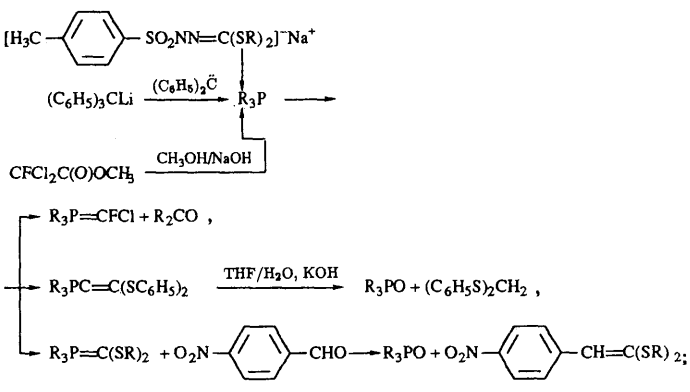
Dihalomethylenephosphoranes (XXVII, Hal = F, Cl, Br) have been obtained from trialkyl- and triaryl-phosphines and dihalocarbenes, generated from haloform by the treatment with potassium t-butoxide,[107–109] by the thermolysis of phenyl(bromodichloromethyl)mercury[110] or the sodium salt of chlorodifluoroacetic

acid,[111] or from dibromodifluoromethane by treatment with lithium butoxide:[112]

$$R_3P + \ddot{C}HHal_2 \longrightarrow \underset{(XXVII)}{R_3P{=}CHHal_2} + R_2CO \longrightarrow R_3PO + Hal_2C{=}CR_2;$$

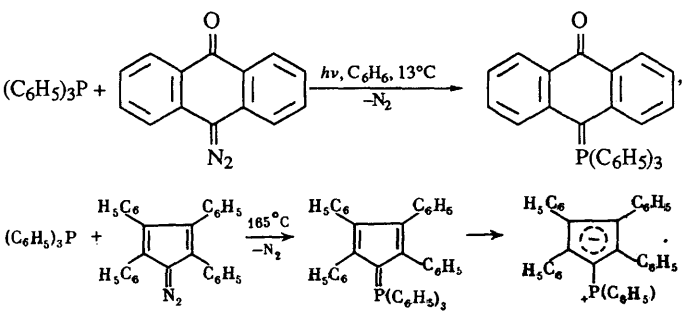
R = Alk, Ar; Hal = Cl, Br, F.

Chlorofluoromethylene, obtained from methyl dichlorofluoroacetate and sodium hydride,[109,113] bis(phenylthio)carbene, generated from tris(phenylthiomethyllithium)[114] and bis(alkylthio)carbene, generated by the thermal decomposition of the sodium salt of tosylhydrazone[115] enter into similar reactions with phosphines:



Phosphorus ylids are formed when the carbene precursor is a diazo-compound, for example, in the reaction with triphenylphosphine under the conditions of catalytic, photolytic, or thermal decomposition of the corresponding diazo-compound:[93,95,96,116]

$$(C_6H_5)_3P + CH_2N_2 \xrightarrow[-N_2]{CuCl} (C_6H_5)_3P{=}CH_2,$$



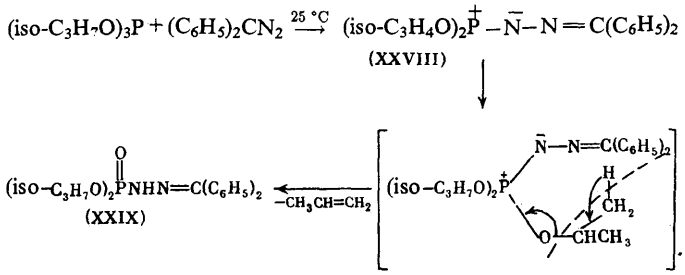
3. Phosphites in reactions with diazo-compounds and carbenes

Kabachnik and Arbuzov[13,117–119] showed that trialkyl phosphites behave similarly to phosphines in reactions with diazomethane and diazoacetic acid esters, forming trialkyl phosphate *N*-methylene- and *N*-ethoxycarbonyl-azines respectively in yields of at least 60%:

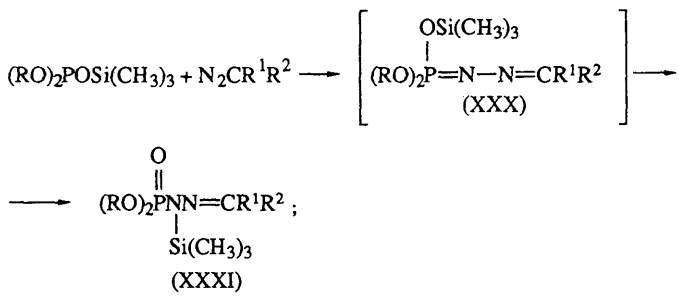
$$(RO)_3P + N_2CHR^1 \longrightarrow (RO)_3P{=}N{-}N{=}CHR^1;$$

R^1 = H, C(O)CH$_3$, C(O)OC$_2$H$_5$.

It has been observed[120] that the reaction of triisopropyl phosphite with diphenyldiazomethane does not stop at the stage involving the formation of benzophenone triisopropylphosphorazine (XXVIII). Instead, a compound with the hydrazone structure, namely diisopropyl *N*-(diphenylmethylene)phosphorohydrazidate (XXIX), is formed in 75% yield, provided that the reaction is carried out under severe conditions:



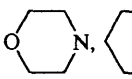
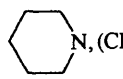
In the case of dialkyl trimethylsilyl phosphites, the intermediate phosphorazines (XXX) almost wholly isomerise already under experimental conditions with migration of the trimethylsilyl group to the phosphimine nitrogen atom and the quantitative formation of dialkyl *N*-trimethylsilylphosphorohydrazidates (XXXI):[121,122]



$R^1 = R^2$ = H, C$_6$H$_5$; R^1 = H, R^2 = C(O)CH$_3$, C(O)OCH$_3$, C(O)OC$_2$H$_5$.

Phosphorous triamides react vigorously with various acyclic and cyclic diazo-compounds similarly to trialkyl phosphites. About 60 compounds of the class of tris(dimethylamino)phosphorazines were obtained:[123–125]

$$R_3P + N_2CR^1R^2 \longrightarrow R_3P{=}N{-}N{=}CR^1R^2,$$

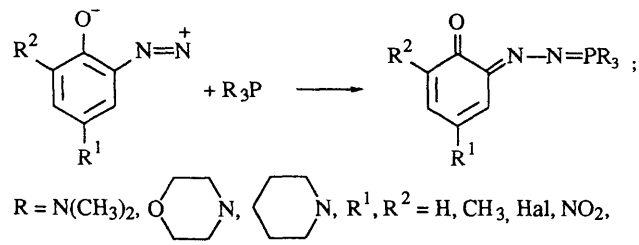
R =  ,  , (CH$_3$)$_2$N, (C$_2$H$_5$)$_2$N; $R^1 = R^2$ = H, C(O)OCH$_3$,

C(O)OC$_2$H$_5$, C$_6$H$_5$, R^1 = H, R^2 = C(O)OC$_2$H$_5$, C(O)OCH$_3$;

R^1 = C(O)CH$_3$, R^2 = C(O)C$_6$H$_5$; $R^1 + R^2$ = (CH$_3$)$_3$C(CH$_2$)$_2$CO$_2$,

o-C$_6$H$_4$(CO)$_2$.

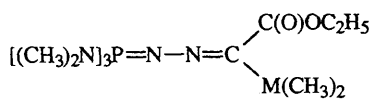
The reaction with *O*-diazoquinone and its various derivatives 4,6-disubstituted in the aromatic ring proceeds similarly:[126]



$R = N(CH_3)_2$, O, N, N, $R^1, R^2 = H, CH_3$, Hal, NO_2, $C(O)CH_3$, $C(O)OCH_3$.

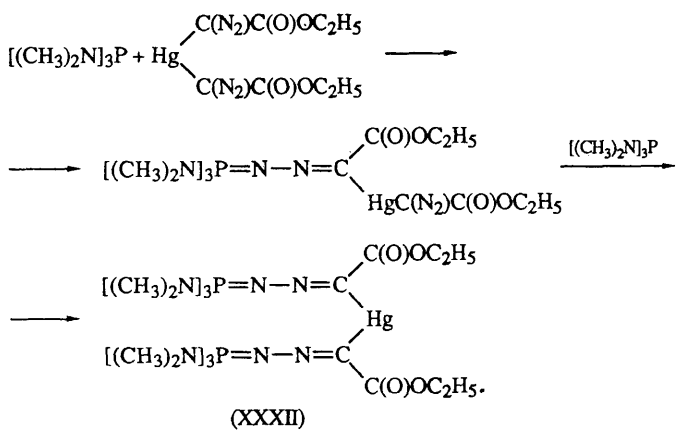
Towards the end of the 1970s, Krommes and Lorberth[124,127] investigated the reactions of phosphorous tris(dimethylamides) with a whole series of organoelement derivatives of diazomethane: $(CH_3)_nMCN_2$ [M = Si, Ge, Sn, Pb, As, Sb, Bi: n = 2, 3; R = H, $C(O)OC_2H_5$].

From the available literature data on the chemistry of organoelement diazoalkanes,[128] it was postulated that the introduction of any element into the molecule of the diazo-compound does not alter the chemical behaviour of organoelement derivatives or diazomethane in their reactions with phosphorous tris(dimethylamides). Indeed, the tris(dimethylamino)phosphorazines



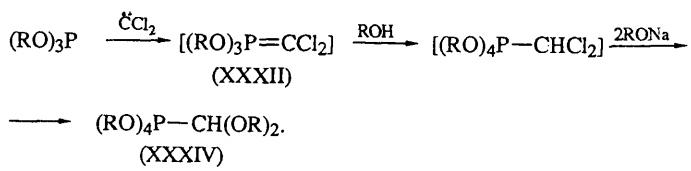
were obtained for M = As or Sb. When R = H, M = Si, Ge, or As, and n = 2 or 3, a mixture of the *cis*- and *trans*-isomers of tris(dimethylamino)phosphorazines is formed.

The interaction of phosphorous tris(dimethylamide) with bis(ethyl diazoacetate)mercury to form the tris(dimethylamino)phosphorazine (XXXII) can proceed in stages:



(XXXII)

As regards the interaction of trialkyl phosphites with carbenes, it was found that, in contrast to phosphines, trialkyl phosphites, in the presence of which dichlorocarbene is generated from chloroform and sodium alkoxide, give rise to the adducts (XXXIII), which undergo further changes and are converted into tetraalkoxy(dialkoxy-methylene)phosphoranes (XXXIV):[129]

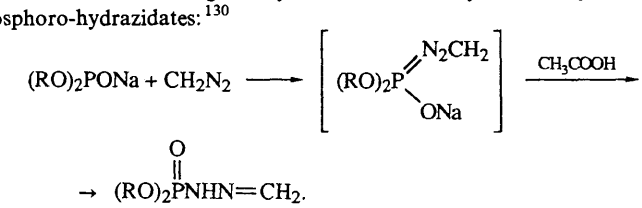


(XXXII) (XXXIV)

Thus a common feature of the reactions of phosphines and phosphites with diazo-compounds is the formation of a new phosphorus–nitrogen bond. Evidently, these reactions are based on addition to the lone pair of the phosphorus atom, probably as a result of the electrophilic attack by the terminal nitrogen atom and the conversion of the trivalent phosphorus derivative into the corresponding pentavalent phosphorus derivative.

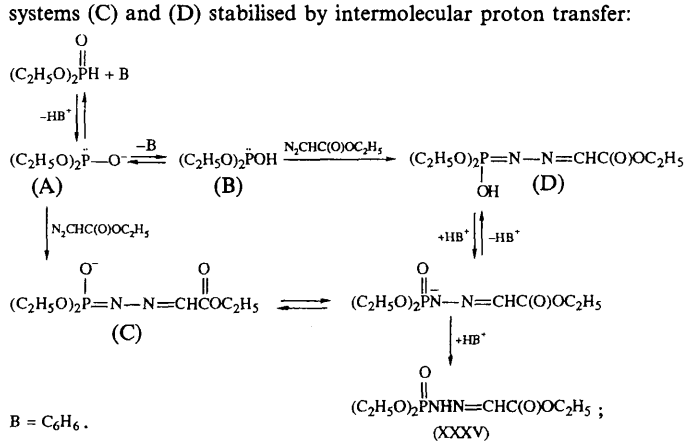
4. Dialkyl phosphites in reactions with diazo-compounds

In contrast to trialkyl- and triaryl-phosphines, trialkyl phosphites, and phosphorous triamides, dialkyl phosphites do not react with aliphatic diazo-compounds under the usual conditions. Only their sodium salts react vigorously to form dialkyl *N*-methylene-phosphoro-hydrazidates:[130]



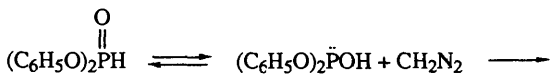
The inability of dialkyl phosphites to react with diazoalkanes has been attributed to the low acidity of dialkyl phosphites, because their tautomeric equilibrium is strongly displaced towards the form with pentavalent phosphorus[131] and the insertion of the methylene group in the P–H bond, specially investigated in relation to hypo-phosphorous acid esters, was not observed.[10]

However, the use of benzene as the solvent, which promotes the shift of the tautomeric equilibrium of diethyl phosphite towards the formation of the trivalent form (B) according to the authors,[119] leads to the interaction between the diethyl phosphite and diazoacetic ester with formation of diethyl *N*-ethoxycarbonylmethylene-phosphorohydrazidate (XXXV). A mechanism is proposed for the formation of the reaction product via the intermediate phosphazine systems (C) and (D) stabilised by intermolecular proton transfer:



B = C_6H_6.

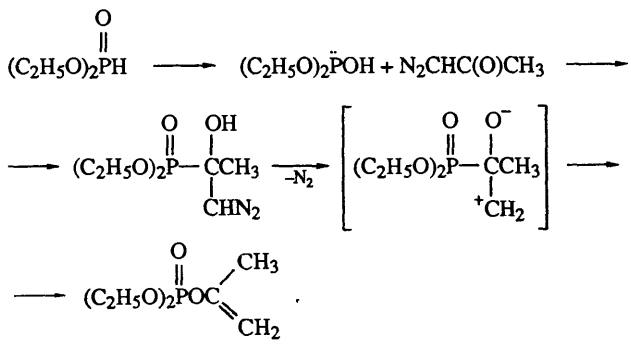
Diphenyl phosphite, which has more acid properties than diethyl phosphite, reacts with diazomethane to form methyl diphenyl phosphite due to the presence of the tautomeric equilibrium between the pentavalent and trivalent forms:[132]



$$(C_6H_5O)_2\overset{O}{\overset{\|}{P}}H \rightleftharpoons (C_6H_5O)_2\ddot{P}OH + CH_2N_2 \longrightarrow$$

$$\rightarrow (C_6H_5O)_2POCH_3 + N_2.$$

The unusual behaviour of diazoacetone in the reaction with diethyl phosphite and the formation of diethyl isopropenyl phosphate have been noted:[87,133]

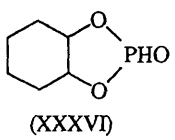


$$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}H \longrightarrow (C_2H_5O)_2\ddot{P}OH + N_2CHC(O)CH_3 \longrightarrow$$

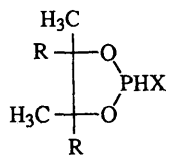
$$\longrightarrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}-\underset{CHN_2}{\overset{OH}{\overset{|}{\underset{|}{C}}}}CH_3 \xrightarrow{-N_2} \left[(C_2H_5O)_2\overset{O}{\overset{\|}{P}}-\underset{{}^{+}CH_2}{\overset{O^-}{\overset{|}{\underset{|}{C}}}}CH_3\right] \longrightarrow$$

$$\longrightarrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}OC(CH_3)=CH_2.$$

In contrast to acyclic dialkyl phosphites, the high reactivity of cyclic phosphorous acids and their sulphur and nitrogen analogues (XXXVI)–(XXXIX) in reactions with diazomethane indicates a greater shift of the tautomeric equilibrium of the acid towards the trivalent form, which is the reason for their acid properties:[134,135]

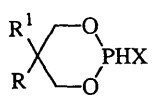


(XXXVI)



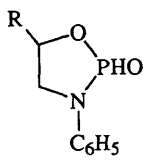
(XXXVII)

R = H, CH_3, X = O, S



(XXXVIII)

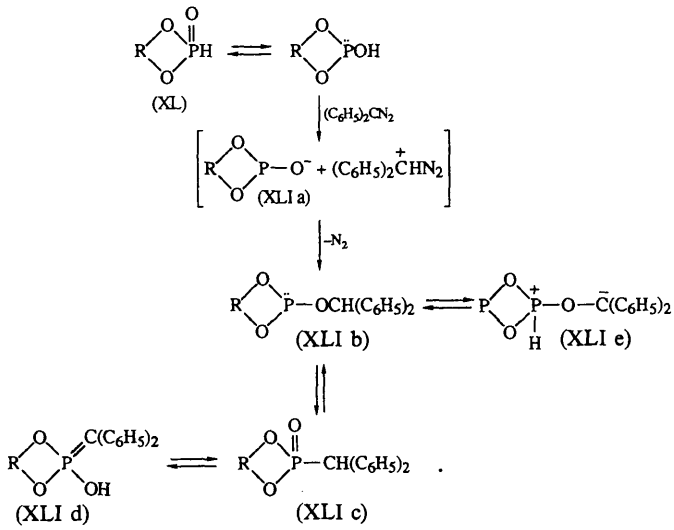
R = CH_3, R^1 = H, X = O;
R = H, R^1 = CH_3, X = S



(XXXIX)

R = H, CH_3.

Thus, when equimolar amounts of 2,3-butylene-, *o*-phenylene, and neopentylene-phosphorous acids (XL) are mixed with diphenyldiazomethane at 20–25 °C, an equilibrium mixture of products (XLIb–e) is formed:



(XL) $\rightleftharpoons$ $\xrightarrow{(C_6H_5)_2CN_2}$ [(XLI a)] $\xrightarrow{-N_2}$ (XLI b) $\rightleftharpoons$ (XLI e)

(XLI d) $\rightleftharpoons$ (XLI c)

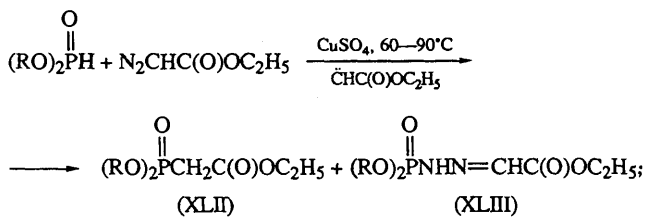
From the entire set of experimental data and the results of kinetic studies of the reactions of cyclic phosphorous acids with diphenyldiazomethane, it was established that the reaction proceeds via a two-stage mechanism. In the first stage, diphenyldiazomethane is protonated with formation of the ion pair (XLIa), while in the second stage the ion pair is converted into the final reaction products (XLIb–e).

Thus the kinetic studies indicate the existence of common mechanisms in the reactions of phosphorous acids and cyclic phosphoromonothioic and phosphorodithioic acids[36,37] as well as acyclic phosphorus monothio acids[22,26] with diazo-compounds.

5. Reactions of dialkyl phosphites and dialkyl phosphorothioites with carbenes

Until the beginning of the 1960s, there was no information in the literature about the reactions of organophosphorus compounds containing a P–H bond in the molecule with diazo-compounds under carbene generation conditions.

The formation of dialkyl phosphonoacetate esters (XLII) and small amounts (5–6%) of dialkyl *N*-ethoxycarbonylmethylene-phosphorohydrazidates (XLIII, R = CH_3, C_3H_7) was achieved for the first time[12,13] in the $CuSO_4$-catalysed decomposition of diazoacetic ester in the corresponding dialkyl phosphites. The authors represent the formation of the phosphorohydrazidates as a result of the interaction of dialkyl phosphites with still undecomposed diazoacetic ester:



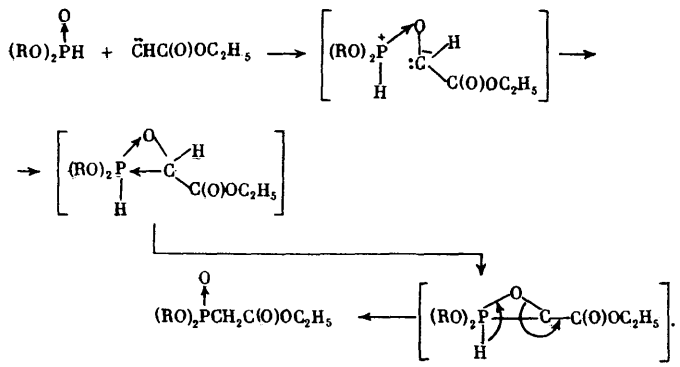
$$(RO)_2\overset{O}{\overset{\|}{P}}H + N_2CHC(O)OC_2H_5 \xrightarrow[\ddot{C}HC(O)OC_2H_5]{CuSO_4,\ 60—90°C}$$

$$\longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}CH_2C(O)OC_2H_5 + (RO)_2\overset{O}{\overset{\|}{P}}NHN{=}CHC(O)OC_2H_5;$$

(XLII) (XLIII)

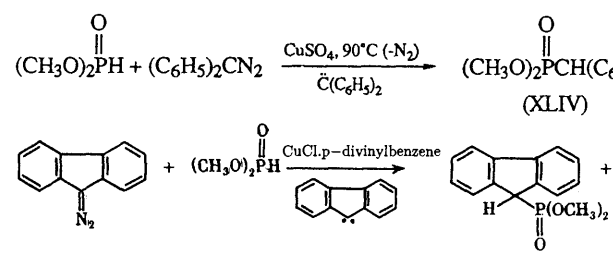
R = CH_3, C_2H_5, C_3H_7.

The mechanism proposed for the formation of compounds (XLII) includes electrophilic attack by the ethoxycarbonylcarbene on the oxygen of the dialkyl phosphite with subsequent redistribution of bonds in the intermediate complex formed:[13]

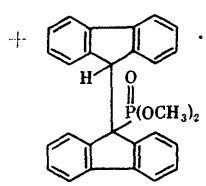


According to the authors, the hypothesis of the possible direct insertion of the ethoxycarbonylcarbene in the P–H bond is no less likely.

The product of insertion in the P–H bond, namely dimethyl diphenylmethylphosphonate (XXIV) [136] and, in the case of diazofluorene, the adducts (XLV) and (XLVI),[137] were obtained similarly in the thermocatalytic decomposition of diphenyldiazomethane in dimethyl phosphite:



(XLV)



(XLVI)

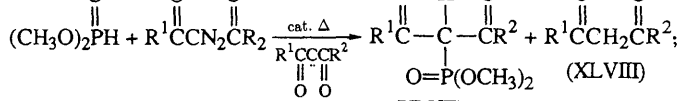
The reactions with diazoindene and 7-diazo-8-naphthene are likewise similar.[137]

As regards diazodicarbonyl compounds, especially diazodiketones which are known to be capable of the specific Wolff rearrangement in the decomposition process,[138] by suppressing this process or by creating conditions promoting the occurrence of the Wolff rearrangement, it is possible to alter the mode of the reactions of diazoketones with organophosphorus compounds.

It has been established that, under conditions promoting the Wolff rearrangement, phosphorus-containing products cannot be isolated. The only reaction product was alkyl 2-oxo-1,2-diphenylpropionate.[139]

In order to suppress the Wolff rearrangement and to make it possible to synthesise the products of insertion in the P–H bond, a study has been made[139–146] of the thermocatalytic decomposition,[139–142], direct photolysis,[142] and photosensitised decomposition[142,144–146] of a whole series of 2-diazo-1,3-diketones in dialkyl phosphites and phosphorothioites.

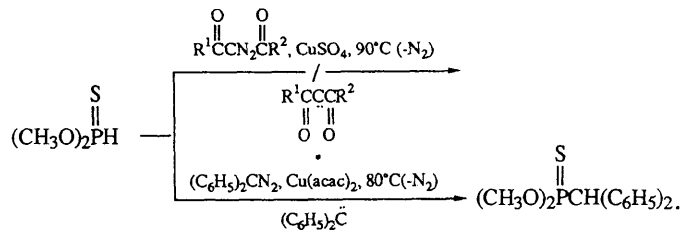
The thermocatalytic decomposition of 2-diazo-1,3-diketones ($CuSO_4$ or copper acetylacetonate; 80–90 °C) in dimethyl phosphite led to the isolation in 16.5–46% yield of 2-phosphono-1,3-diketones (XLVII) — the products of the insertion of the corresponding diketocarbene in the P–H bond of dimethyl phosphite and the products of the reduction of the diketocarbenes (XLVIII). The reaction constitutes a general method for the *C*-phosphorylation of 1,3-dicarbonyl compounds:



(XLVII)

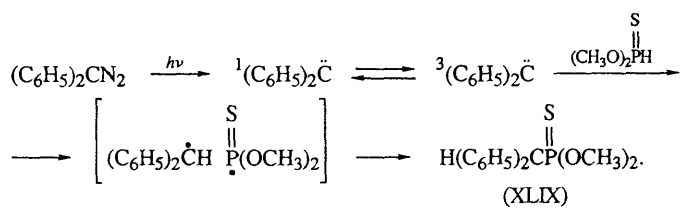
$R^1 = R^2 = CH_3$, OCH_3, C_6H_5; $R^1 + R^2 = (CH_3)_2C(CH_2)_2$.

In the case of dialkyl phosphorothioites, the insertion of diketocarbenes, obtained under similar conditions, in the P–H bond could not be achieved,[142] in contrast to diphenylcarbene:[136]



Until recently, there was no information in the literature about the insertion of photochemically generated carbenes in the P–H bond.

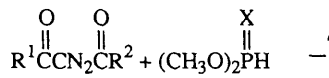
It was not until 1989[136] that the product of the insertion of diphenylcarbene in the P–H bond, namely dimethyl diphenylmethylphosphonothioate (XLIX), was obtained by the direct photolysis of diphenyldiazomethane in dimethyl phosphorothioite. The formation of compound (XLIX) was represented as a reaction proceeding via the mechanism involved in the recombination of the radical pairs generated from the triplet form of diphenylcarbene:[147]



(XLIX)

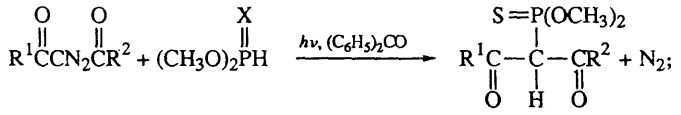
There are no literature data indicating that the diketocarbenes obtained by the direct photolysis of diazodicarbonyl compounds exist predominantly in the triplet form. This is apparently the

reason why the attempt in 1986 to obtain the products of insertion in the P–H bond was unsuccessful:[142]



$R^1 = CH_3$, $R^2 = OCH_3$, CH_3; $R^1 + R^2 = (CH_3)_2(CH_2)_2$; X = O, S.

However, 2-(thio)phosphono-1,3-dicarbonyl compounds — the products of insertion in the P–H bond — were obtained in 6.5–3.9% yields by the photosensitised decomposition of 2-diazo-1,3-dicarbonyl compounds in dimethyl phosphite (phosphorothioite) in the presence of benzophenone:[142,144,145]



$R^1 = R^2 = OCH_3$, X = S; $R^1 = CH_3$, $R^2 = OCH_3$, X = S;

$R^1 = R^2 = CH_3$; X = O, S;

$R^1 + R^2 = (CH_3)_2C(CH_2)_2$, X = S.

Thus the results obtained for the reactions of the photochemically generated diketocarbenes in dialkyl phosphites (phosphorothioites) led the investigators[142,144] to put forward the hypothesis that a triplet carbene is the main intermediate in the insertion in the P–H bond, which was confirmed by a study, using the chemically induced dynamic nuclear polarisation method (^{31}P CIDNP), of the mechanism of the insertion of carbenes in the P–H bond.[145,146]

Thus it is evident from the literature data on the reactions of organophosphorus compounds with a P–H bond in the molecule that the formation of the products of insertion in this bond in the reactions of dialkyl phosphites (phosphorothioites) with diazo-compounds occurs in two cases: (a) under the conditions of the thermocatalytic generation of carbenes and (b) in the photosensitised decomposition of diazodicarbonyl compounds. In the reactions with diphenyldiazomethane, such products are formed under the conditions of direct photolysis owing to the specific properties of the diphenylcarbene generated.

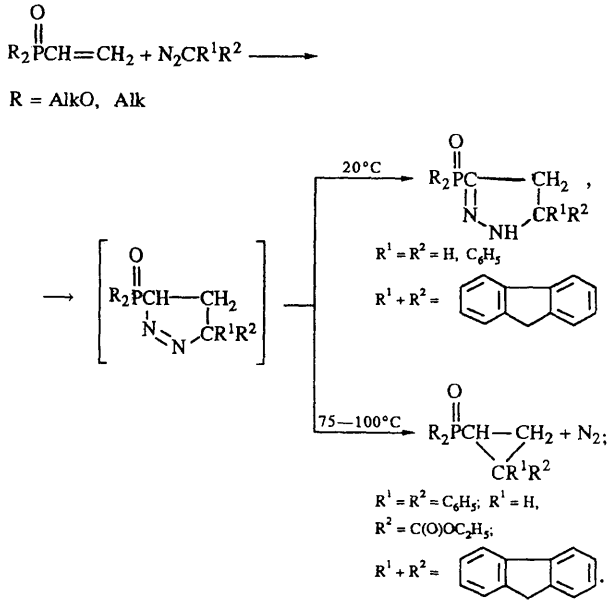
IV. Reactions of diazo-compounds and carbenes with phosphorus-containing systems having multiple bonds

1. Reactions involving the 1,3-dipolar cycloaddition of diazo-compounds and the cycloaddition of alkoxycarbonylcarbenes to phosphorus-containing systems with multiple bonds

A series of studies devoted to the comprehensive investigation of the reactions of aliphatic diazo-compounds and carbenes with unsaturated organophosphorus compounds has been carried out since the beginning of the 1960s by the Kazan School of organophosphorus chemists[148–157,159–161,169–180] and have been described in a review.[3] There exist also communications and reviews by foreign authors.[4,5,158,162–168,181–193]

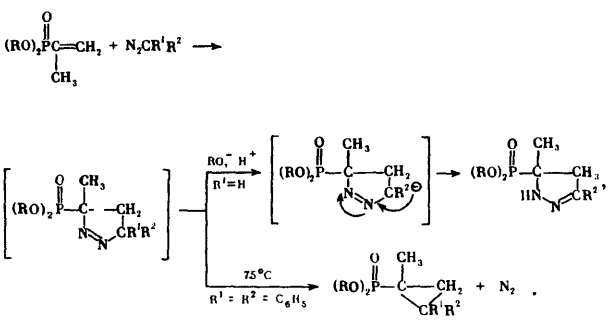
The study of the 1,3-dipolar cycloaddition reactions of diazo-compounds is of considerable interest not only for the elucidation of the reactivity of unsaturated organophosphorus compounds with which the mode of the reactions and the nature of the products formed are associated, but also as a possible way of synthesising five-membered heterocycles.

It has been shown that the 1,3-dipolar cycloaddition of diazomethane, diazoacetic ester, diphenyldiazomethane, and diazofluorene to dialkyl vinylphosphonates[148–153] and of diphenyldiazomethane to tertiary vinylphosphine oxides[154] proceeds via the intermediate formation of phosphorylated 3-Δ^1-pyrazolines, which, depending on the experimental conditions, either isomerise to phosphorylated 3-Δ^2-pyrazolines, or eliminate nitrogen and are converted into cyclopropane derivatives:



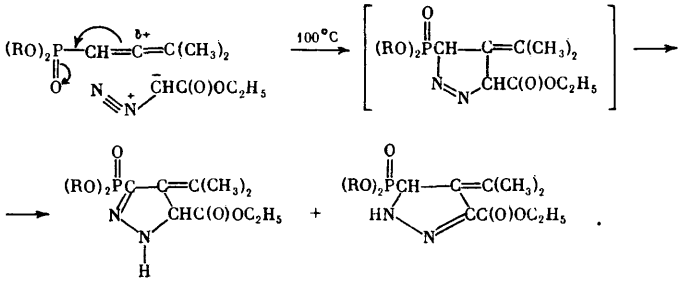
The reactions of diethyl allylphosphonate and diethylallylphosphine oxide with diazomethane and diphenyldiazomethane proceed similarly via the 1,3-dipolar cycloaddition mechanism.[148,154]

As a result of the 1,3-dipolar cycloaddition of diazo-compounds, dialkyl isopropenylphosphonates give rise to either phosphorylated 5-Δ^2-pyrazolines or to cyclopropane derivatives, depending on the experimental conditions:[155–157]



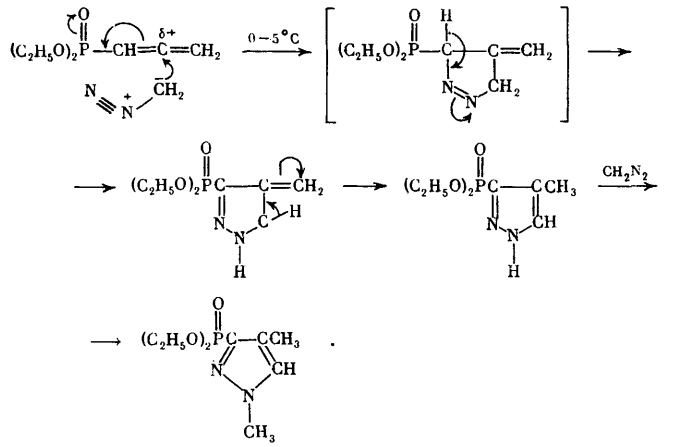
The addition of diazomethane to α-cyanovinylphosphonates takes place similarly with formation of phosphorylated 5-Δ^2-pyrazolines.[158]

The interaction of diazoalkanes with organophosphorus compounds containing cumulated or conjugated double bonds also proceeds via the mechanism involving 1,3-dipolar cycloaddition to the α,β-double bond. The reaction of γ,γ-dimethylallenylphosphonate with diazoacetic ester affords under these conditions a mixture of phosphorylated 3(5)-Δ^2-pyrazolines with exocyclic isopropenyl groups:[159]

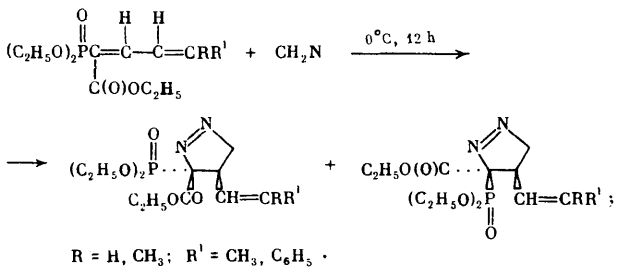


The cycloaddition of diphenyldiazomethane to allenylphosphonate takes place regiospecifically with the exclusive formation of 3-Δ^2-phosphorylated pyrazoline containing an exocyclic methylene group.[160]

In the case of the reaction with diazomethane, the analogous product, namely phosphorylated 3-Δ^2-pyrazoline, fully isomerises during distillation to 3-diethoxyphosphono-4-methylpyrazole. After *N*-methylation with diazomethane, 3-diethoxyphosphono-1,4-dimethylpyrazole was isolated:[161]

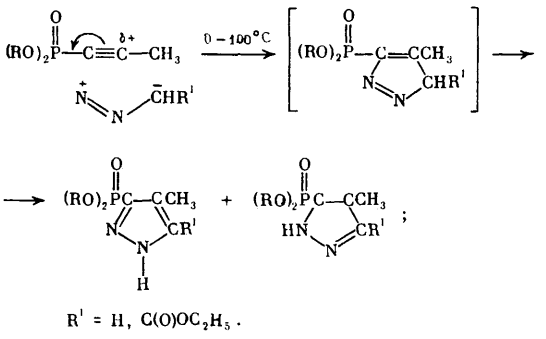


The cycloaddition of diazomethane to diethyl buta-1,3-dienylphosphonates proceeds with formation of a mixture of isomeric phosphorylated 3-Δ^2-pyrazolines, which are stable under the reaction conditions:[162]



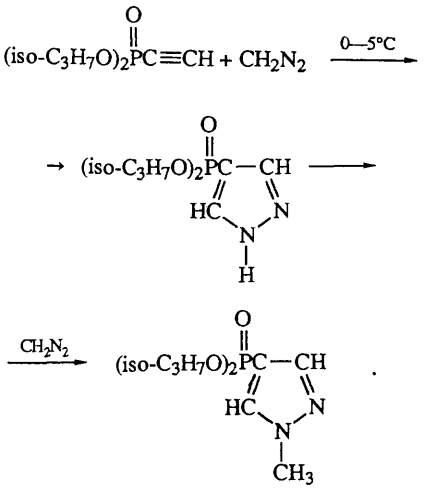
R = H, CH_3; R' = CH_3, C_6H_5.

The 1,3-dipolar cycloaddition of diazoacetic ester and diazomethane to the triple bond of dialkyl propynylphosphonates has been described.[159,161] A mixture of isomeric 3(5)-dialkoxyphosphono-5(3)-ethoxycarbonyl-4-methylpyrazoles was obtained as a result of the reaction:

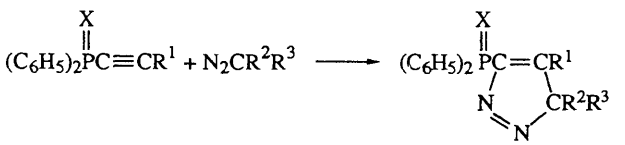


R' = H, $C(O)OC_2H_5$.

Diisopropyl ethynylphosphonate reacts with an excess of diazomethane to form diisopropyl 1-methylpyrazol-5-ylphosphonate only:[163]



The reactions involving the 1,3-dipolar cycloaddition of diazomethane, diazopropane, diphenyldiazomethane, and methylphenyldiazomethane to alkynyldiphenylphosphine oxides (sulphides) and alkynylbis(diphenylphosphine) oxides (sulphides) involve only the triple bond with formation of diphenyl [3*H*]-pyrazol-5-ylphosphonates and diphenyl [3*H*]-pyrazol-5-ylthiophosphonates:[4,164]

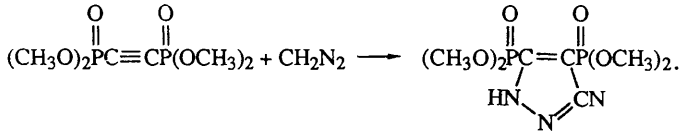


R^1 = H, CH_3, C_6H_5, $P(C_6H_5)_2$; R^2 = R^3 = H, CH_3, C_6H_5;

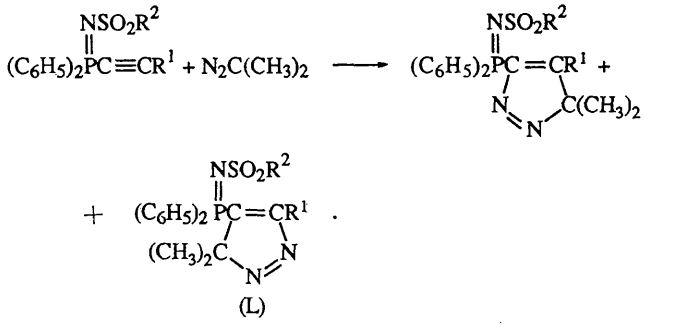
R^2 = CH_3, R^3 = C_6H_5;

X = O, S.

The reaction of tetramethyl acetylenebisphosphonate with diazomethane proceeds similarly:[165]

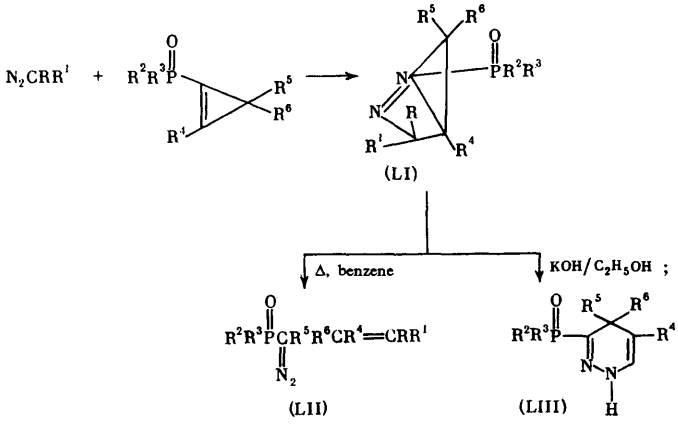


The reaction of *N*-[alkynyl(diphenyl)phosphorandiyl]sulphonamide with diazopropane either affords a mixture of isomeric 3*H*-pyrazoles (if R^1 = C_6H_5 and R^2 = CH_3, C_6H_5, *p*-$CH_3C_6H_4$, *p*-ClC_6H_4, or *p*-$NO_2C_6H_4$) or the cycloaddition takes place regiospecifically with the exclusive formation of the cyclic adduct (L) (if R^1 = H or CH_3 and R^2 = CH_3, C_6H_5, *p*-ClC_6H_4, *p*-FC_6H_4, or *p*-$CH_3C_6H_4$ [164]). The phosphimine bond remains unreactive:



(L)

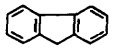
Regitz and co-workers[166,167] investigated the reactions involving the 1,3-dipolar cycloaddition of diazo-compounds to phosphorylated cyclopropenylphosphonates and cyclopropenylphosphine oxides. It was shown that the reactions proceed regiospecifically with formation of homopyrazolylphosphonates (LI), the cyclic adduct formed isomerising on heating either to allylphosphoryldiazomethane (LII) or to 3-phosphorylated 1,4-dihydropyridazine (LIII) in the presence of a strong base as the catalyst:



(LI)

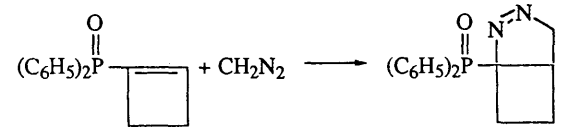
(LII) (LIII)

R = R' = H, CH_3, C_6H_5; R = H, R' = $C(O)OC_2H_5$, C_6H_5;

R + R' =  ; R^2 = R^3 = CH_3O, C_6H_5;

R^4 = H, CH_3, C_6H_5, $P(O)(C_6H_5)_2$; R^5 = H, CH_3, C_6H_5;
R^6 = CH_3, $C(CH_3)_3$.

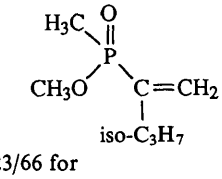
1-Cyclobutenyldiphenylphosphine oxide reacts with diazomethane to form Δ^1-pyrazolinylphosphine oxide:[168]



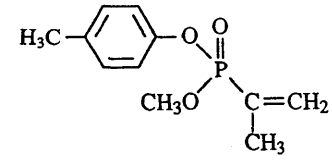
The 1,3-dipolar cycloaddition mechanism is a single-stage many-centre process with cyclic electron transfer as was confirmed in a study of the kinetics of the cycloaddition of diazoacetic ester to allenylphosphonates and allenylphosphine oxides[169] and of diphenyldiazomethane to vinylphosphonates and vinylphosphine oxides.[170,171]

The mutual orientation of the 1,3-dipole and of the dipolarophile in the transition state constitutes an important condition for reactions involving the 1,3-dipolar cycloaddition of diazoalkanes to phosphorus-containing dipolarophiles with a chiral phosphorus atom, which proceeds via a many-centre synchronous mechanism. The stereochemistry of such reactions has been investigated in relation to vinylphosphonates and vinylphosphinates and their α,β-substituted derivatives,[172–176] as well as allenyl- and ethynylphosphonates.[177]

It was shown that the stereospecificity of the reactions, determined by the diastereoisomeric composition of the isomers of 3-phosphorylated Δ^1-pyrazolines (the *threo*/*erythro* percentage ratio) depends both on the immediate steric environment of the chiral centre and on the effective volume of the substituents at the double bond. The approach of the diazoalkane molecule from the less hindered side determines the preferential formation of the *threo*-diastereoisomer, while its approach from the opposite side gives rise to the preferential formation of the *erythro*-diastereoisomer. For example, the ratio of the *threo*- and *erythro*-diastereoisomers varies from 90/10 for

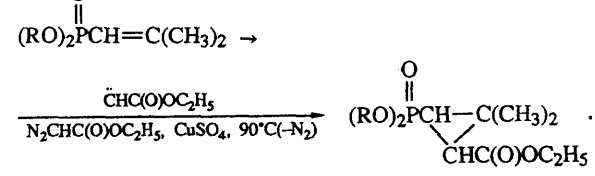


to 23/66 for



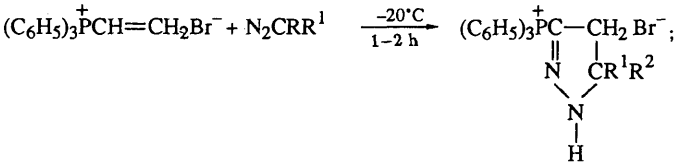
Ref. 172.

The reactions involving the cycloaddition of alkoxycarbonylcarbenes to vinyl- and allyl-phosphonic and vinylphosphoric esters proceed via the carbene mechanism with formation of cyclopropane derivatives. The direct dependence of the reactivity on the nucleophilicity of the double bond has been established:[148,151,178,179,180]



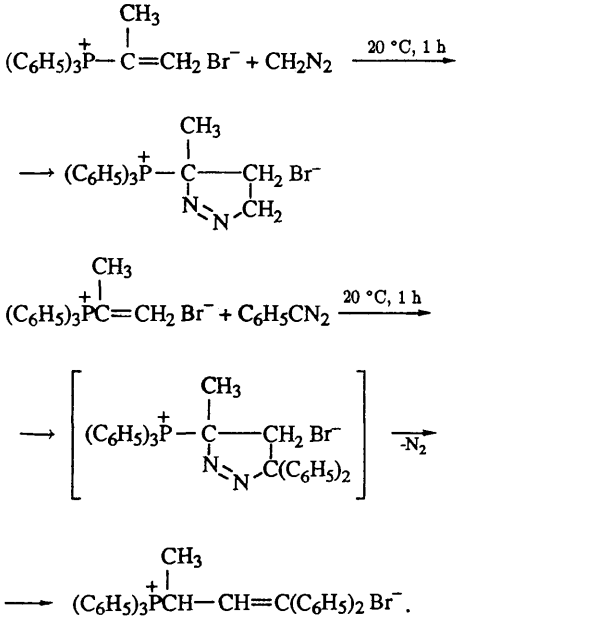
The reactions of phosphonium salts containing multiple bonds with diazo-compounds also involve 1,3-dipolar cycloaddition. It has been shown[5,168,181–183] that the final result of the reaction depends on the structure of the phosphonium salt and the diazo-compound.

Triphenylvinylphosphonium bromide gives rise to triphenyl-3-Δ^2-pyrazolinylphosphonium bromide:[181,182]



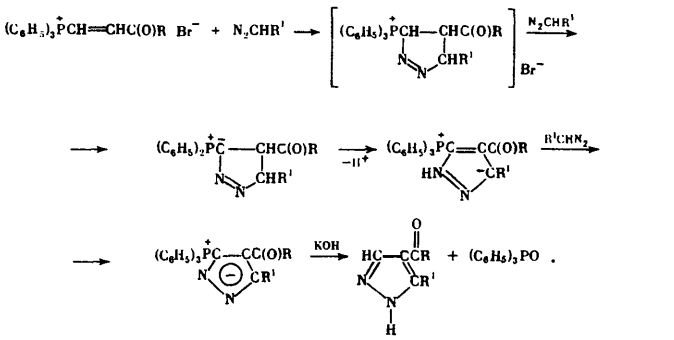
$R = R^1 = H,\ CH_3,\ C_6H_5;\ R = H,\ R^1 = CH_3,\ C_6H_5.$

Isopropenyltriphenylphosphonium bromide reacts with diazomethane to form triphenyl-5-Δ^1-pyrazolinylphosphonium bromide, while in the reaction with diphenyldiazomethane under the same conditions the analogous reaction products proved to be unstable, substituted allyltriphenylphosphonium bromide being formed after the evolution of nitrogen:[182]

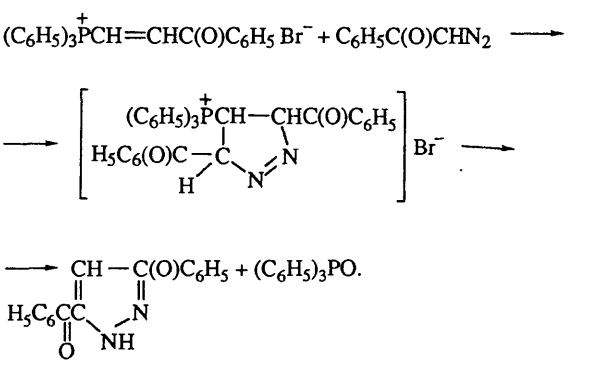


It is of interest that β-substituted triphenylvinylphosphonium and allyltriphenylphosphonium bromides do not react with diazoalkanes.[182] On the other hand, the introduction of an acyl group into the triphenylvinylphosphonium bromide alters its reactivity.

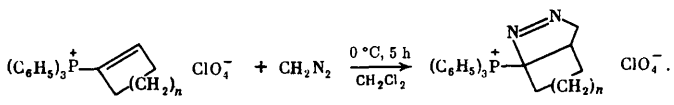
Although the cycloaddition of diazomethane and diazoacetic ester to β-acylvinyltriphenylphosphonium bromide does in fact proceed via the stage involving the formation of the intermediate triphenyl-5-Δ^1-pyrazolinylphosphonium salt, the reaction product isolated was the phosphorus-containing ylide (LIV), which is converted into 4-acylpyrazole on alkaline hydrolysis:[183]



After the reaction of β-acylvinyltriphenylphosphonium bromide with diazoacetophenone, 3,5-diacylpyrazole was isolated:[183]



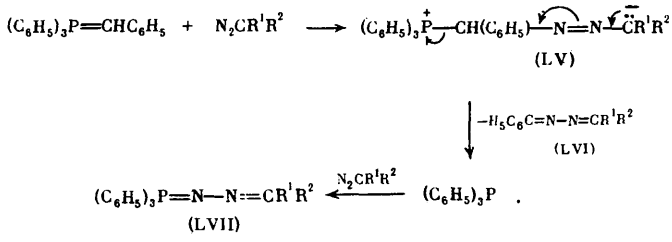
The 1,3-dipolar cycloaddition of diazomethane to 1-cycloalkenylphosphonium salts takes place with formation of bicyclic adducts:[168]



2. Phosphorus-containing ylids in reactions with diazo-compounds and carbenes

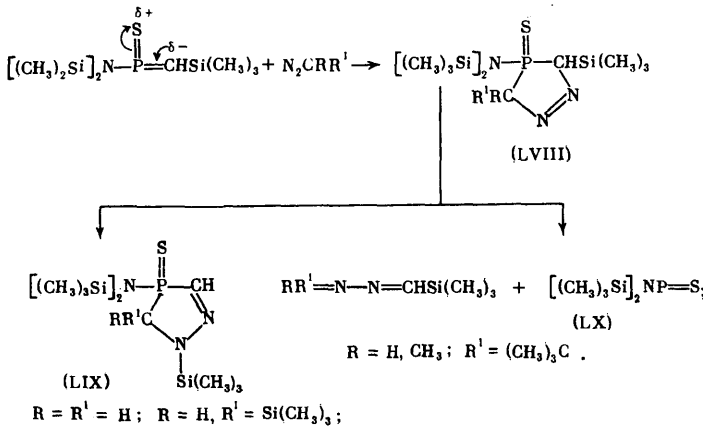
Phosphorus-containing ylids react unambiguously with diazo-compounds depending on the structure of the ylid and the reaction conditions. It has been shown[185,185] that the reaction of benzylidenetriphenylphosphorane with diazoacetophenone and phenyldiazomethane proceeds readily at room temperature with formation of a mixture of the azine (LVI) and triphenylphosphazine (LVII). It is assumed that the reaction proceeds via the intermediate formation of the betaine (LV), its decomposition to the

azine (LVI) and triphenylphosphine, and subsequent interaction of triphenylphosphine with the diazo-compound:

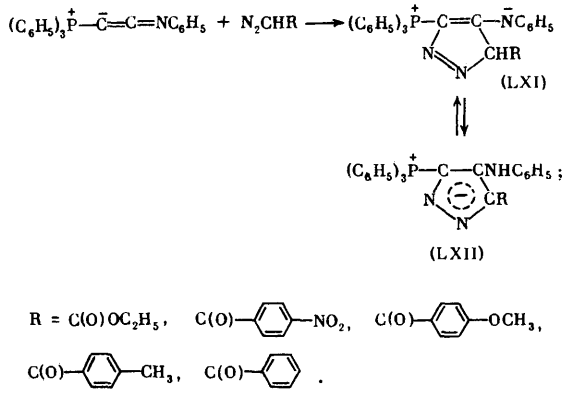


A much more complex reaction occurs between benzoylmethylenetriphenylphosphorane and diazoacetophenone; it leads to 4-benzylidene-2,6-diphenylpyran.[186,187]

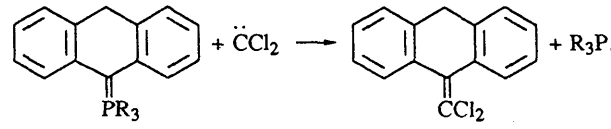
Silylated aminothionophosphorane reacts differently with diazoalkanes. The 1,3-dipolar cycloaddition to the P=C double bond lead to the formation of 3-trimethylsilysl-Δ^1-diazophospholene (LVIII), which either isomerises to 1-trimethylsilyl-Δ^2-diazaphospholene (LIX) as a result of the migration of the trimethylsilyl group or it decomposes to an azine and bis(trimethylsilyl)aminothionophosphorane (LX):[188]



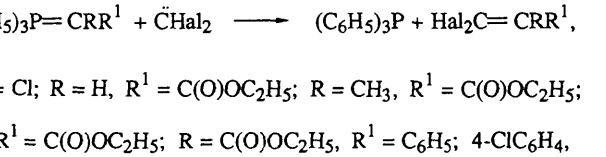
The reaction of *N*-phenylaminoketenylidenetriphenylphosphorane with diazocarbonyl compounds proceeds as 1,3-dipolar cycloaddition with formation of a phosphorylated pyrazoline derivative (LXI), which is involved in a tautomeric equilibrium with the phosphorylated imidopyrazole (LXII):[189]



The interaction of phosphorus-containing ylids with dihalocarbenes proceeds in most cases with formation of the corresponding olefins and phosphines and is believed to occur as a result of the electrophilic attack by the dihalocarbene on the negatively charged carbon atom of the phosphorus ylid.[190–192] The reactions of fluorenylidenetriphenyl(butyl)phosphorane and phosphorus-containing ylids having different electron-accepting groups proceed via the same mechanism:[190–192]



$R = C_6H_5$, C_4H_9;



Hal = Cl; R = H, $R^1 = C(O)OC_2H_5$; $R = CH_3$, $R^1 = C(O)OC_2H_5$;

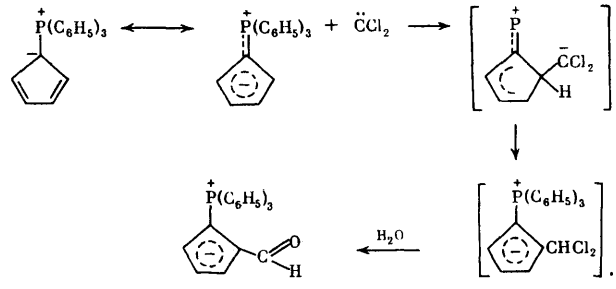
$R = R^1 = C(O)OC_2H_5$; $R = C(O)OC_2H_5$, $R^1 = C_6H_5$; 4-ClC_6H_4,

4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$;

Hal = F; R = H, $R^1 = C_3H_7$, C_6H_{13}, $C_{11}H_{23}$; $R = CH_3$, $R^1 = C_2H_5$;

$R = R^1 = CH_3$; $R + R^1 = (CH_2)_4$, $(CH_2)_5$.

Cyclopentadienylidenetriphenylphosphorane reacts differently with dichlorocarbene, generated from chloroform and potassium t-butoxide at 0 °C; it gives rise to a monoformyl derivative — triphenylphosphonium 2-formylcyclopentadienylide:[193]

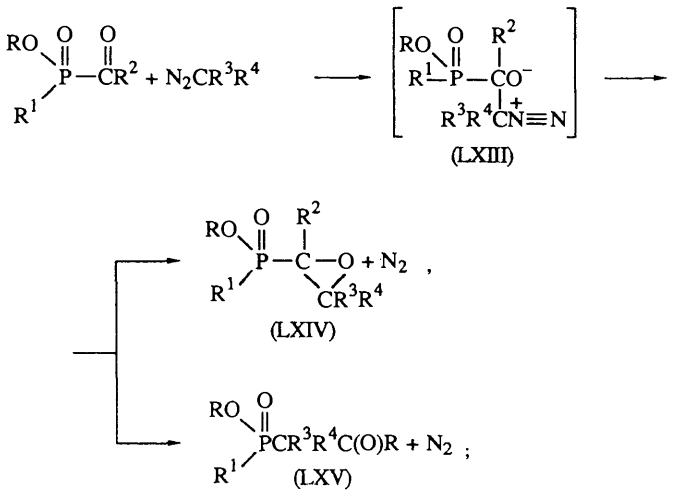


3. Reactions of diazoalkanes with ketophosphoryl compounds and phosphoryl isothiocyanates

The available literature data on the reactivities of organophosphorus compounds containing a carbonyl group with aliphatic diazo-compounds are restricted mainly to those obtained in the studies by Pudovik and co-workers.[194,197–199,202–204] Since the results of these studies have been described in detail in a review[6] and in a review report,[200] we shall confine ourselves to their brief consideration only.

The authors showed that, depending on the nature of the substituent at the carbonyl group and of the diazo-compound, the interaction of α-ketophosphonates and α-ketophosphinates with diazo-compounds proceeds with formation of either phosphorylated

oxiran derivatives (LXIV) or β-ketophosphonates and β-ketophosphinates—the products of insertion in the P—C bond of the initial organophosphorus compound (LXV):[194–200]

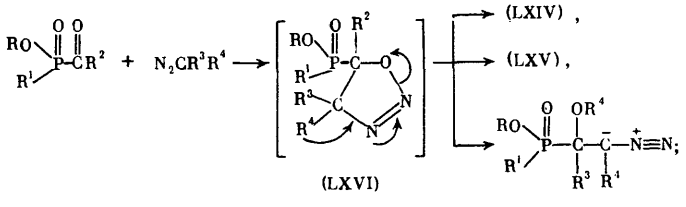


R = Alk; R^1 = AlkO, Alk, C_6H_5; R^2 = CH_3, C_6H_5, X = C_6H_4;

R^3 = R^4 = H, C_6H_5; R^3 = H, R^4 = CH_3.

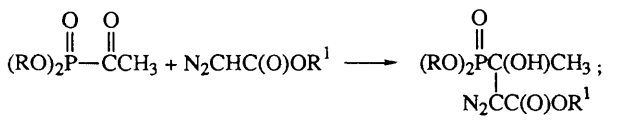
The formation of the reaction products (LXIV) and (LXV) is explained, in conformity with the generally accepted mechanism of the reactions of diazoalkanes with carbonyl compounds,[201] by the stabilisation of the intermediate dipolar ion (LXIII).

However, Pudovik et al.[194] do not exclude also the 1,3-dipolar cycloaddition mechanism with formation of the intermediate 1,2,3-oxadiazoline derivative (LXVI), which, depending on the substitution at the C(4) ring atom, either decomposes with evolution of nitrogen and the formation of the products (LXIV) and (LXV) or isomerises with formation of the phosphorus-containing diazo-compound (LXVII):



R = Alk; R^1 = AlkO, Alk, C_6H_5;
R^2 = CH_3, C_6H_5, X-C_6H_4;
R^3 = R^4 = H, C_6H_5; R^3 = H, R^4 = CH_3.

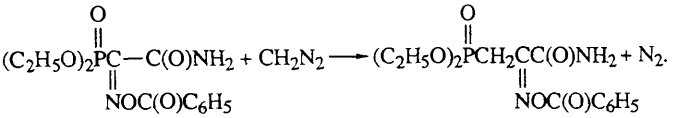
It is of interest that an adduct, similar to compound (LXVII), was obtained by the reaction of diazoacetic esters with acetylphosphonates:



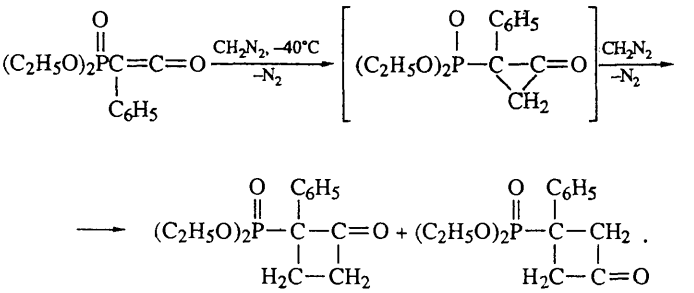
R = R^1 = CH_3, C_2H_5.

Neither the product with the oxiran structure (LXIV) nor the product (LXV) of insertion in the P—C bond were detected in the reaction mixture.[202–204]

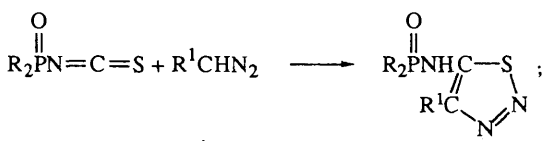
Similarly to the reaction with α-ketophosphoryl compounds, the reaction of acyloxyiminoalkylphosphonate with diazomethane leads to the product of the insertion of the methylene group in the P—C bond:[205]



The interaction of diethylphosphonophenylketene, which is an extremely reactive compound, with an excess of diazomethane involves not the carbonyl group but the C=C double bond and proceeds via the formation of the reactive phosphorylated cyclopropanone and leads to a mixture of isomeric phosphorylated cyclobutanes:[206]



One study is described in the literature,[207] where it was shown that phosphorylated isothiocyanates enter into reactions involving the 1,3-dipolar cycloaddition of diazomethane and phenyldiazomethane with formation of the corresponding 5-phosphinamido-1,2,3-thiadiazoles:



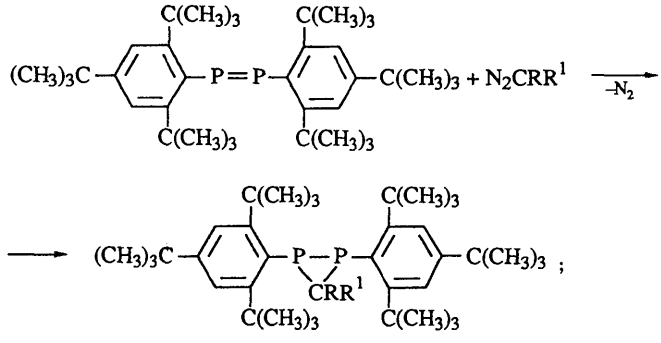
R = C_6H_5, CH_3; R^1 = H, C_6H_5.

V. Derivatives of di- and mono-coordinate phosphorus in reactions with diazo-compounds and carbenes

1. Reactions of diazo-compounds and carbenes with acyclic derivatives of dicoordinate and monocoordinate phosphorus

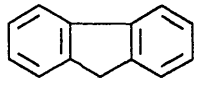
Acyclic derivatives of dicoordinate phosphorus containing the —P=P—, —P=C—, and —P=N— bonds have been investigated in reactions with diazo-compounds and carbenes.

The stable diphosphirans (LXVIII) have been obtained by cyclising a diphosphene, a derivative of dicoordinate phosphorus, with diazomethane at 0 °C [208] and with diphenyldiazomethane and diazofluorene on heating and UV irradiation:[209]



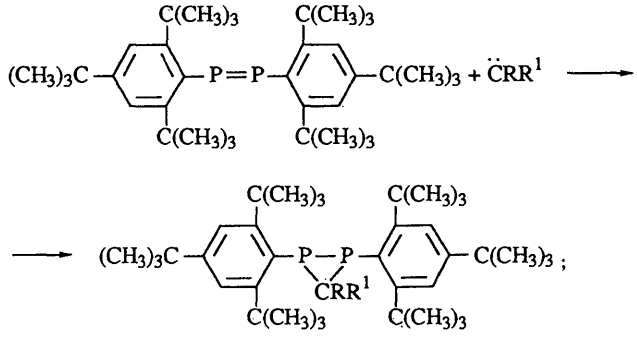
(LXVIII)

R = R^1 = H, C_6H_5; R + R^1 =



.

The hypothesis of the carbene mechanism of the formation of compound (LXVIII) under the conditions involving the generation of diphenyl- and fluorenylidene-carbenes (UV irradiation) was confirmed by the fact that the diphosphirans (LXIX) are formed from the diphosphene and dichloro-, dibromo-, and phenylbromocarbenes:[209]

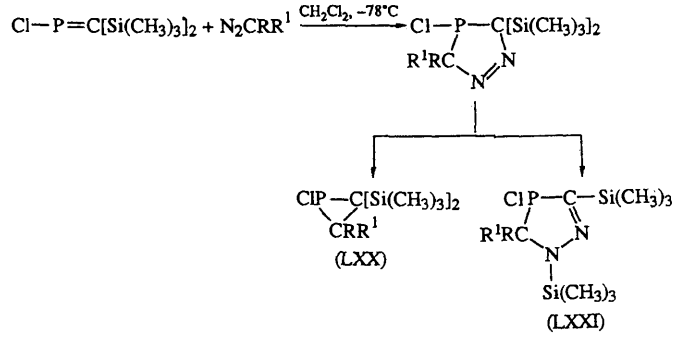


(LXIX)

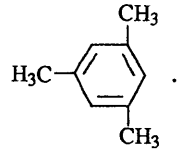
R = R^1 = Cl, Br; R = Br, R^1 = C_6H_5.

The interaction of *P*-chlorophosphaalkenes with diazocompounds, except organometallic derivatives of diazomethane, proceeds as 1,3-dipolar cycloaddition to the P=C double bond of the *P*-chlorophosphaalkene.[210–212] It was shown that the nature of the reaction product formed depends on the structure of the diazocompound and the *P*-chlorophosphaalkene.

Thus the reaction of 1-chloro-2-bis(trimethylsilyl)-1-phosphaalkenes with both mono- and di-substituted derivatives of diazomethane occurs even at a very low temperature with formation of unstable 3*H*-1,2,4-diazaphospholenes at room temperature, which either decompose with elimination of nitrogen and the formation of 1-chlorophosphirans (LXX) or are converted into 4,5-dihydro-1,2,4-diazaphospholenes (LXXI) as a result of the migration of the trimethylsilyl group:[212]

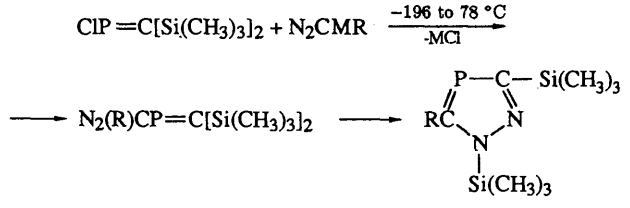


R = H, CH_3; R^1 = t-C_4H_9; R = H, R^1 = $Si(CH_3)_3$.



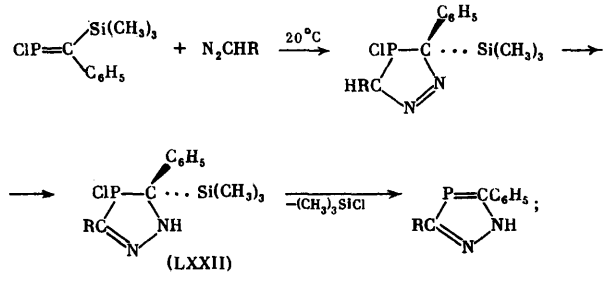
.

Organometallic derivatives of diazomethane react quite differently. The reaction proceeds with retention of the P=C bond of the initial 1-chloro-2-bis(trimethylsilyl)-1-phosphaalkene and the formation of phosphavinyldiazoalkane which cyclises to 1,2,4-diazaphosphole on subsequent heating:[213]



M = Li, $HgC(N_2)OC(O)C(CH_3)_3$; R = $Si(CH_3)_3$, 2, 4, 6-$(CH_3)_3C_6H_2$, $CH_3C(O)O$.

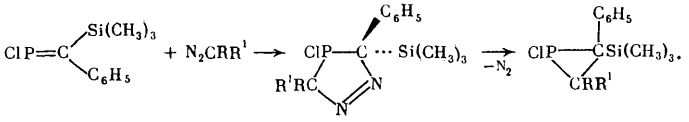
Monosubstituted derivatives of diazomethane react with 1-chloro-2-phenyl-2-trimethylsilyl-1-phosphaalkene at room temperature to form 1*H*-1,2,4-diazaphospholes via the intermediate cyclic adduct (LXXII) and subsequent elimination of chlorotrimethylsilane:[210]



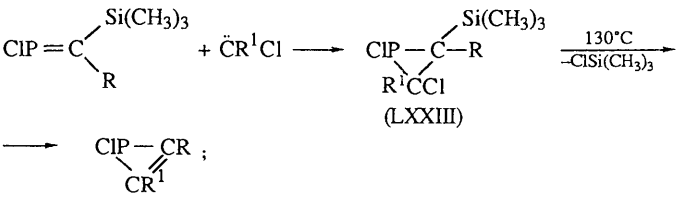
(LXXII)

R = H, C_6H_5, $C(O)OC_2H_5$, $C(O)C_6H_5$.

However, the reaction with disubstituted derivatives of diazomethane proceeds with the exclusive formation of 1-chlorophosphirans:[211]

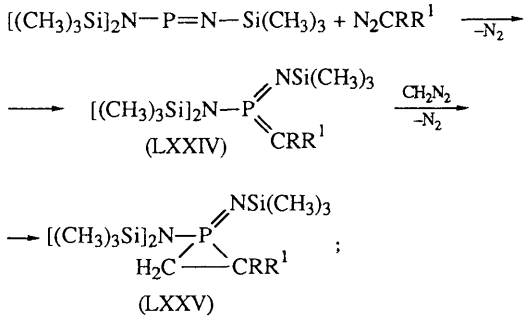


The reaction of *P*-chlorophosphaalkenes with chloro(phenyl)- and chloro(phenoxy)-carbenes has been described recently.[214] The analogous 1-chlorophosphirans (LXXIII) were obtained, their thermal decomposition resulting in the elimination of chlorotrimethylsilane and the formation of 1-chloro-1*H*-phosphirenes:



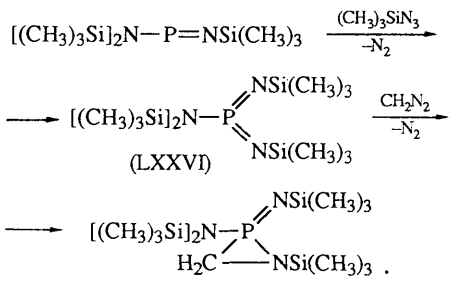
R = C_6H_5, $Si(CH_3)_3$; R^1 = C_6H_5, C_6H_5O.

In contrast to *P*-chlorophosphaalkenes, silylated amino-iminophosphanes react with diazo-compounds not via the 1,3-dipolar cycloaddition mechanism but with retention of the P=N bond and the formation of stable diylide structures. Thus the interaction of bis(trimethylsilyl)aminotrimethylsilyliminophosphane with diazoalkanes leads to the formation of bis(trimethylsilyl)aminotrimethylsilyliminophosphoranes (LXXIV), the subsequent reaction of which with diazomethane, proceeding as 1,2-cycloaddition, results in the formation of bis(trimethylsilyl)trimethylsilylimino-λ^5-phosphirans (LXXV):[215–217]

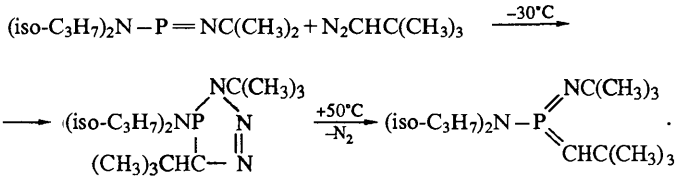


R = CH_3, H; R^1 = CH_3, C_2H_5, $CH(CH_3)_2$, $C(CH_3)_3$.

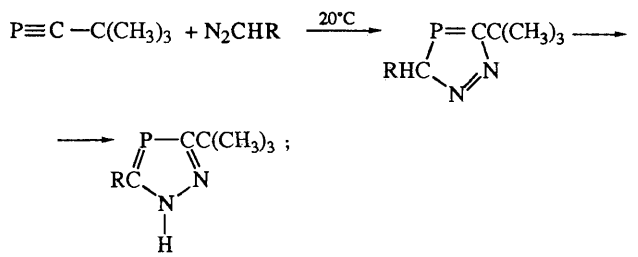
The 1,2-cycloaddition of diazomethane to one of the P=N bonds of aminodiiminophosphorane (LXXVI) leads to the formation of 1,2-λ^5-azaphosphoridine:[215]



An aminoiminophosphorane is also formed on interaction of t-butyliminodiisopropylaminophosphane with t-butyldiazopropane. It is suggested that the reaction proceeds as 1,3-dipolar cycloaddition to the P=N bond with formation of cyclic adducts and subsequent elimination of nitrogen on raising the temperature:[218]



The interaction of diazo-compounds with derivatives of monocoordinate phosphorus has been reported.[219] 1,3-Dipolar cycloaddition to a phosphaalkyne results in the formation of 1*H*-1,2,4-diazaphospholes:



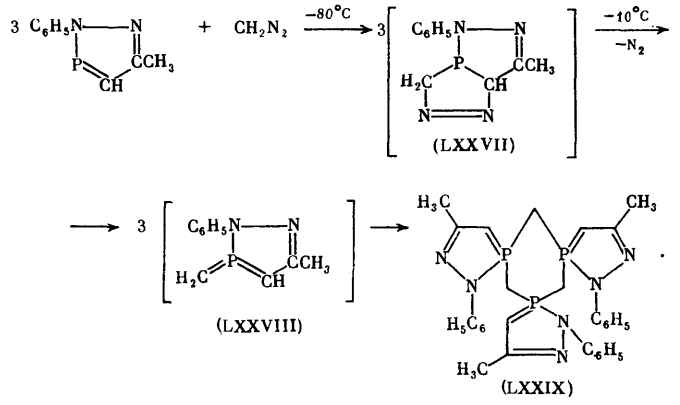
R = H, CH_3, t-C_4H_9, $C(O)C_6H_5$, $C(O)OCH_3$.

2. Reactions of diazo-compounds and carbenes with cyclic derivatives of dicoordinate phosphorus

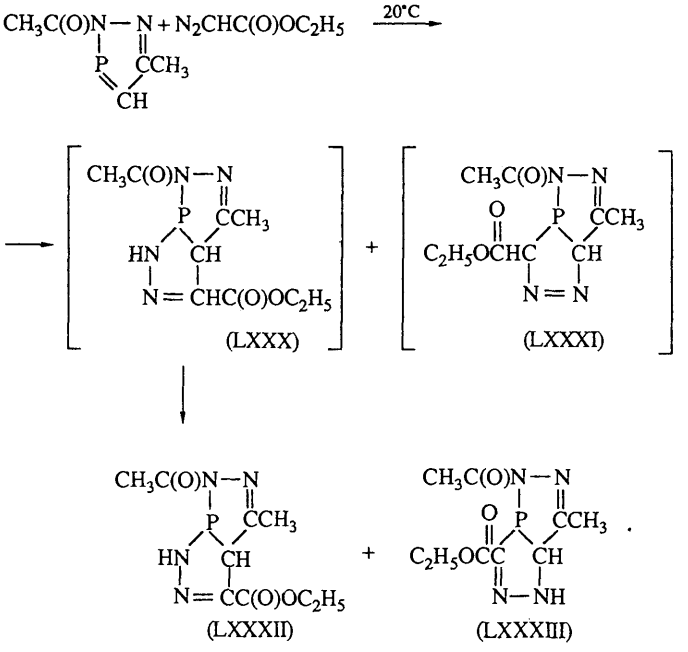
The reactions of five-membered cyclic derivatives of dicoordinate phosphorus with diazo-compounds have been investigated by Arbuzov and co-workers in relation to substituted 1,2,3-diazaphospholes. It was shown that the final reaction product depends to a considerable extent on the structures of both initial reactants and on the experimental conditions.[220–241]

Thus diazomethane readily reacts at room temperature with 5-methyl-2-phenyldiazaphosphole with evolution of nitrogen and the formation of an adduct having the structure of the trimer (LXXIX).[220]

It was later established[221] that this reaction proceeds via the formation of the unstable cyclic [2 + 3]adduct (LXXVII), having the pyrazoline structure, with subsequent elimination of nitrogen, the formation of the reactive phosphorus diylid (LXXVIII), and its subsequent trimerisation:

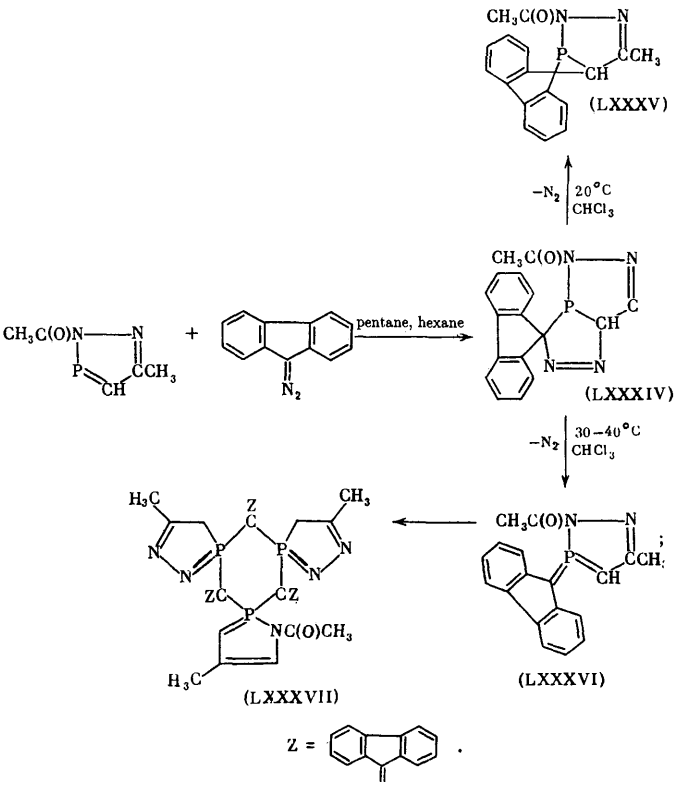


In contrast to the reaction with diazomethane, the reaction of 2-acetyl-5-methyl-1,2,3-diazaphosphole with diazoacetic ester proceeds via the 1,3-dipolar cycloaddition mechanism without the evolution of nitrogen, a mixture of compounds (LXXX) and (LXXXI) being formed, regardless of the nature of the solvent, and isomerising to the Δ^2-phosphapyrazoline derivatives (LXXXII) and (LXXXIII) respectively:[222]



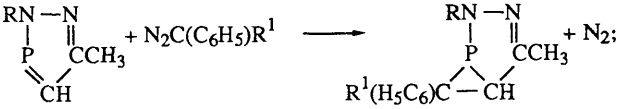
2-Acetyl-5-methyl-1,2,3-diazaphosphole reacts differently with diazoacetone depending on the experimental temperature.[221] At room temperature, the reaction proceeds with evolution of nitrogen and the formation of a trimer, whose structure is similar to that of compound (LXXIX). At 10 °C, the reaction takes place without the evolution of nitrogen and, as in the reaction with diazoacetic ester, a mixture of isomeric derivatives of Δ^2-phosphapyrazoline is formed.

The reactions of 2-acetyl-5-methyldiazaphosphole with 9-diazofluorene, proceeding via the 1,3-dipolar cycloaddition mechanism, proved to be of interest.[220,223] Thus at room temperature in pentane and hexane, the product is the Δ^1-phosphapyrazoline derivative (LXXXIV), which is converted in chloroform at room temperature into the bicyclic phosphiran (LXXXV), while at 30–40 °C it is converted into the trimer of the diazaphosphole ylid (LXXXVII) via a stage involving the formation of the diylid structure (LXXXVI):



The trimer (LXXXVII) is formed without the isolation of the bicyclic compound (LXXXIV) when the reaction is carried out in benzene, methylene chloride, and carbon tetrachloride. In diethyl ether, the reaction proceeds with formation of a mixture of the products (LXXXIV) and (LXXXVII).[220]

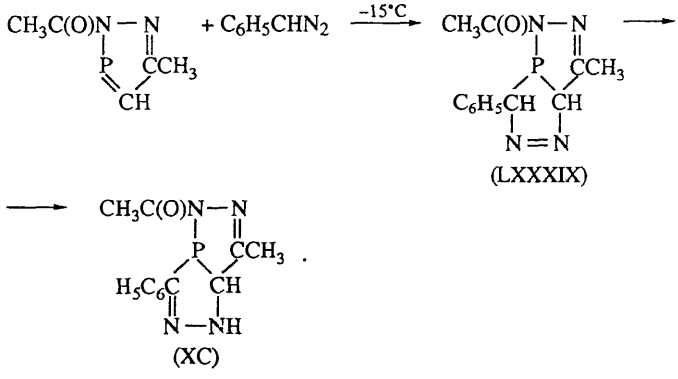
The possibility of cycloaddition to the P=C bond involving a dicoordinate phosphorus atom with formation of stable bicyclic phosphirans (LXXXVIII) was first demonstrated in relation to the reactions of *N*-substituted diazaphospholes with diphenyldiazomethane in different solvents[224–227] and later with methylphenyldiazomethane.[228] The structure of the bicyclic phosphirans was established by X-ray diffraction.[229–232]



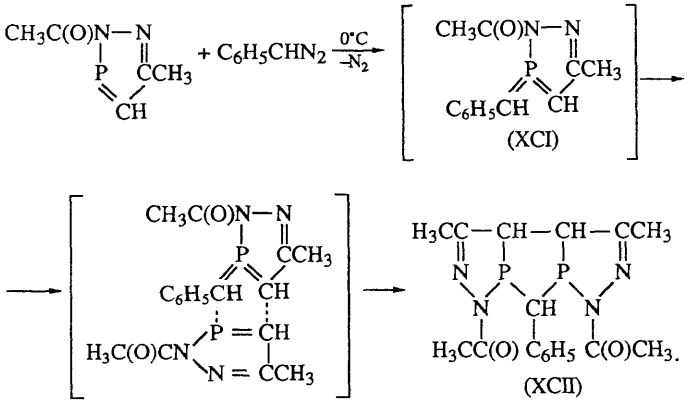
R = C_6H_5, $CH_3C(O)$; R^1 = C_6H_5, CH_3.

In the study of the mechanism of the reaction of 5-methyl-2-phenyl(acetyl)diazaphospholes with diphenyldiazomethane, it was shown that the reaction is of the non-carbene type and proceeds via the 1,3-dipolar cycloaddition mechanism.[233]

In contrast to diphenyldiazomethane, phenyldiazomethane does not give rise to a bicyclic phosphiran in its reaction with 2-acetyl-5-methyl-1,2,3-diazaphosphole. In hexane at −15 °C, the reaction product is the Δ^1-phosphapyrazoline derivative (LXXXIX), which isomerises to the Δ^2-phosphapyrazoline derivative (XC):[234]

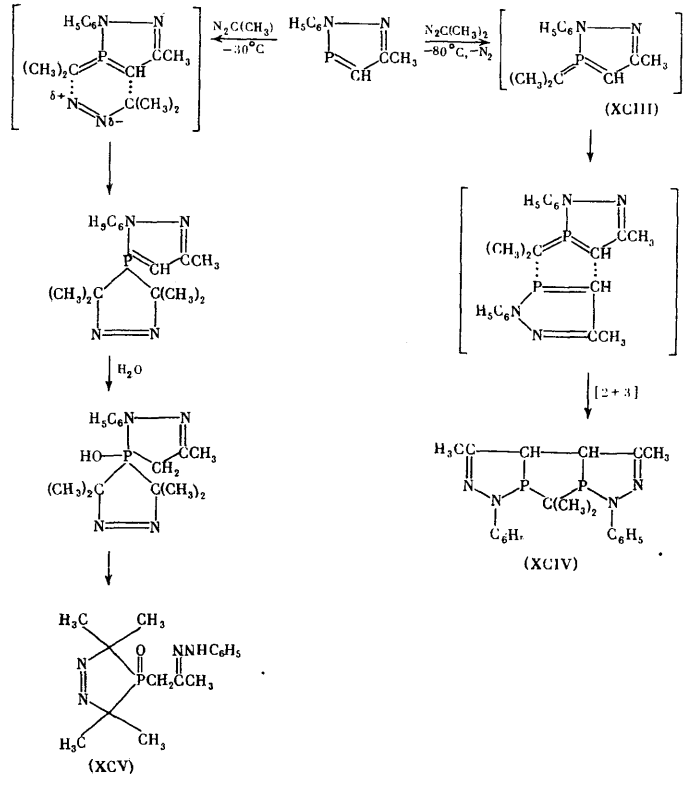


When the temperature is raised to 0 °C and the reactants are added in the opposite order, nitrogen is evolved and the tricyclic compound (XCII) is formed. It is the product of the cyclic [2 + 3]addition of the intermediate diylid (XCI) to the initial diazaphosphole:[234]



The reaction of 5-methyl-2-phenyl-1,2,3-diazaphosphole with diazopropane proceeds, in contrast to the reaction with diphenyldiazomethane, in a much more complex manner with formation of products of different structure as the experimental conditions are varied.[235–239] As in the reaction with phenyldiazomethane, bicyclic phosphirans were not obtained in any of the experiments.

It was established by X-ray diffraction that the reaction of 5-methyl-2-phenyl-1,2,3-diazaphosphole with diazopropane, which proceeds with evolution of nitrogen on intensive cooling, results in the formation of the diphosphorus tricyclic compound (XCIV), whose structure is similar to that of compound (XCII).[235–238] Compound (XCIV) is evidently formed as a result of the 1,3-dipolar cycloaddition of the intermediate reactive phosphorus diylid (XCIII), which behaves as the dipole:

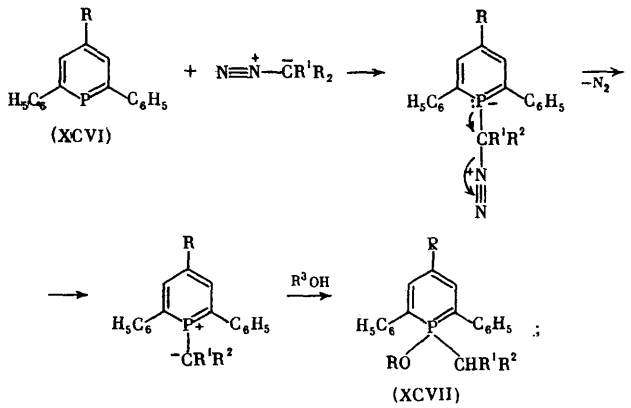


The reaction of 5-methyl-2-phenyl-1,2,3-diazaphosphole with an excess of diazopropane at −30 °C takes place differently and leads to the formation of the phosphorylated phenylhydrazone derivative (XCV), evidently as a result of the 1,3-dipolar cycloaddition of the intermediate phosphorus diylid, acting as the dipolarophile, to the diazopropane molecule.[237]

5-Methyl-2-phenyl-1,2,3-diazaphosphole reacts with 1-diazo-2-methylpropane and 1-diazo-2,2-dimethylpropane to form only a tricyclic diphosphorus compound, whose structure is analogous to that of compound (XCIV).[240]

The reaction of diazo-compounds and carbenes with a six-membered cyclic derivative of dicoordinate phosphorus, such as the trisubstituted phosphabenzene (XCVI), have also been investigated.[242–244] Thus treatment of 2,4,6-trisubstituted λ^3-phosphorins with alcoholic or phenolic solutions of diazo-compounds afforded 39 different derivatives of the λ^5-phosphorins (XCVII).[242,243] It is assumed that compounds (XCVII) are formed as a result of the nucleophilic attack by the diazo-compound on the phosphorus atom of the phosphabenzene with subsequent elimination of nitrogen and

the formation of a dipolar ion, which then reacts with the alcohol or the phenol:

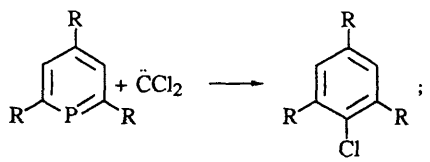


(XCVI) (XCVII)

R = C_6H_5, $C_6H_5CH_2$; $R^1 = R^2 = H$, C_6H_5; $R^1 = H$, $R^2 = C(O)OC_2H_5$;

$R^3 = CH_3$, C_2H_5, $CH(CH_3)_2$, C_6H_5, $C_6H_5CH_2$, $CH_2{=}CH{=}CH_2$, CH_2CH_2Cl, CH_2CCl_3.

The reactions of trisubstituted phosphabenzenes — 2,4,6-triphenyl- and 2,4,6-tributyl-phosphabenzenes — with dichlorocarbene, generated by the thermolysis of $Cl_3CC(O)ONa$ and $C_6H_5HgCCl_2Br$ or obtained from CH_2Cl_2 and $CHCl_3$ in the presence of t-C_4H_9OK, proceed in an unusual way. They result in the formation of trisubstituted benzenes:



R = C_6H_5, t-C_4H_9.

The reaction with chloro(phenyl)carbene, generated from dichloro(phenyl)methane and potassium t-butoxide, takes place similarly. The reaction mechanism has been discussed.[244]

Thus the study of the reactivities of various phosphorus-containing systems in relation to diazo-compounds and carbenes has led to interesting possibilities both for the synthetic organic chemistry of phosphorus and for the development of theoretical ideas in the chemistry of organophosphorus compounds and carbenes.

References

1. T A Mastryukova, M I Kabachnik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, (9) 2040–2061
2. B S Khaskin *Usp. Khim.*, 1984, **53**(8) 1325–1351 [English translation in *Russ. Chem. Rev.*, 1984(8)]
3. N G Khusainova, A N Pudovik *Usp. Khim.*, 1978, **47**(9) 1507–1527 [English translation in *Russ. Chem. Rev.*, 1978(9)]
4. G Guillerm, A L Honore, L Veniard, et al. *Bull. Soc. Chim. Fr.*, 1973, (10) 2739–2746
5. E Zbiral *Synthesis*, 1974, (10) 775–797
6. Yu A Zhdanov, L A Uzlova, Z I Glebova *Usp. Khim.*, 1980, **49**(9) 1730–1750 [English translation in *Russ. Chem. Rev.*, 1980(9)]
7. S Reichstein *Helv. Chim. Acta*, 1940, **23** 669
8. F R Atherton, H T Howard, A R Todd *J. Chem. Soc.*, 1948, (8) 1106–1111
9. D A March, J G Turcotte *ACS Symp. Ser.*, 1981, **171** 195–198
10. M I Kabachnik, A E Shipov, T A Mastryukova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1960, (1) 146
11. L D Anin, M R Dysart *J. Org. Chem.*, 1962, **27**(3) 1012–1014
12. A N Pudovik, R D Gareev *Zh. Obshch. Khim.*, 1964, **34**(12) 3942–3946
13. B A Arbuzov, A O Vizel' *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1963, (4) 749–750
14. G M Steinberg, C N Lieske, A B Ash, P Blumbergs, US P. 3 729 558, 1973
15. M Hoffman, Polish P. 93 173, 1977
16. M Hoffman, C Wasielewski *Rocz. Chem.*, 1976, **50**(1) 139–146
17. M Hoffman *Pol. J. Chem.*, 1979, **53**(12) 2639–2641
18. M Hoffman *Pol. J. Chem.*, 1982, **56**(9) 1191–1194
19. J S Loran, R A Naylor, A Williams *J. Chem. Soc., Perkin Trans. II*, 1976, (12) 1444–1447
20. M H Akhtar *J. Agric. Food Chem.*, 1982, **30**(6) 1048–1050
21. T A Mastryukova *Phosphorus Sulfur*, 1976, **1**(2–3), 211–229
22. T A Mastryukova, M Orlov, L S Butorina, et al. *Zh. Obshch. Khim.*, 1974, **44**(5) 1001–1011
23. M Orlov, T B Sakharova, L S Butorina, et al. *Khimiya i Primenenie Fosfororganicheskikh Soedinenii. Trudy V Konferentsii, Moskva* (The Chemistry and Applications of Organophosphorus Compounds. Proceedings of the Vth Conference, Moscow), Nauka, Moscow, 1974, pp 358–363
24. T A Mastryukova, R M Kalyanova, T K Genkina, et al. *Zh. Obshch. Khim.*, 1977, **47**(12) 2723–2730
25. T A Mastryukova, J Michalski, A B Uryupin, et al. *Zh. Obshch. Khim.*, 1978, **48**(2) 463
26. T A Mastryukova, M Orlov, D Eremich, M I Kabachnik *Zh. Obshch. Khim.*, 1974, **44**(11) 2403–2408
27. T A Mastryukova, A B Uryupin, M I Kabachnik *Zh. Obshch. Khim.*, 1978, **10** 2174–2179
28. T A Mastryukova, A B Uryupin, M I Kabachnik, et al. *Croat. Chem. Acta*, 1982, **55**(4) 413–427
29. T A Mastryukova, J Michalski, A B Uryupin, et al. *Zh. Obshch. Khim.*, 1978, **48**(7) 1447–1455
30. T A Mastryukova, L S Butorina, V I Kushnir, M I Kabachnik *Zh. Obshch. Khim.*, 1977, **47**(5) 981–989
31. T A Mastryukova, L S Butorina, E I Matrosov, M I Kabachnik *Zh. Obshch. Khim.*, 1977, **47**(4) 748–756
32. T A Mastryukova, L S Butorina, M I Kabachnik *Zh. Obshch. Khim.*, 1973, **43**(9) 2083–2084
33. T A Mastryukova, A B Uryupin, M Orlov *Zh. Obshch. Khim.*, 1981, **51**(7) 1475–1477
34. T A Mastryukova *Izv. Khim. B'lg. Akad. Nauk*, 1978, **10**(4) 471–490
35. T A Mastryukova, L S Butorina, A B Uryupin, et al. *Zh. Obshch. Khim.*, 1978, **48**(2) 257–263
36. V V Ovchinnikov, V I Galkin, R A Cherkasov, A N Pudovik *Dokl. Akad. Nauk SSSR*, 1976, **229**(6) 1386–1388
37. V V Ovchinnikov, R A Cherkasov, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, (4) 934–935
38. V V Ovchinnikov, V I Galkin, E G Yarkova, et al. *Dokl. Akad. Nauk SSSR*, 1977, **235**(1) 118–120

39. A S Ishmuratov, Candidate's Thesis in Chemical Sciences, All-Union Institute of Chemical Plant Protecting Agents, Moscow, 1989, pp 56–67
40. B A Khaskin, A S Ishmuratov, N A Torgasheva, T I Koroleva *Sovershenstvovanie Pestitsidnykh Preparatov. Sbornik Nauchnykh Trudov* (Improvement of Pesticidal Preparations. Collected Scientific Reports), Izd. VNIIKhSZR, Moscow, 1987, pp 35–40
41. B A Khaskin, O D Sheluchenko, N A Torgasheva, et al., USSR P. 944314; *Byull. Izobret.*, 1991, (7)
42. B A Khaskin, N A Torgasheva, O D Molodova *Zh. Obshch. Khim.* (in the Press).
43. P S Skell, A Y Garner *J. Am. Chem. Soc.*, 1956, **78**(20) 5430–5433
44. J Hine, A M Dowell *J. Am. Chem. Soc.*, 1954, **76**(10) 2688–2692
45. W E Doering, W A Henderson, *J. Am. Chem. Soc.*, 1958, **80**(19) 5274–5277
46. W E Doering, K Hoffmann *J. Am. Chem. Soc.*, 1954, **76**(23) 6162–6165
47. L Almasi, I Fenesan, V Biro *J. Prakt. Chem.*, 1979, **321**(6) 913–920
48. A Schmidpeter, H Groeger *Z. Anorg. Allg. Chem.*, 1966, **345**(1) 106–118
49. A Schmidpeter, H Brecht, J Ebeling *Chem. Ber.*, 1968, **101**(11) 3902–3912
50. J Bödeker *Organomet. Chem.*, 1973, **56**(2) 255–260
51. L Almasi, A Hant *Rev. Roum. Chim.*, 1964, **9**(6–7) 433–440
52. L Almasi, R Popescu *Chem. Ber.*, 1975, **108**(3) 856–861
53. L Almasi, L Paskucz *Chem. Ber.*, 1966, **99**(10) 3293–3297
54. A Schmidpeter, H Groeger *Chem. Ber.*, 1967, **100**(9) 3052–3062
55. O O Orazi, R A Corral, H Schuttenberg *J. Chem. Soc., Perkin Trans. 1*, 1974, (18) 2087–2091
56. L Almasi, L Paskucz *Chem. Ber.*, 1970, **103**(9) 2972–2975
57. B A Khaskin, N A Tomacheva, O D Sheluchenko, V K Promonenkov, USSR P. 717059; *Byull. Izobret.*, 1980, (7)
58. B A Khaskin, O D Sheluchenko, N A Torgasheva, V K Promonenkov *Zh. Obshch. Khim.*, 1980, **50**(9) 1990–1994
59. B A Khaskin, O D Sheluchenko, N A Torgasheva, et al. *Zh. Obshch. Khim.*, 1980, **50**(11) 2629–2630
60. B A Khaskin, O D Sheluchenko, N A Torgasheva, *Zh. Obshch. Khim.*, 1982, **52**(3) 597–601
61. B A Khaskin, N A Torgasheva, O D Sheluchenko, A S Ishmuratov *Zh. Obshch. Khim.*, 1988, **58**(5) 1041–1046
62. B A Khaskin, O D Sheluchenko, N A Torgasheva *Zh. Obshch. Khim.*, 1983, **53**(4) 780–784
63. N A Torgasheva, B A Khaskin, A S Ishmuratov *Zh. Obshch. Khim.*, 1991, **61**(6) 1325–1328
64. B A Khaskin, N A Tolmacheva, T I Koroleva, V V Negrebetskii *Zh. Obshch. Khim.*, 1980, **50**(11) 1781–1784
65. B A Khaskin, N A Tolmacheva, T I Koroleva *Zh. Obshch. Khim.*, 1983, **53**(6) 1219–1222
66. B A Khaskin, N A Tolmacheva, T I Koroleva, V K Promonenkov *Zh. Obshch. Khim.*, 1980, **50**(10) 2233–2235
67. B A Khaskin, O D Sheluchenko, N A Torgasheva, N A Tolmacheva *Trudy VII Vsesoyuznoi Konferentsii po Khimii FOS* (Proceedings of the VIIth All-Union Conference on the Chemistry of Organophosphorus Compounds), Nauka, Moscow, 1982, p. 56
68. B A Khaskin, O D Sheluchenko, N A Torgasheva *Trudy IV Vsesoyuznoi Konferentsii po Khimii Karbenov* (Proceedings of the IVth All-Union Conference on the Chemistry of Carbenes), Nauka, Moscow, 1987, pp 76, 77
69. B A Khaskin, N A Torgasheva, A S Ishmurata *XI International Conference on Phosphorus Chemistry*, Tallin, 1989, p. 39
70. L Field, C J Banks *J. Org. Chem.*, 1975, **40**(19) 2774–2779
71. W Ando, T Yagihara, S Tozune, et al. *J. Org. Chem.*, 1972, **37**(11) 1721–1727
72. T Miyamoto, J Yamamoto *Nippon Noyaku Gakkaishi*, 1977, **2**, 303
73. T Miyamoto, J Yamamoto *Agric. Biol. Chem.*, 1980, **44**(11) 2581–2586
74. M Toru, Y Izuru *J. Pesticide Science*, 1977, (3) 303–310
75. J Michalski, J Wasiak *J. Chem. Soc.*, 1962, (12) 5056–5061
76. B A Khaskin, N N Mel'nikov, N A Torgasheva *Zh. Obshch. Khim.*, 1973, **43**(9) 1916–1918
77. K A Petrov, A A Neimysheva *Zh. Obshch. Khim.*, 1959, **29**(9) 3030–3032
78. L Almasi, L Paskucz *Chem. Ber.*, 1965, **98**(2) 613–616
79. N A Torgasheva, A S Ishmuratov, B A Khaskin *Zh. Obshch. Khim.*, 1989, **59**(4) 956–958
80. B A Khaskin, A S Ishmuratov, N A Torgasheva *Zh. Obshch. Khim.*, 1991, **61**(5) 1095–1100
81. B A Khaskin, A S Ishmuratov, N A Torgasheva *Zh. Obshch. Khim.*, 1991, **61**(5) 1090–1095
82. A Ya Yakubovich, V A Ginzburg *Zh. Obshch. Khim.*, 1952, **22**(9) 1534–1542
83. L M Yagupol'skii, P A Yufa *Zh. Obshch. Khim.*, 1958, **28**(10) 2853–2856
84. H Staudinger, J Meyer, *Helv. Chim. Acta*, 1919, **2** 619–635; H Staudinger, E Hauser, 1921, **4** 861–886; H Staudinger, G Lüscher, 1922, **5** 75–86
85. H Bestmann, H Buckschewski, H Leube *Chem. Ber.*, 1959, **92**(6) 1345–1354
86. G Märkl *Tetrahedron Lett.*, 1961, **22** 811–813
87. F Weygand, H Bestmann *Angew. Chem.*, 1960, **72**(16) 535–554
88. M Regitz *Chem. Ber.*, 1966, **99**(10) 3128–3147
89. A Schönberg, K Brosowski *Chem. Ber.*, 1959, **92**(10) 2602–2605
90. G Wittig, K Schwarzenbach *Ann. Chem.*, 1961, **650** 1–20
91. D E Worrall *J. Am. Chem. Soc.*, 1930, **52**(5) 2933–2937
92. I G Cadogan, A G Rowley, N H Wilson *Ann. Chem.*, 1978, **1** 74–77
93. J C Fleming, H Shechter *J. Org. Chem.*, 1969, **34**(12) 3962–3969
94. T Severin, H Pehr *Chem. Ber.*, 1979, **112**(11) 3559–3565
95. H Bestmann, L Gothlich *Ann. Chem.*, 1962, **655** 1–19
96. M Regitz, A Liedhegener *Tetrahedron*, 1967, **23**(6) 2701–2708
97. H Goetz, H Juds *Ann. Chem.*, 1964, **678** 1–9
98. D Bethell, S F Dunn, M M Khodaei, A K Newall *J. Chem. Soc., Perkin Trans. 2*, 1989, (11) 1829–1834
99. I F Lutsenko, M V Proskurina, N B Karlstedt *Zh. Obshch. Khim.*, 1978, **48**(4) 765–767
100. O I Kolodyazhnyi *Zh. Obshch. Khim.*, 1976, **46**(9) 2386–2387
101. O Dick, K F Gerrit *Tetrahedron Lett.*, 1989, **30**(27) 3525–3528
102. I G M Campbell, R C Cookson, M B Hocking, A N Hughes *J. Chem. Soc.*, 1965, (3) 2184–2193
103. D Seyferth, S Grim, T Read *J. Am. Chem. Soc.*, 1960, **82**(6) 1510–1511
104. D G Wittig, M Schlosser *Angew. Chem.*, 1960, **72**(9) 324

105. D Seyferth, S Grim, T Read *J. Am. Chem. Soc.*, 1961, **83**(7) 1617–1620
106. D Seyferth, H D Simmons, G Singh, Jr. *J. Organomet. Chem.*, 1965, **3**(4) 337–339
107. A J Speziale, G J Marco, K W Ratts *J. Am. Chem. Soc.*, 1960, **82**(5) 1260
108. A J Speziale, K W Ratts, D E Bissing *Org. Synth. Coll.*, 1973, **5** 361–364
109. A J Speziale, K W Ratts *J. Am. Chem. Soc.*, 1962, **84**(5) 854–859
110. D Seyferth, J K Heeren, G Singh *J. Organomet. Chem.*, 1966, **5**(3) 267–274
111. S A Fuqua, W G Duncan, R M Silverstein *J. Org. Chem.*, 1965, **30**(4) 1027–1029
112. V F Heidelberg *Angew. Chem.*, 1960, **72**(16) 566
113. H Yamanaka, T Ando, W Funasaka *Bull. Chem. Soc. Jpn.*, 1986, **41**(3) 756–759
114. D Seebach *Angew. Chem.*, 1967, **79**(10) 469–470
115. D M Lemal, E H Banitt *Tetrahedron Lett.*, 1964, **5** 245–251
116. G Wittig, M Schlosser *Tetrahedron*, 1962, **18** 1023–1028
117. M I Kabachnik, V A Gilyarov *Dokl. Akad. Nauk SSSR*, 1956, **106**(3) 473–475
118. V A Gilyarov *Khimiya i Primenenie Fosfororganicheskikh Soedinenii. Trudy I Konferentsii, Moskva* (The Chemistry and Applications of Organophosphorus Compounds. Proceedings of the Ist Conference, Moscow), Nauka, Moscow, 1957, pp 275–282
119. A N Pudovik, R D Gareev *Zh. Obshch. Khim.*, 1975, **45**(8) 1674–1685
120. A C Poshkus, J E Herweh *J. Org. Chem.*, 1962, **27**(7) 2700–2702
121. A N Pudovik, R D Gareev *Zh. Obshch. Khim.*, 1975, **45**(1) 235–236
122. R D Gareev, A N Pudovik *Zh. Obshch. Khim.*, 1976, **46**(8) 1717–1729
123. H Malz, E Roos, BRD P. 1 158 971, 1963
124. P Krommes, J Lorberth *J. Organomet. Chem.*, 1977, **127**(1) 19–31
125. B A Arbuzov, A M Polozov, N A Polezhaeva *Zh. Obshch. Khim.*, 1984, **54**(9) 1968–1970
126. W Reid, H Appel *Ann. Chem.*, 1964, **679** 56–77
127. P Krommes, J Lorberth *J. Organomet. Chem.*, 1976, **110**(2) 195–200
128. M F Lappert, J S Poland *Adv. Organomet. Chem.*, 1970, **9** 397–435
129. L V Nesterov, N E Krepysheva *Trudy III Vsesoyuznoi Konferentsii po Khimii Karbenov, Moskva* (Proceedings of the IIIrd All-Union Conference on the Chemistry of Carbenes, Moscow), Nauka, Moscow, 1982, p. 60
130. V A Gilyarov *Khimiya i Primenenie Fosfororganicheskikh Soedinenii. Trudy II Konferentsii, Moskva* (The Chemistry and Applications of Organophosphorus Compounds. Proceedings of the IInd Conference, Moscow), Nauka, Moscow, 1962, pp 133–135
131. M I Kabachnik *Dokl. Akad. Nauk SSSR*, 1952, **83**(3) 407–410
132. M I Kabachnik, Yu M Polikarpov *Dokl. Akad. Nauk SSSR*, 1957, **115**(3) 512–515
133. N Kreutzkamp, H Kayser *Chem. Ber.*, 1956, **89**(7) 1614–1619
134. V V Ovchinnikov, V I Galkin, E G Yarkova, et al. *Dokl. Akad. Nauk SSSR*, 1977, **235**(1) 118–120
135. V V Ovchinnikov, V I Galkin, R A Cherkasov *Dokl. Akad. Nauk SSSR*, 1979, **249**(1) 128–132
136. B A Arbuzov, A M Polozov, N A Polezhaeva, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, (3) 726–727
137. B A Arbuzov, A V Fuzhenkova *Trudy IV Vsesoyuznoi Konferentsii po Khimii Karbenov, Moskva* (Proceedings of the IVth All-Union Conference on the Chemistry of Carbenes, Mosçow), Nauka, Moscow, 1987, p. 148
138. W Kirmse *Carbene Chemistry* (Russian translation from English), Mir, Moscow, 1966, pp 141–150
139. B A Arbuzov, A M Polozov, N A Polezhaeva *Zh. Obshch. Khim.*, 1984, **54**(7) 1517–1520
140. B A Arbuzov, A M Polozov, N A Polezhaeva, USSR P. 1 203 095; *Byull. Izobret.*, 1986, (1)
141. O N Kataeva, I A Litvinov, V A Naumov, et al. *Zh. Obshch. Khim.*, 1990, **60**(3) 555–563
142. B A Arbuzov, N A Polezhaeva, A M Polozov *Dokl. Akad. Nauk SSSR*, 1986, **287**(4) 849–852
143. H Meier, K Zeller *Angew. Chem., Int. Ed. Engl.*, 1975, **14**(1) 32–43
144. A M Polozov, N A Polezhaeva, B A Arbuzov *Zh. Obshch. Khim.*, 1987, **57**(10) 2200–2206
145. A M Polozov, Ya A Levin, E I Gol'dfarb, et al. *Trudy IV Vsesoyuznoi Konferentsii po Khimii Karbenov, Moskva* (Proceedings of the IVth All-Union Conference on the Chemistry of Carbenes, Moscow), Nauka, Moscow, 1987, pp 138, 139
146. A M Polozov, Ya A Levin, E I Gol'dfarb, et al. *Zh. Obshch. Khim.*, 1989, **59**(6) 1262–1267
147. G L Closs, B E Rabinov *J. Am. Chem. Soc.*, 1976, **98**(25) 8190–8198
148. A N Pudovik, R D Gareev *Zh. Obshch. Khim.*, 1964, **34**(12) 3942–3946
149. A N Pudovik, R D Gareev, A V Aganov *Zh. Obshch. Khim.*, 1971, **41**(5) 1017–1022
150. A N Pudovik, R D Gareev, L A Stabrovskaya, et al. *Zh. Obshch. Khim.*, 1970, **40**(10) 2181–2186
151. A N Pudovik, R D Gareev, L I Kuznetsova *Zh. Obshch. Khim.*, 1969, **39**(7) 1536–1543
152. A N Pudovik, R D Gareev, O E Raevskaya *Zh. Obshch. Khim.*, 1970, **40**(6) 1189–1195
153. A N Pudovik, R D Gareev, L A Stabrovskaya, A V Aganov *Zh. Obshch. Khim.*, 1973, **43**(6) 1236–1240
154. A N Pudovik, R D Gareev, A V Aganov, et al. *Zh. Obshch. Khim.*, 1971, **41**(5) 1008–1016
155. A N Pudovik, R D Gareev, L A Stabrovskaya, et al. *Zh. Obshch. Khim.*, 1972, **42**(1) 80–87
156. A N Pudovik, R D Gareev *Zh. Obshch. Khim.*, 1970, **40**(5) 1025–1030
157. A N Pudovik, R D Gareev, A V Aganov, L A Stabrovskaya *Zh. Obshch. Khim.*, 1971, **41**(5) 1173
158. D Danion, R Carrie *Bull. Soc. Chim. Fr.*, 1972, (3) 1130–1135
159. A N Pudovik, N G Khusainova, G V Timoshina *Zh. Obshch. Khim.*, 1974, **44**(2) 272–276
160. A N Pudovik, N G Khusainova, G V Timoshina *Zh. Obshch. Khim.*, 1972, **42**(10) 2159–2166
161. A N Pudovik, N G Khusainova, G V Timoshina, O E Raevskaya *Zh. Obshch. Khim.*, 1971, **41**(7) 1476–1481
162. T Minamo, S Tokumasi, R Mimasu, I Hirao *Chem. Lett.*, 1985, **8** 1099–1102
163. B C Saunders, P Simpson *J. Chem. Soc.*, 1963, **6** 3351–3360

164. H Heydt, M Regitz *Ann. Chem.*, 1977, **10** 1766–1786
165. D Seyferth, J D Paetsch *J. Org. Chem.*, 1969, **34**(5) 1483–1484
166. M Regitz, W Welter, A Hartmann *Chem. Ber.*, 1979, **112**(7) 2509–2527
167. H Heydt, K-H Busch, M Regitz *Ann. Chem.*, 1980, 4 590–599
168. T Minami, T Hanamoto, I Hirao *J. Org. Chem.*, 1985, **50**(8) 1278–1281
169. N G Khusainova, G V Timoshina, A N Pudovik *Zh. Obshch. Khim.*, 1976, **46**(11) 2624
170. A N Pudovik, R D Gareev, L A Stabrovskaya, et al. *Zh. Obshch. Khim.*, 1973, **43**(8) 1674–1682
171. A N Pudovik, G I Stabrovskaya, A B Evstaf'ev', et al. *Zh. Obshch. Khim.*, 1972, **42**(8) 1862–1863
172. R D Gareev, G M Loginova, A N Pudovik *Zh. Obshch. Khim.*, 1979, **49**(3) 493–503
173. R D Gareev, Yu Yu Samitov, A N Pudovik *Zh. Obshch. Khim.*, 1977, **47**(2) 278–290
174. R D Gareev, A N Pudovik *Zh. Obshch. Khim.*, 1979, **49**(4) 728–738
175. R D Gareev, A N Pudovik *Zh. Obshch. Khim.*, 1982, **52**(11) 2637–2638
176. Yu Yu Samitov, R D Gareev, L A Stabrovskaya, A N Pudovik *Zh. Obshch. Khim.*, 1972, **42**(6) 1227–1235
177. N G Khusainova, V I Galkin, R A Cherkasova *Zh. Obshch. Khim.*, 1990, **60**(5) 995–997
178. A N Pudovik, R D Gareev *Zh. Obshch. Khim.*, 1963, **33**(10) 3441–3442
179. A N Pudovik, R D Gareev *Zh. Obshch. Khim.*, 1968, **38**(6) 1291–1295
180. A N Pudovik, R D Gareev, L E Kazakova *Zh. Obshch. Khim.*, 1969, **39**(6) 1239–1243
181. E E Schweizer, C S Kim, R A Jones *J. Chem. Soc., Chem. Commun.*, 1970, **1** 39–40
182. E E Schweizer, C G Kim *J. Org. Chem.*, 1971, **36**(26) 4033–4041
183. E Zbiral, E Bauer *Tetrahedron*, 1972, **28**(15) 4189–4196
184. G Wittig, M Schlosser *Tetrahedron*, 1962, **18**(9) 1023–1028
185. G Märkl *Tetrahedron Lett.*, 1961, **22** 811–813
186. H Strzelecka, M S Siemiatycki, C Prevost *C. R. Seances Acad. Sci.*, 1962, **254**(4) 696–697
187. H Strzelecka, M H Moureu *C. R. Seances Acad. Sci.*, 1962, **255**(4) 731–733
188. E Niecke, J Boeske, B Krebs, M Dartmann *Chem. Ber.*, 1985, **118**(8) 3227–3240
189. H Bestmann, G Schmid *Tetrahedron Lett.*, 1981, **22**(18) 1679–1680
190. R Oda, Y Ito, M Okano *Tetrahedron Lett.*, 1964, (1) 7–9
191. Y Ito, M Okano, R Oda *Tetrahedron*, 1966, **22**(8) 2615–2619
192. G A Wheaton, D J Burton *Tetrahedron*, 1976, (12) 895–898
193. Z Yoshida, S Yoneda, Y Murato *J. Org. Chem.*, 1973, **38**(20) 3537–3541
194. A N Pudovik, R D Gareev, A V Aganov, L A Stabrovskaya *Zh. Obshch. Khim.*, 1971, **41**(6) 1232–1239
195. B A Arbuzov, V S Vinogradova, N A Polezhaeva, A K Shamsutdinova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1963, (4) 675–683
196. D Kost, M S Sprecher *Tetrahedron Lett.*, 1975, **49** 4483–4486
197. R D Gareev, A N Pudovik, Yu Yu Samitov *Khimiya Elementorganicheskikh Soedinenii* (The Chemistry of Organoelement Compounds), Nauka, Leningrad, 1976, pp 135–147
198. R D Gareev, A N Pudovik *Zh. Obshch. Khim.*, 1977, **47**(2) 475
199. A N Pudovik, R D Gareev, L A Stabrovskaya *Zh. Obshch. Khim.*, 1970, **40**(3) 698
200. A N Pudovik, I V Konovalova, R D Gareev, et al. *Khimiya i Primenenie Fosfororganicheskikh Soedinenii. Trudy V Konferentsii, Moskva* (The Chemistry and Applications of Organophosphorus Compounds. Proceedings of the Vth Conference, Moscow), Nauka, Moscow, 1974, pp 62–76
201. V D Sviridov, G A Nikiforov, V V Ershov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, (8) 1862–1863
202. A N Pudovik, R D Gareev, S E Shtil'man, USSR P. 396344; *Byull. Izobret.*, 1973, (6)
203. A N Pudovik, A M Remizov, L A Stabrovskaya, et al. *Zh. Obshch. Khim.*, 1972, **42**(6) 1421
204. A N Pudovik, R D Gareev, A B Remizov, A B Aganov *Zh. Obshch. Khim.*, 1973, **43**(3) 559–567
205. A D Mikityuk, B A Kashemirov, I I Chervin, G S Khokhlov *Zh. Obshch. Khim.*, 1985, **55**(12) 2798–2799
206. O I Kolodyazhnyi, V N Yakovlev, V P Kukhar' *Zh. Obshch. Khim.*, 1980, **50**(6) 1418–1419
207. G Tomaschewski, D Zanke *Z. Chem.*, 1970, **10**(4) 145–146
208. J Bellan, G Etemad-Moghadam, M Payard, M Koenig *Tetrahedron Lett.*, 1986, **27**(10) 1145–1146
209. G Etemad-Moghadam, J Bellan, C Tachon, M Koenig *Tetrahedron*, 1987, **43**(8) 1793–1797
210. G Märkl, I Trötsch *Angew. Chem.*, 1984, **96**(11) 899–901
211. G Märkl, W Hölzl, I Trötsch-Schaller *Tetrahedron Lett.*, 1987, **28**(24) 2693–2696
212. W Schnurr, M Regitz *Z. Naturforsch., B*, 1988, **43**(10) 1258–1292
213. W Schnurr, M Regitz *Synthesis*, 1989, (7) 511–515
214. W Schnurr, M Regitz *Tetrahedron Lett.*, 1989, **30**(30) 3951–3954
215. E Niecke, W Flick *Angew. Chem.*, 1975, **87**(9) 355–356
216. E Niecke, D-A Wildbredt *Angew. Chem.*, 1978, **90**(3) 209–210
217. E Niecke, D-A Wildbredt *Chem. Ber.*, 1980, **113**(4) 1549–1565
218. E Niecke, A Seyer, D-A Wildbredt *Angew. Chem.*, 1981, **93**(8) 687–688
219. W Rösch, M Regitz *Angew. Chem.*, 1984, **96**(11) 898–899
220. B A Arbuzov, E N Dianova, S M Sharipova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, (5) 1113–1116
221. B A Arbuzov, E N Dianova, E Ya Zabotina *Zh. Obshch. Khim.*, 1987, **57**(8) 1699–1702
222. B A Arbuzov, A F Lisin, E N Dianova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, (10) 2395–2397
223. B A Arbuzov, E N Dianova, R T Galiaskarova, et al. *Zh. Obshch. Khim.*, 1987, **57**(9) 1949–1955
224. B A Arbuzov, E N Dianova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, (6) 1453–1454
225. B A Arbuzov, E N Dianova, E Ya Zabotina *Zh. Obshch. Khim.*, 1987, (12) 2819–2821
226. B A Arbuzov, E N Dianova, Yu Yu Samitov *Dokl. Akad. Nauk SSSR*, 1979, **244**(5) 1117–1121
227. B A Arbuzov, E N Dianova, R T Galiaskarova, A Schmidpeter *Chem. Ber.*, 1987, **120**(4) 597–599
228. B A Arbuzov, E N Dianova, E Ya Zabotina *Dokl. Akad. Nauk SSSR*, 1983, **273**(3) 613–616
229. I A Latvinov, Yu T Struchkov, B A Arbuzov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, (10) 2275–2279
230. B A Arbuzov, V D Cherepinskii-Malov, E N Dianova, et al. *Dokl. Akad. Nauk SSSR*, 1978, **243**(2) 358–360

231. B A Arbuzov, V D Cherepinskii-Malov, E N Dianova, et al. *Dokl. Akad. Nauk SSSR*, 1979, **247**(5) 1150–1152
232. B A Arbuzov, E N Dianova, E Ya Zabotina, et al. *Vsesoyuznoe Soveshchanie po Difraktsionnym Metodam v Khimii. Tezisy Dokladov, Suzdal'* (All-Union Conference on Diffraction Methods in Chemistry. Abstracts of Reports, Suzdal), Suzdal, 1988, p. 91
233. B A Arbuzov, E N Dianova, R T Galiaskarova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, (6) 1376–1380
234. B A Arbuzov, E N Dianova, R T Galiaskarova, P P Chernov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, (2) 412–418
235. B A Arbuzov, E N Dianova, I Z Galeeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, (5) 1196
236. A V Il'yasov, A N Chernov, A A Nafikova, et al. *Zh. Obshch. Khim.*, 1984, **54**(7) 1511–1517
237. B A Arbuzov, E N Dianova, I Z Galeeva, et al. *Zh. Obshch. Khim.*, 1985, **55**(1) 3–11
238. I A Litvinov, Yu T Struchkov, B A Arbuzov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, (12) 2718–2723
239. I A Litvinov, Yu T Struchkov, B A Arbuzov, et al. *Izv. Akad. Nauk SSSR, Ser Khim.*, 1983, (10) 2280–2284
240. B A Arbuzov, E N Dianova, E Ya Zabotina *Zh. Obshch. Khim.*, 1985, **55**(7) 1471–1475
241. B A Arbuzov, E N Dianova, A F Lisin *Khimiya i Primenenie Fosforganicheskikh Soedinenii. Trudy VII Konferentsii, Leningrad* (The Chemistry and Applications of Organophosphorus Compounds. Proceedings of the VIIth Conference, Leningrad), Nauka, Leningrad, 1987, pp 347–352
242. P Kieselack, K Dimroth *Angew. Chem.*, 1974, **86**(3) 129–130
243. P Kieselack, C Helland, K Dimroth *Chem. Ber.*, 1975, **108**(11) 3656–3670
244. G Märkl, A Merz *Tetrahedron Lett.*, 1971, (17) 1269–1272

Translated from *Uspekhi Khimii* **61** 616–645 (1992) U.D.C. 547.1127'118

Compounds containing phosphorus and boron

G N Nikonov, A S Balyeva
Arbuzov Institute of Organic and Physical Chemistry, Kazan

ABSTRACT. This review examines the synthesis and properties of phosphorus-boron-containing compounds containing the fragments P=B, B–C–B, P–N–B, P–O–B, P–C–C–B, P–C=C–B, P=C–O–B, P–C–O–B, P–C≡C–B, and P–$(C)_n$–B, and also phosphorus-containing borohydrides, carboranes, and coordination compounds containing phosphorus- and boron-containing ligands. The interaction of heteroatomic functional groups has received special attention. Wherever possible the acquisition of new properties by the compounds as a result of these interactions has been noted.

The bibliography contains 139 references.

Contents

I. Introduction 335
II. Compounds containing fragment P=B 336
III. Compounds containing fragment P–C–B 336
IV. Compounds containing fragment P–N–B 338
V. Compounds containing fragment P–O–B 341
VI. Compounds containing fragments P–C–C–B and P–C=C–B 342
VII. Compounds containing fragment P=C–O–B 343
VIII. Compounds containing fragment P–C–O–B 343
IX. Compounds containing fragment P–C≡C–B 345
X. Compounds containing fragment P–$(C)_n$–B and others 346
XI. Phosphaborohydrides 346
XII. Coordination compounds 347

I. Introduction

The introduction of different heteroatom-containing groups into an organic molecule leads to the mutual enrichment of the chemistry of the corresponding classes of organic compounds. One of the most interesting examples of this type is the introduction of phosphorus atoms into organoboron compounds. Phosphorus and boron are known to have different electronic compositions (an atom with an unshared electron pair, an atom with a vacant orbital, a donor and an acceptor, a base and an acid) and have the ability to change reversibly their coordination and to form coordinate bonds with metals, while the variety of properties and types of compounds obtained may be attributed to the diversity of fragments by means of which the phosphorus- and boron-containing groups may be linked. New properties appear as a result of the mutual effect of the functional groups containing these elements. In this regard it is appropriate to examine the currently known classes of P- and B-containing compounds (PBC) and to attempt to follow the change in the interaction of the heteroatoms. In the phosphinoboranes and phosphineboranes a chemical bond is involved in this interaction. When a particular fragment is present between the P and B atoms, the effect of the heteroatomic functions is equivalent to a supplementary interaction, and the type and method of transfer of the latter are determined by several factors, i.e. the remoteness of the heteroatoms from each other, the spatial arrangement, the ability of the separating fragment to "conduct" electronic effects, etc. With such an approach different classes of P- and B-containing compounds may be combined into a single review. A study of the coordination compounds is one of the most promising avenues for the advancement of the chemistry of functionally substituted phosphorus compounds including the phosphorus-boron compounds. The introduction of boron-containing functional groups into a molecule of a phosphorus-containing ligand may lead to fundamental changes in the coordination sphere of the metal. Numerous examples of PBC coordination compounds are considered in the review.

In a study and comparison of the properties of different types of PBC such an approach may be extended also to other systems possessing two or several heteroatomic functions, for example P–Al, As–B, etc.

The currently known phosphorus-boron containing compounds may be separated into three major groups: 1) compounds in which the P and B atoms are linked by a coordinate bond, the phosphineboranes; 2) compounds containing three-coordinate P and B atoms linked directly to each other, the acyclic and cyclic monomeric phosphinoboranes; 3) compounds in which the P and B atoms are separated by some fragment, carbon atoms, heteroatoms, metal atoms, C–O and C–N fragments, etc. The present review focuses on the latter group of compounds which are presently attracting the attention of many research workers. A number of monographs and reviews have examined methods used to prepare and the properties of PBC including those in which the P and B atoms are separated by fragments.[1–7] However in these communications no reference was made to the mutual effect of heteroatom-containing groups leading to the appearance of new properties in the compounds, and in addition the relationship between the interaction of the heteroatoms and the nature of the fragments separating them has not been revealed.

To achieve these objectives the compounds presented below have been classified according to the type of the fragments which separate the phosphorus and boron atoms.

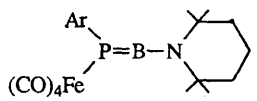
Three types of interaction between the phosphorus-boron-containing functional groups are possible, the interaction being transmitted along the bond system of the separating fragment, the trans-annular intramolecular (coordinate bond P→B), and the trans-annular intermolecular interaction (coordinate bond P→B). These interactions which are evident from the behaviour of the functional groups are determined by the coordination of the P and B atoms,

the type of fragment between them, and by the structural features of the molecule.

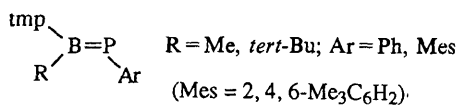
II. Compounds containing fragment P=B

The most obvious route, which can be used to obtain compounds containing the P=B fragment (boraphosphenes), is the interaction of phosphines with haloboranes or halophosphines with boron hydrides in the presence of hydrogen halide acceptors, but this route does not lead to the expected result. In this case phosphinoboranes are usually formed as dimers, trimers, or oligomers. Nevertheless the diphosphadiboretenes may be regarded as original compounds for obtaining boraphosphenes, which is confirmed by the appearance of cation radicals of the corresponding boraphosphenes in their mass spectra.[8,9]

Boraphosphenes were observed in the gas phase for the first time in the mass-spectrometer for (tmpB = PAr)$_2$ (tmp = 2,2,6-tetramethylpiperidino; Ar = 2,4,6-(*tert*-Bu)$_3$C$_6$H$_2$).[10,11] The authors[10] involved in this study suggested that they were able to identify boraphosphene as a complex with iron tetracarbonyl.



The dimer (tmp−PAr)$_2$ was obtained as a result of the interaction of tmpBCl$_2$ and ArP(SiMe$_3$)Li in Et$_2$O at 0 °C. Thermolysis of this compound at 250 °C yielded boraphosphene in the gas phase, which was confirmed by the mass spectra. It followed from *ab initio* calculations of a model molecule of boraphosphene H−B=P−H that the energy minimum for the boraphosphenes corresponds to a structure with a free unshared electron pair at the P atom and a P=B double bond (H−P=B−H) in contrast to the iminoboranes in which the N≡B triple bond is found (H−N≡B−B).[10] In an attempt to obtain boraphosphene by treatment of MeLi or the *tert*-BuLi compound (tmp)B(Cl)PHAr in Et$_2$O at 25 °C a new phosphide anion was found.

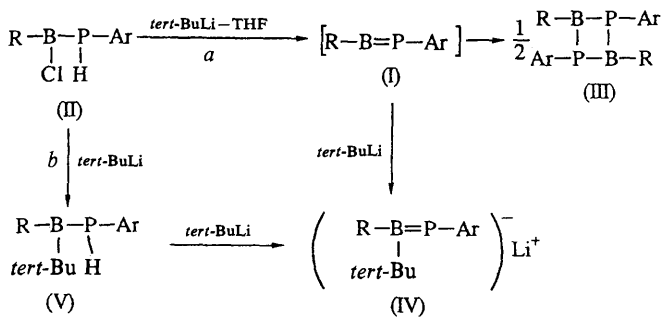


R = Me, *tert*-Bu; Ar = Ph, Mes

(Mes = 2, 4, 6-Me$_3$C$_6$H$_2$).

Thus a series of compounds containing the P=B multiple bond was synthesised. The structural parameters of double-bonded P and B atoms in complexes [Li(Et$_2$O)RPBMes$_2$] (R = Ph, C$_6$H$_{11}$, Mes) and in the ion pairs [Li(12-crown-4)$_2$][RPBMes$_2$], THF, obtained by the action of two equivalents of 12-crown-4 on these complexes have been presented for the first time.[12,13] The environment of the P and B atoms is planar, and a slight twisting is found between the planes in which the atoms lie, and there is a short bond between them (1.823 Å). The P=B bond length is significantly shorter than the known bond lengths in the borophosphines (1.96 Å). The Li ion is coordinated through the P atom. For the complexes the chemical shift in the ^{31}P NMR spectra is equal to +55−73 p.p.m. During the action of the crown ether the signal is displaced to +91−103 p.p.m.

Using chemical methods attempts were made to demonstrate the existence of compounds containing two-coordinate P and B atoms but without an ionic structure. For this the behaviour of borylphosphine in the reaction with *tert*-BuLi was studied.[14]



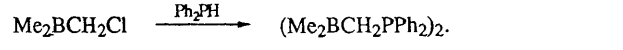
On account of the absence of compound (V) in the reaction mixture it was concluded that the reaction occurs via route *a*. Certain information is available on the reactivity of the compounds containing a double bond between the P and B atoms. Thus type (I) compounds are air-sensitive and readily react with proton donors such as water and methanol (forming in this case the type (V) structures) and also with alkyl halides and triemthylchlorosilane.[7]

Generalised data on the methods used for synthesis and on the structures of compounds containing the P=B fragment have been described.[15] In these works the synthesis and spectral data of 17 boron-phorphorus-containing compounds, relating to the synthesis of the Li(Et$_2$O)P(R)BR$_2$ type of structures, have been examined in detail. Here it is necessary to distinguish the compound with the P=B−P structure which has two different phosphorus atoms and one boron atom (δ^{31}P 32 and −117.0 p.p.m., the constant J_{P-P} is absent, J_{P-H} = 247 Hz, the P−B bond length is 1.927, and the P=B bond length is 1.810 Å). It has the shortest P=B bond.[13]

Thus of the currently known compounds containing the P=B fragment the only stable compounds are the phosphinidene borates in which the boron atom is three-coordinate. Moreover stabilisation is ensured by the bulky substituents in both heteroatoms.

III. Compounds containing the P−C−B fragment

Substances containing this fragment have long been known.[6,16] Two types of structures are possible, compounds in which the P and B atoms occur in the three-coordinate state, and substances containing a phosphonium cation and a borate anion in the molecule. Only a few representatives of the first type have been described, and furthermore they usually exist as dimers. Thus the interaction of dimethylchloromethylborane with nucleophilic reagents including phosphines has been studied.[16]



The reaction was carried out in sealed ampoules. Borylmethylenephosphine exists as the dimer in the gas phase.

Much more work has been done on the synthesis of boratomethylenephosphonium betaines. The method used to obtain such compounds is based on the reaction of phosphorus ylides with halogen boranes[17–22] or boron hydrides.[22–27]

$$R_3P{=}CHR' + BX_3 \longrightarrow R_3\overset{+}{P}{=}CHR'{-}\overset{-}{B}X_3,$$

R = Me, Et, Ph, R' = H, Alk, X = Hal;

$$Ph_3P{=}CHR' + B_2H_6 \xrightarrow[0°C]{Et_2O} Ph_3\overset{+}{P}\underset{R^1}{CH}\overset{-}{B}H_3;$$

$$Ph_3P{=}CH_2 + H_2RB{\leftarrow}NEt_3 \xrightarrow[-NEt_3]{C_6H_6,\ 80°C} Ph_3\overset{+}{P}CH_2\overset{-}{B}RH_2.$$

The borate alkylidene phosphonium betaines are of interest in that as a result of intramolecular regroupings they may give rise to a phosphine complex with borane in which the alkylidene fragment of the molecule is found to be at the boron atom. This regrouping is used in organic syntheses.[28–30]

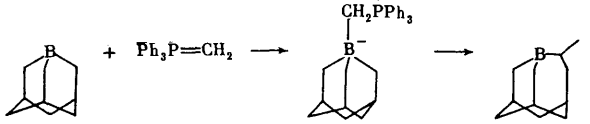
$$R^1CH{=}PPh_3 \xrightarrow{BH_3THF} R^1\underset{\overset{-}{B}H_3}{CH}\overset{+}{P}Ph_3 \longrightarrow$$

$$\longrightarrow R^1CH_2{-}H_2B{\leftarrow}PPh_3 \xrightarrow[-R^5\overset{+}{P}Ph_3\overset{-}{I}]{R^2HC{=}CR^3R^4,\ R^5I}$$

$$\longrightarrow R^1CH_2B\underset{R^2}{\overset{R^4}{(CH{-}CH)_2}}\underset{R^3}{} \xrightarrow[3)H_2O_2/NaOH]{1)\ Cl_2CHOMe,\ 2)LiOCEt_3}$$

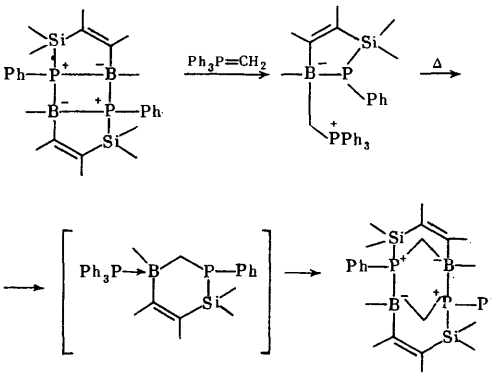
$$\longrightarrow R^1CH_2{-}\underset{HO\ R^2}{\overset{R^4}{C(CH{-}CH)_2}}\underset{\ R^3}{} .$$

An analogous regrouping has been acheived for boradamantane derivatives. On interaction of triphenylphosphine ylide with boradamantane the corresponding phosphonium salt is formed which regroups with a change of the boradamantyl framework into the homodamantyl framework. After triphenylphosphine is removed, 4-alkyl-3-borohomoadamanatane separates out.[31]



The X-ray diffraction analysis of borataphosphonium betaine formed in this reaction shows that certain geometric parameters in the P atom environment differ significantly from the corresponding characteristics of the phosphonium systems and are intermediate between the values observed in them and in the ylide molecules.[32]

The regrouping of the borataalkylenephosphonium salts may involve two phosphorus atoms.[33] In this case one $\overset{+}{P}{-}C{-}\overset{-}{B}$ fragment is disrupted and a new fragment is formed.



By substitution of boron hydride by the haloboranes in reactions with phosphorus ylides it is possible to obtain borylalkylidene phosphoranes,[34] i.e. compounds containing the P=C–B fragment.

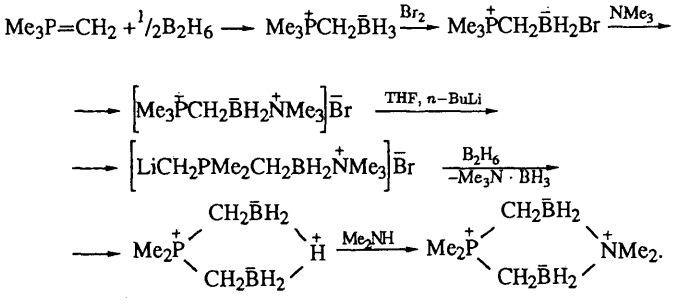
$$R'CH{=}PPh_3 \xrightarrow{R^2_2BCl} R'\underset{Ph_3P^+}{CH}{-}\underset{Cl}{\overset{-}{B}}R^2_2 \rightleftharpoons R'\underset{Ph_3P^+}{CH}{-}BR^2_2Cl^- \longrightarrow$$

$$\xrightarrow[-\ R'CH_2{-}\overset{+}{P}Ph_3Cl^-]{R'CH{=}PPh_3} R'C(=PPh_3){-}BR^2_2 \longleftrightarrow R'C{=}\overset{-}{B}R^2_2.$$

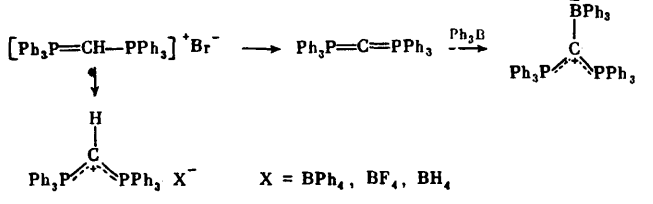
$$\qquad\qquad\qquad

On account of the ability of the borylalkylidene phosphoranes to react with the proton donors and bromine it is possible to obtain deuterated and brominated phosphorus ylides, which in turn provide a means to achieve the stereoselective synthesis of deuterated and bromo-substituted vinyl compounds according to the Wittig reaction.[37]

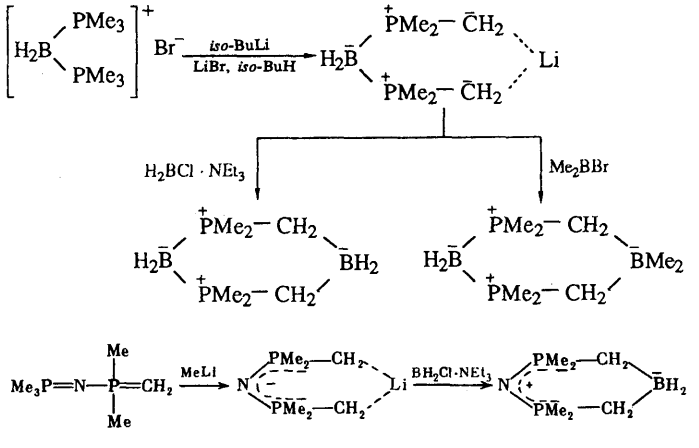
Two novel and unusual heterocycles containing P–C–B fragments were synthesised according to the following scheme:[38]



On account of the ability of the P and B atoms to change their coordination and to form ionic structures it is possible to obtain a diversity of compounds. Thus in the PBC series containing the P–C–B fragment compounds having a mesoionic structure are known.[39,40]

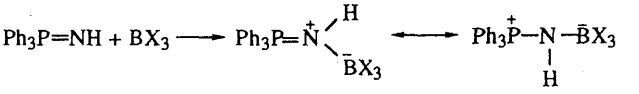


The synthesis of new heterocyclic systems containing P and B atoms in the four-coordinate state, borata-*bis*-(dimethylphosphoniamethylene) borate and nitrido-*bis*-(dimethylphosphoniamethylene)-borate has been studied.[40]

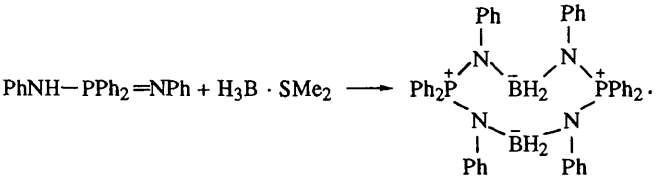


IV. Compounds containing fragment P–N–B

PBS containing such a fragment are most numerous among compounds in which the P and B atoms are separated by one atom. Such compounds were described a considerable time ago. Substances containing 3- or 4-coordinate P and B atoms depending on the original reagents and the synthetic route have been obtained. Thus betaines, which may be presented as two boundary mesomeric structures, were obtained from iminophosphoranes and boranes, triphenylborane or trifluoroborane.[41,42]



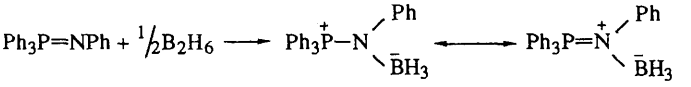
On interaction with a borane complex containing diethylsulphide the amino(imino)phosphoranes form a diazaboraphosphetidine dimer in which there are two atoms of four-coordinate boron and two phosphonium centres:[43]



The structures of phenyl-, *p*-fluorophenyl-, and benzylamino-triphenylphosphorane complexes with boron trifluoride have been studied by i.r. and ^{31}P NMR spectroscopy.[44]

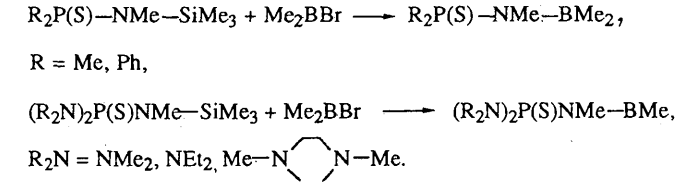
The complexes have the phosphorane structure towards which the phosphonium salt structure makes a significant contribution.

Phenyliminophosphorane forms a complex with diborane and the composition of this complex may also be presented as two resonance structures.[42]



It will be found impossible subsequently to describe the structure of the compounds containing the P–N–B fragment as a simple structure, which can be attributed to the ability of the heteroatoms of the P–N–B system to change reversibly their coordination and to the possibility of charge delocalisation at several atoms.

Borylaminophosphine sulphides are formed on substitution of the trimethylsilyl group in the silyaminophosphine sulphides during the action of bromoboranes.[45]



Use of lithium amides increases the yield to 90%.[45,46]

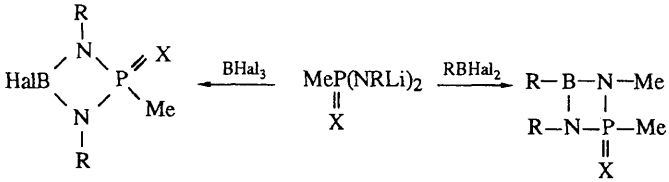
$$Me_2P(S)NRLi + Me_2BBr \longrightarrow Me_2P(S)NRBMe_2,$$

R = H, Me,

$$MeP(X)(NRLi)_2 \xrightarrow{2R_2BHal} MeP(X)(NR{-}BR_2)_2,$$

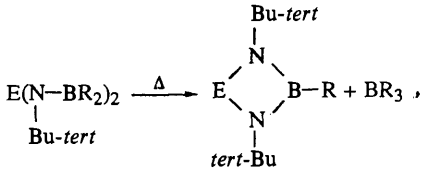
X = O, S; R = H, Me, Et.

It is noteworthy that of the boron dihalides or trihalides it has not been possible to obtain *bis*-(borylamino)methylphosphine sulphides or oxides, since cyclisation to diazaboraphosphetidines occurs.[46]



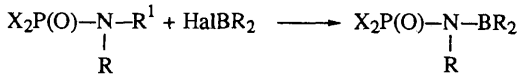
X = O, S.

Certain authors have noted that formation of borylaminophosphine sulphides does not occur on interaction of thiochlorophosphines and silylated aminoboranes.[45] In subsequent studies these authors extended the range of starting reagents,[46–50] using boron trihalides,[46,47] dichloro(silylamino)phosphine sulphide, and lithium phosphamides. Three methods used to synthesise borylaminophosphine sulphides were analysed,[48] and their degradation routes on thermolysis were studied.[47,49] It was shown that 1,3,2,4-diazaboraphosphetidines are formed, when a bulky substituent (*tert*-Bu) is present at the atom.



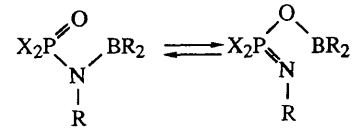
E = PPh, PMe.

A series of phosphoryl aminoboranes obtained by substitution of the hydrogen, silyl group, or lithium at the nitrogen atom in the corresponding oxides of aminophosphines or aminochlorophosphines by the boryl group has been described.[50]



X = Cl, Me, NMe_2; R = Me, Et, Cl, Br; R^1 = H, Li, $SiMe_3$.

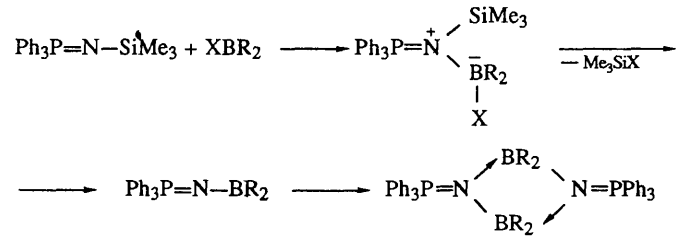
These compounds exist in solutions (X = R = NMe_2) as monomers. When X = Cl or NMe_2 and When R = Me borotrophic tautomerism was observed.



These authors later described the synthesis of borated iminophosphoranes,[51] which were previously obtained during thermal transformations of the triphenylboron complex with iminotriphenylphosphorane.[41]

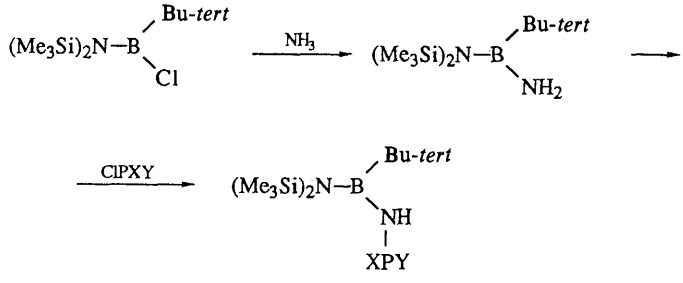
$$Ph_3P{=}\overset{+}{N}H{-}\overset{-}{B}Ph_3 \xrightarrow[-C_6H_6]{\Delta} Ph_3P{=}N{-}BPh_2.$$

Using the same method, the substitution of the silyl group at the nitrogen atom by the boryl group in the reaction with boron halides, it was possible to obtain a series of borated iminophosphoranes, which underwent association into dimers in the solutions but which were monomeric in the gas phase.



X = F, Cl, Br; R = F, Cl, Br, *n*-Bu, Ph.

Although these authors do not recommend the use of silylated aminoboranes and the acid chlorides of phosphorous-containing acids to obtain compounds containing the P–N–B fragment,[45–50] such a synthetic route has previously been described,[52] and the yield of the compounds was 40–90%.



X, Y = NMe_2, Ph, CH_2SiMe_3, $N(SiMe_3)_2$, Cl.

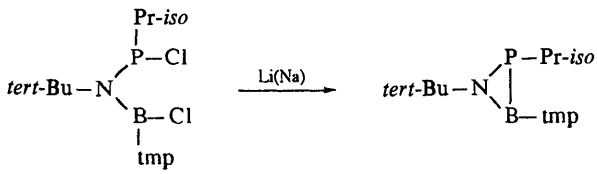
Fluoro(amino)phosphines and their sulphides with halides give phosphinoaminoboranes,[53,54] and derivatives of *tris*, *bis*, and monophosphinoaminoboranes may be obtained depending on the number of halogen atoms at the boron and the ratios of the reagents.

$$F_2PNH_2 + BF_3 \longrightarrow F_2B{-}NH{-}PF_2,$$

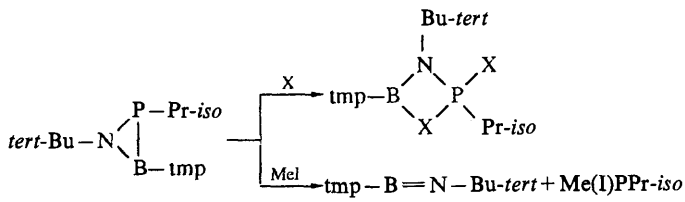
$$nF_2(S)PNH_2 + Cl_nBPh_{3-n} \longrightarrow (F_2(S)PNH)_nBPh_{3-n}$$

$n = 2, 3.$

The most characteristic property of the borylaminophosphine derivatives is their ability to form heterocyclic structures. Cyclisation may arise by the action of some reagent owing to the detachment of the halogen atoms.[55]

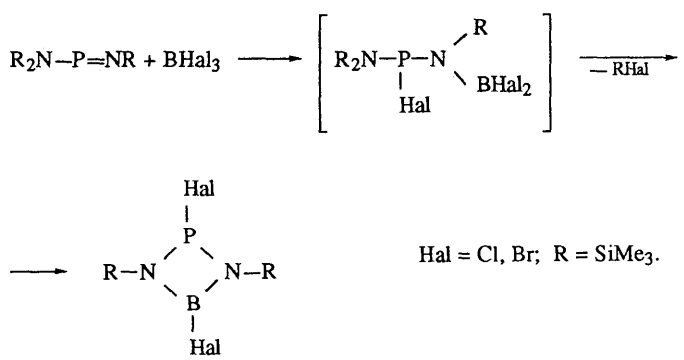


Breakage of the three-membered ring formed by the action of S(Se) or methyl iodide occurs at the P—B bond:



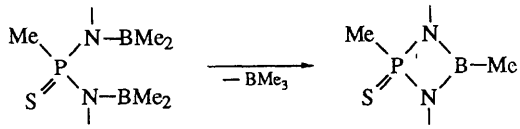
X = S, Se.

The formation of the four-membered ring, diazaboraphosphetidine, may arise as a result of intramolecular cyclisation in the N-boryl(sily)aminophosphines.[56]

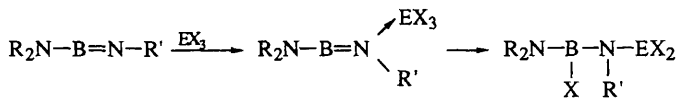


Hal = Cl, Br; R = $SiMe_3$.

Intramolecular cyclisation may appear not only because of the detachment of the halosilane, as in the above example, but also owing to the release of trialkylborane.[57,58]



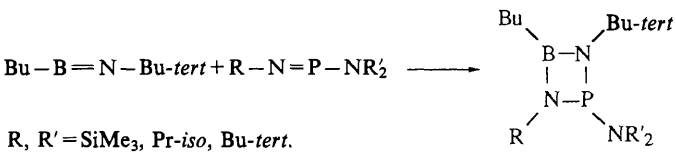
Compounds containing the P—N—B fragment in the molecule have been obtained as a result of the addition of halogenphosphines to two-coordinate boron compounds, amino-iminoboranes. This is a general method and halogenarsines, halogenstibines, and also the $E(OMe)_3$ or $E(OMe_2)_3$ type of derivatives, where E = P, As, Sb, may be used in this reaction. The reaction initially involves complex formation at the imonium atom, after which hetero-aminoboranes are formed,[59,60] as a result of the migration of the substituent from the phosphorus atom (arsenic, tin) to the boron atom.



E = P, As, Sb; X = Cl, Br, F, OMe, NMe_2;

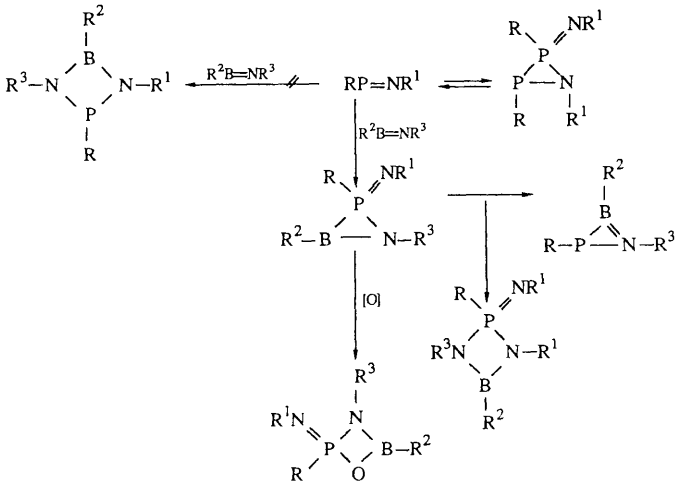
R' = Alk, Ar; R_2 =

The borylaminophosphines may be synthesised by using compounds containing P and B atoms with low coordination numbers. The method is based on the cycloaddition reaction of iminoboranes and iminophosphenes. It has been shown that depending on the radicals the reaction may occur either as a [2 + 2]-cycloaddition, or as a [2 + 1]-cycloaddition. Thus the iminoborane Bu—B=N—Bu-*tert* and aminoiminophosphene react via [2 + 2]-cycloaddition giving rise to diazaboraphosphetidine.[61]

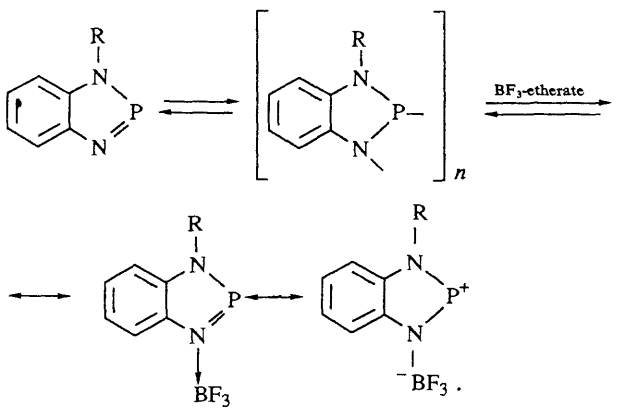


R, R' = $SiMe_3$, Pr-*iso*, Bu-*tert*.

Otherwise the reaction proceeds at the P and B atoms in the case of the alkyl substituents. The iminophosphene RP = NR· undergoes autocyclisation and an iminophosphorane is obtained. When it interacts with iminoborane, [2 + 2]-cycloaddition does not occur, while a reaction analogous to autocyclisation of iminophosphene is acheived. The azaboraphosphyrene formed readily oxidises with the disruption of the P—B bond, giving rise to oxazaboraphosphetidine or it undergoes disproportionation.[62]

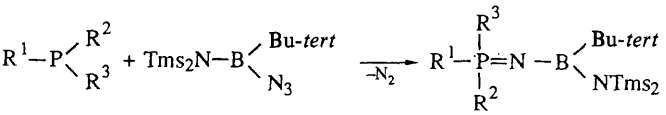


1,3-Diazaphosphols existing as oligomers or tetramers undergo monomerisation by the action of boron trifluoride etherate with the formation of the complexes[63]

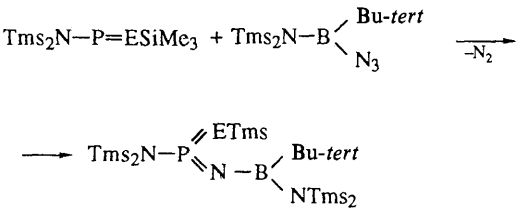


It is proposed that the complex may be described by two boundary structures.

Yet another example of the diversity of the original reagents which may be used to synthesise PBC containing the P–N–B fragment is the interaction of azidoboranes with phosphines leading to the formation of boryliminophosphoranes, and depending on the type of the original phosphorus-containing reagent a four- or three-coordinate phosphorane containing the P=N–B fragment is formed.[64]



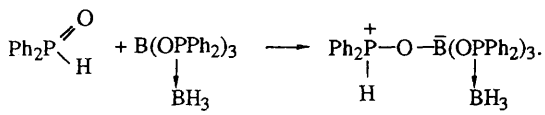
$R^1 = Ph$; $R^2 = Me, NMe_2$; $R^3 = NMe_2, NTms_2$.



E = CH, N.

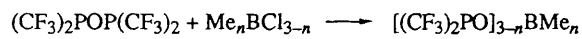
V. Compounds containing fragment P–O–B

Compounds containing fragment P–O–B have been known since 1951.[65,66] The reactions of phosphoric acid esters with various boron hydrides have been examined in earlier reviews.[67,68] In the P–O–B system the P atom preserves its ability to form complexes with boranes. Thus the compound containing four-coordinate P and B atoms in the P–O–B fragment have been obtained by the following scheme:



The structure of the betaine has been confirmed by X-ray diffraction studies.[68]

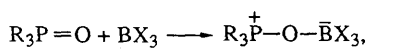
Borophosphinites containing strong electron-acceptor substituents have been obtained on disruption of the phosphinite fragment by the action of halogenboranes.[69]



$n = 0, 1, 2$.

The authors note the stability of the borphosphinites to the Arbuzov reaction type of regrouping. Trifluoromethyl groups such as strong electron acceptors increase the acidity of the boron atom as a result of which all three borophosphinites form complexes with dimethyl ether.

Compounds with the P–O–B fragments in which P and B atoms are in the four coordinate state can be obtained by the action of halogenboranes or phosphine[70] or aminophosphine oxides.[71,72]



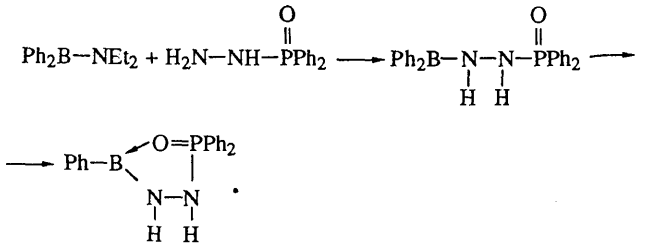
R = Alk, NMe_2; X = Cl, F.

If bromides or iodides of the boranes are used in the reaction with the aminophosphine oxides, it is possible to isolate unusual ions of compounds in which the cation contains an anionic borate fragment.[71]

$$(Me_2N)_3P{=}O + BX_3 \longrightarrow [(Me_2N)_3P{-}O{-}BX_2{-}O{-}P(NMe_2)_3]^+X^-,$$

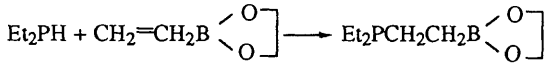
$$(Me_2N)_3P{=}O + R_3NBHI_2 \longrightarrow [((Me_2N)_3P{-}O{-})_2BH{-}NR_3]^{2+}2I^-.$$

Reference should be made to yet another study concerning the formation of aminoboranes but describing the synthesis of a compound with a phosphorus-containing fragment.[73] The spectral data indicated that the boron atom in this compound is in the following state:



VI. Compounds containing fragments P–C–C–B and P–C=C–B

Only a few compounds of this type have been described. Phosphorylation of vinyl derivatives of boron is the most obvious route for the synthesis of these compounds.[74,75]

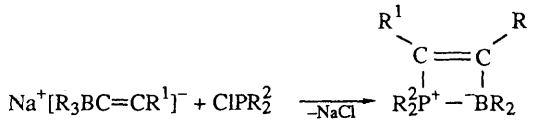


This is a general type of reaction in which silicon, tin, and sulphur hydrides may be added to the ethylene fragment.[74]

There are many reports in the literature describing the synthesis and study of the properties of compounds containing the P–C=C–B fragment. 1,2-Heteroethenes containing P, As, Si, Sn, B, O, N and Al atoms in different combinations are known. Those compounds in which heteroatoms, for example phosphorus and boron atoms, possess different electronic characteristics are of especial interest. Such a combination leads to the appearance of new properties in the compounds.

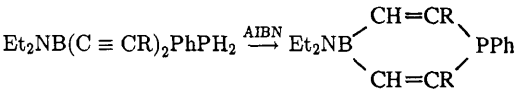
The first member of the borylphosphinoethenes has been described.[76] The principal method used to synthesise compounds containing the P–C=C–B fragment with three-coordinate P and B atoms is the interaction of halogenphosphines or phosphines with alkinyl borates or alkinyl boranes respectively.[76–79] Thus in the reaction of sodium trialkyl(alkinyl)borates with diorganylchlorophosphines, substituted 1-borata-4-phosphoniacyclobutenes-2 were isolated.[76,79]

A four-membered cyclic structure was assigned to these compounds on the basis of ^{11}B- and ^1H-NMR and mass-spectroscopic data and from a cryoscopic determination of the molecular mass and structure of the hydrolysis products. Their structure was subsequently confirmed by an X-ray diffraction analysis,[80] by determination of the dipole moment, and by studying the chemical properties (see below)



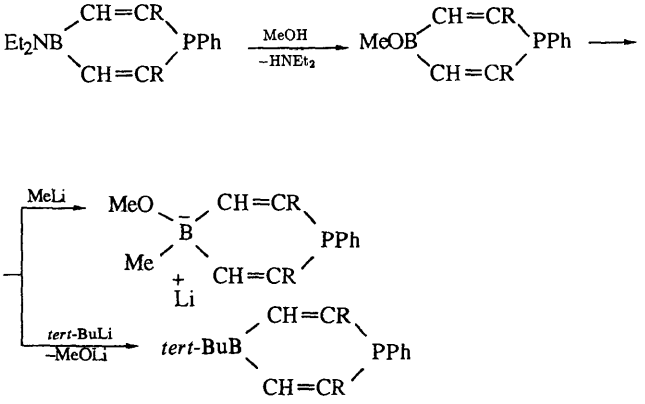
R, R^1, R^2 = Me, Et, Bu, *cyclo*-Hex, Me_3Si.

Addition of phenylphosphine to dialkinyl(diethylamino)boranes is a radical process and leads to the formation of 1,4-boraphosphacyclohexa-2,5-dienes.[77,78]



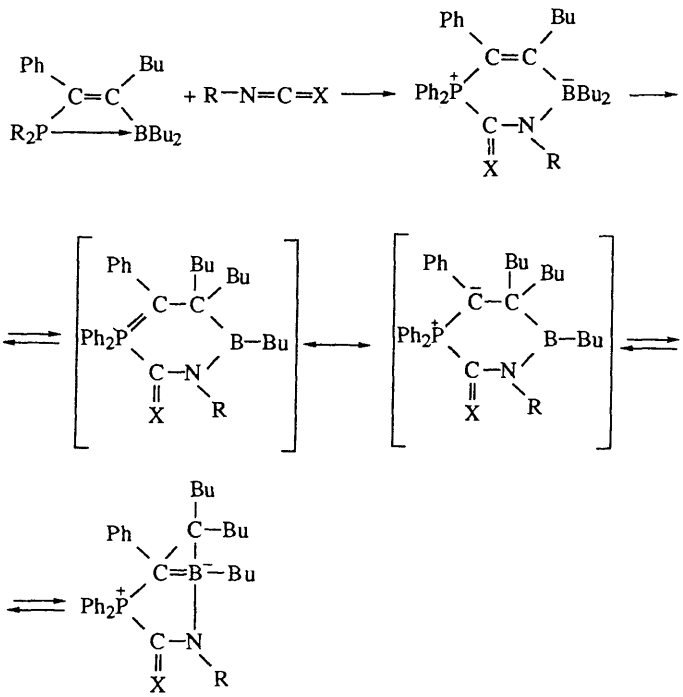
R = H, Me.

These compounds are heat stable but sensitive to oxidation. The reactivity of boron in these compounds is somewhat reduced as a consequence of the coupling of its vacant orbital with that of the unshared electron pair of the N atom, which leads to the absence of intermolecular coordination, although they undergo methanolysis. The resultant methoxy-derivative interacts with alkyllithium compounds, giving rise to borates or B-alkylated derivatives depending on their nature.



The 1-bora-4-phosphacyclohexadienes-2,5 are typically reactive towards tertiary phosphines and together with NMR spectroscopy data there is evidence that the unshared electron pair of the P atom in these rings is not delocalised and the P and B atoms do not have a significant influence on each other. In this regard the heterocycles differ from cyclic compounds containing the P–C–O–B fragment which will be examined below.

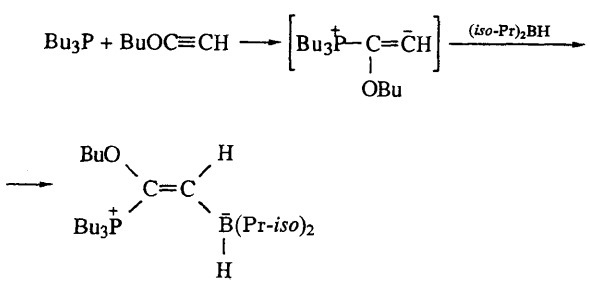
In recent years the authors of the present review have carried out systematic studies of the properties of the 1,2-borylphosphinoethenes,[81–89] and the results obtained have been grouped into one of the sections of a previous review.[4] It has recently been shown that reactions with heterocumulenes are characteristic of the borylphosphinoethenes,[90–93] and these reactions proceed as [4 + 2]-cycloaddition and lead to the formation of 6-oxo(thioxo, imino)-1-aza-5-phosphonia-2-boratacyclohexa-3-enes. These monocyclic betaines undergo anionotropic regrouping leading to the formation of bicyclic betaines, 2-aza-4-phosphonia-1-boratabicyclo[3.1.0]-hexanes. One should particularly note that this is a reversible regrouping and that the reverse process involves the migration of the butyl anion from the sp^3-hybrid C atom to the sp^3-hybrid B atom.



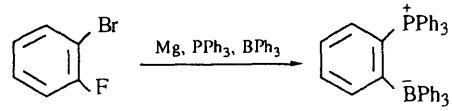
R = Ph; X = NPh, O, S; R = C_6H_{11}, X = NC_6H_{11}.

The structure of the compounds was established by X-ray diffraction studies. The equilibrium processes were studied by NMR and i.r. spectroscopy.

In the studies presented above examples have been described of cyclic betaines containing the P–C=C–B fragment. Such a fragment occurs also in the acyclic molecule 1-borato-2-butoxy-2-phosphonium ethene.[94]

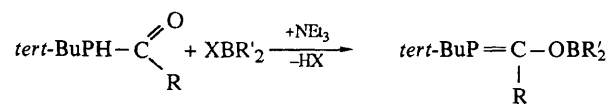


A betaine in which the phosphonium cation and the borate ion are separated by a phenylene fragment was obtained as a secondary product at low yield on interaction of *o*-bromofluorobenzene with Mg, Ph_3P and BPh_3.[95,96]

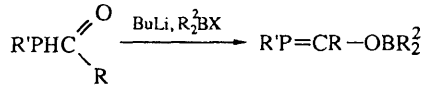


VII. Compounds containing fragment P=C–O–B

This type of compound may be obtained from acylphosphites[97] or from their lithium derivatives[98–100] on interaction with halogenboranes:



X = Cl, Br, R = Alk, R' = Alk, NMe_2;



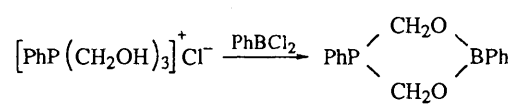
R', R = Alk, Ar; R^2 = Alk, $NAlk_2$.

Germanium, tin and phosphorus halides were used in the reactions, although in these cases not methylenephosphines but hetero-substituted acylphosphines are formed.

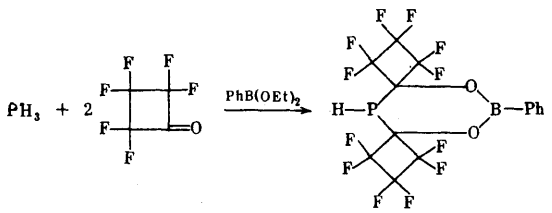
Boryloxymethylenephosphines, i.e. compounds containing a two-coordinate phosphorus atom, constitute an interesting class of hetero-organic derivatives possessing considerable synthetic potential.

VIII. Compounds containing fragment P–C–O–B

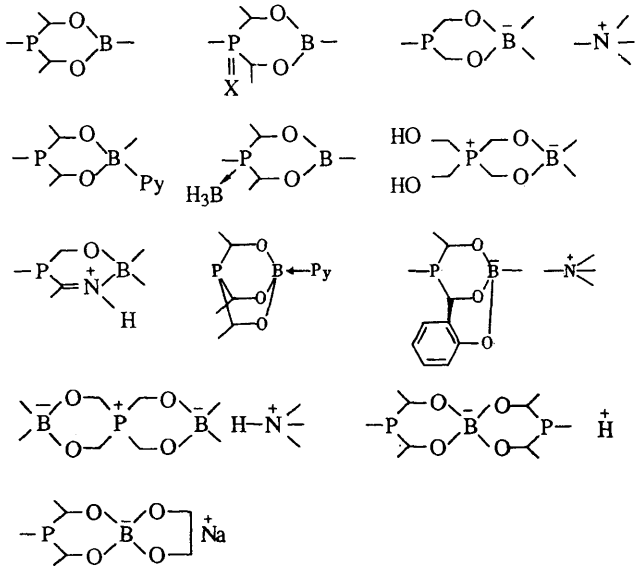
A study of the properties of compounds containing P and B atoms separated by a particular fragment shows that these properties are often determined by the presence of an interaction of heteroatoms, and the nature of the interaction may differ. For chemical compounds containing the P–C–O–B fragment the interaction of the P and B atoms plays a decisive role and is reflected in both the reactivity and the three-dimensional structure of the compounds. The synthesis and properties of the boryloxyalkylphosphines and their analogues are described in a number of articles and reviews.[3,5,90,101] Most of the boroxyalkylphosphines and their derivatives are heterocyclic compounds. The first member in this series was obtained in 1964.[102]



A report was then published which described the synthesis of 1,3,2,5-dioxaboraphosphorinane with hexafluorocyclobutyl substituents in the heterocycle.[103]

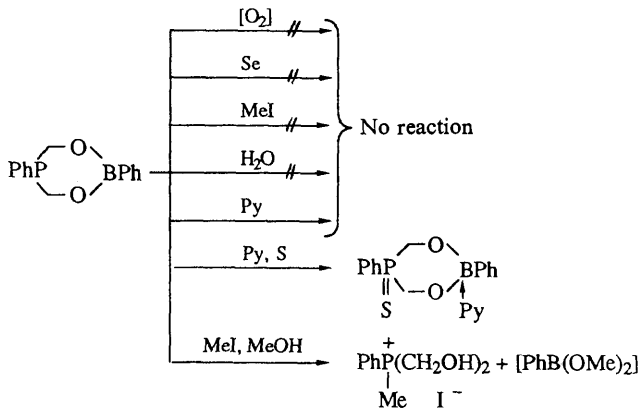


Starting from 1979 a series of studies by B A Arbuzov, O A Erastov, and G N Nikonov was published on the synthesis and properties of boroxyalkyl derivatives of phosphorus. Various heterocyclic compounds containing the P–C–O–B fragment in which the P and B atoms occur in different valence states were synthesised.

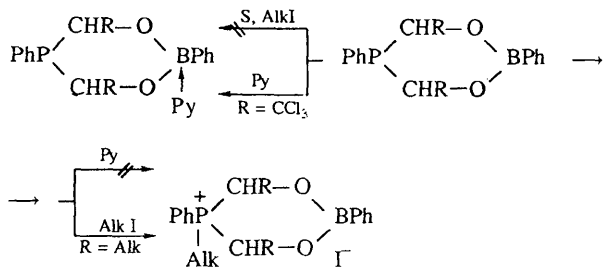


Here we shall emphasise only the properties which illustrate the interaction of the heteroatoms in the P–C–O–B system. They are most clearly apparent in the three-coordinate P and B atoms. Thus the unusually high content of conformer with axial orientation of Ph at the P atom in the conformational equilibrium of 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinone (95%) can be attributed to the n-σ^*-interaction of the unshared electron pair at the P atom and the vacant orbital of the C–O bond. The interaction resulted from the expression of the acceptor properties of the B atom. This type of interaction by the heteroatoms explains satisfactorily the change in content of the stereoisomers or conformers on transition from dioxaboraphosphorinanes to their oxides, sulphides and selenides, which is contrary to the change in ratios of the stereoisomers in the series of dioxaphosphorinanes and their oxides, sulphides and selenides.[101]

The mutual effect of the heteroatoms is even more obviously expressed on examination of the chemical properties of 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane.[3,101] The presence of three-coordination P and B atoms should confer upon this compound properties typical of tertiary phosphines and phenylboric acid esters. However this compound shows anomalous reactivity. Despite the presence of the phosphine fragment it is not oxidised by atmospheric oxygen, it slowly adds sulphur, forms an unstable selenide, and does not interact with methyl iodide. The reactivity of the oxyboryl fragment also fell sharply, which is reflected in the resistance to hydrolysis even by aqueous methanol and in the absence of complex formation with pyridine. However if it operates simultaneously at two reaction centres (the P and B atoms), the reaction proceeds normally, giving rise to the corresponding derivatives with the same reagents.

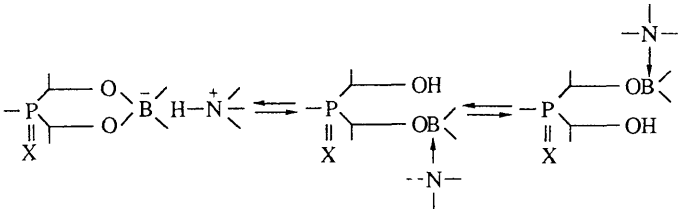


This all indicates the existence of an intramolecular interaction of the heteroatoms (an intermolecular interaction is discounted on the basis of data obtained by using physicochemical techniques). This interaction may be disrupted by varying the nature of the substituent in positions 4 and 6 of the heterocycle. Thus the presence of donor (alkyl) substituents in the 4,6-positions of the 1,3,2,5-dioxaboraphosphinane leads to alkylation by alkyl halides in the absence of methanol. On the contrary 4,6-*bis*-(trichloromethyl)-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane is not alkylated at the P atom and does not add sulphur, but forms a stable complex with pyridine, despite the three-coordinate P atom.



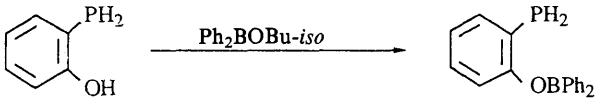
The chemical properties of the boroxialkyl derivatives of phosphorus have been described in a number of reports.[3,101] Reactions with electrophilic reagents leading to an increase in the coordination number of the P atom, the reaction with dipolar reagents (aldehydes) leading to betaines, and reactions with nucleophilic reagents (amines) in which the P–C–O–B fragment is preserved, or disrupted with the formation of aminomethyl derivatives of phosphines, ion-exchange reactions, and thermal transformations, etc. were studied. One of the characteristic features

of the boroxyl derivatives of phosphorus possessing a mobile hydrogen atom is high tautomeric lability, and the tautomeric transformations are caused by the transfer of two particles, a hydrogen atom and a nitrogen atom with the involvement of oxygen and boron atoms, and migration of the boryl grouping also occurs when degenerated tautomerism is taken into account.[3,101]

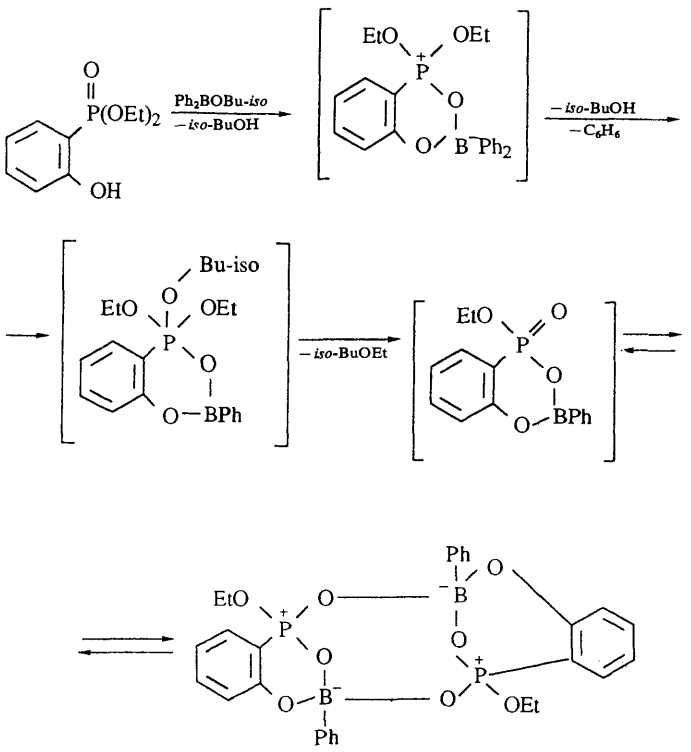


Polymers have been described for this type of tautomerism, ion-complex tautomerism: bicyclo-cyclic ion-complex tautomerism, ion–ion ring-chain, and other.[3,101]

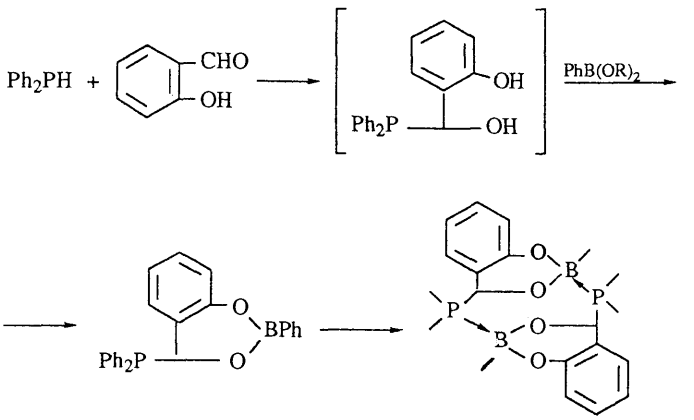
It has been previously shown that borating of *o*-oxyphenylphosphine leads to the formation of *o*-diphenylboryloxyphenylene phosphine and takes place under severe conditions.



The reaction with *o*-oxophenylphosphonate also occurs at high temperatures but in this case the dimer of the corresponding 1,3,2,4-dioxaborophosphinone is formed, which has been shown by X-ray diffraction. The reaction probably takes place with the involvement of isobutyl alcohol formed in the first stage.



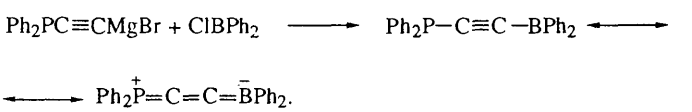
The synthesis of a compound in which the phosphine fragment is the exocyclic substituent relative to the oxyboryl ring has been described. The nature of the interaction of the heteroatoms changed despite the fact that the P–C–O–B fragment was preserved. By combining the data obtained (chemical behaviour, spectral characteristics, RMM, etc.) it was concluded that the P and B atoms undergo intermolecular interaction.[105]



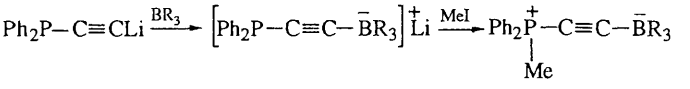
The specific characteristics and the diversity of properties of the boroxyalkyl derivatives of phosphorus can be attribtued to the presence of heteroatoms with opposite electronic behaviour (donor and acceptor) and to the ability of the atoms to change reversibly their coordination and to the presence of an interaction of the heteroatoms transferring in the P–C–O–B system. These features may form the basis of the construction of new structures containing fragments with interacting groups or type A–X–Y–B heteroatoms where A is the donor, B is the acceptor, and X–Y is the fragment with the ability to conduct the interaction of the heteroatoms (C–O, C–N, C–P, C=C, etc.).

IX. Compounds containing fragment P–C≡C–B

Among a large number of acetylene phosphines the synthesis of 1,2-borylphosphinoacetylene with a yield of 64% is presented. Taking into account the ability of the P and B atoms to form betaine structures, the end product structure should be presented as a canonical equation:[106]

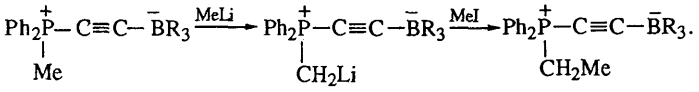


Diphenylphosphinoacetylene may serve as the original compound for the synthesis of phosphinoboratoacetylene[107]



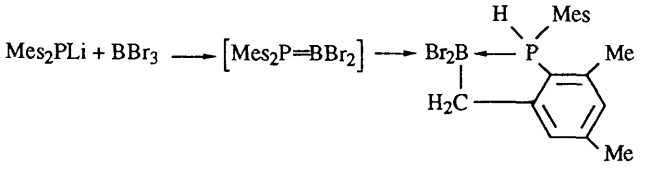
R = CH_2Ph, Ph.

Sequential treatment of this betaine with lithium using MeLi and treatment with MeI leads to the extension of the hydrocarbon chain at the phosphorus atom:

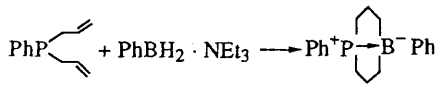


X. Compounds containing fragment P—(C)$_n$—B and others

There are several studies describing P,B-containing compounds in which the P and B atoms are separated by a chain of three carbon atoms and in which these atoms are even more remote from each other. In this case the nature of the interaction of the P and B atoms is different and is manifested as a transannular interaction of the donor and acceptor centres, which leads to the formation of a P→B intramolecular bond. One report is noteworthy in this regard.[108] An attempt was made to obtain dimesitylphosphenylborane from lithium dimesitylphosphide and tribromoborane. However instead a new heterocycle was isolated. The reaction is accompanied by a 1,3-migration of the hydride ion.

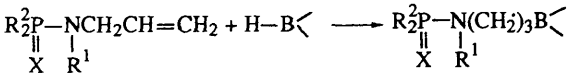


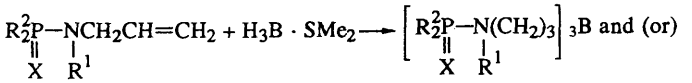
The formation of a strong intramolecular P→B cordinated bond during the hydroboration of dialkylphenylphosphine by triethylaminephenylborane leads to the formation of the bicyclic product, 1-borata-5-phosphoniabicyclo[3.3.0]octane.[109]

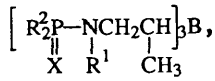


The presence of a coordinate bond in this compound is confirmed by NMR spectra and also by its resistance to oxidation and hydrolysis.

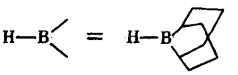
A series of studies has been described of the hydroborination of allyl and propionyl derivatives of N-phosphorylated amines.[110–113]

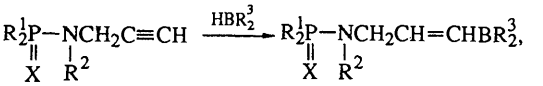






R^1, R^2 = OAlk, Alk, Ar, X = O, S,

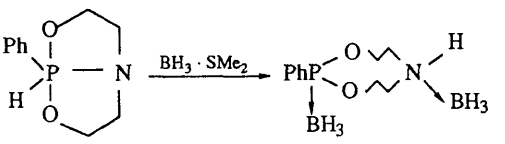




R^1 = OEt, NMe_2; R^2 = Me, CH_2Ph; R^3 = C_5H_{11}, C_6H_{11}, C_8H_{14}; X = O,S.

The hydroboration reactions are regioselective and stereoselective. Compounds in which the boron atom is situated in the δ-position relative to the P atom are formed with a yield of 90–100%. No data are presented on the interaction of the phosphoryl and boryl groups.

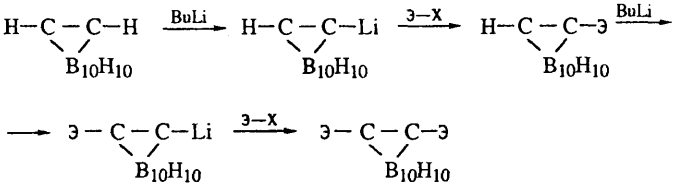
The following is yet another example of a compound containing a δ-atom of boron.[114]



There are also groups of compounds with a different combination of P and B atoms. There are the phosphaborohydrides and coordination compounds in which ligands contain P and B atoms separated by a particular fragment. Compounds of different structure are grouped into one section because the heteroatoms in these compounds are involved in the formation of coordinated or multiple-centre bonds. In line with the general layout of this review only compounds with a fragment between the P and B atoms will be examined.

XI. Phosphaborohydrides

These types of compounds have been known for a long time and have been described in the monograph by B M Mikhailov.[6] However, as before, they continue to attract the attention of research workers. This is because the carborane framework structure imposes certain steric requirements and possesses strong acceptor properties, while on account of the high mobility of the hydrogen atoms at the carbon atoms or in the framework structure different heteroatomic fragments may be introduced via the lithium derivatives.[115,116]



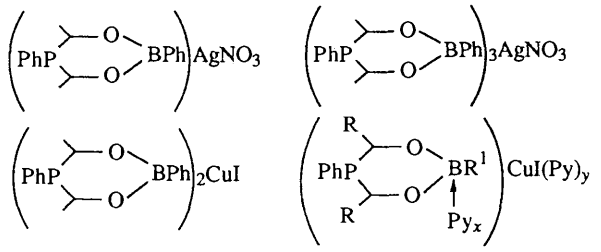
Э = H, As, Si, P.

The opportunity of introducing alkyl or vinyl groups to the C atoms in the *o*-carboranes increases the number of possible compounds. The compounds formed may contain one or two phospha groups separated by one or several carbon atoms from the carborane fragment.

XII. Coordination compounds

On account of the presence of an acceptor or an *o*-carborane group as a functional group in the organophosphorus compound, especially when the P and B atoms interact, these compounds are found to be an interesting type of ligand, and in complexes of these compounds new unusual interactions and bonds may be realised. On the whole all types of PBC compounds may be regarded as potential ligands. The coordination derivatives of PBC may be synthesised by different methods. This is the use of PBC as ligands, the introduction of the phospha group into the coordination compound already containing a boryl fragment in the ligand, or introduction of the boryl group into the complex with a phosphorus-containing ligand.

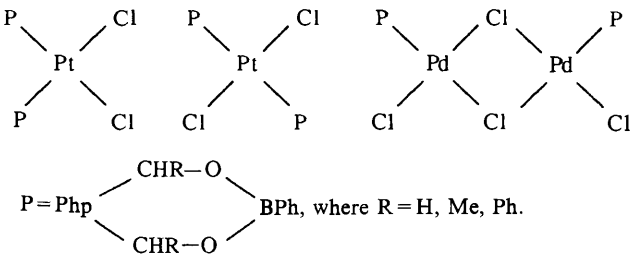
Thus the 1,3,2,5-dioxaboraphosphorinanes have been used as ligands during the synthesis of compounds coordinated to metal salts.[117–119] It was found that Cu(I) and Ag(I) are coordinated at the oxyboryl fragment and depending on the ratio of the reagents complexes of different composition may be obtained.



R = Me, R^1 = Ph, $x = 0, y = 1$
R = Me, R^1 = CBu_3, $x = 0, y = 1$
R = Ph, R^1 = Ph, $x = 1, y = 2$
R = Ph, R^1 = CBu_3, $x = 0, y = 1$

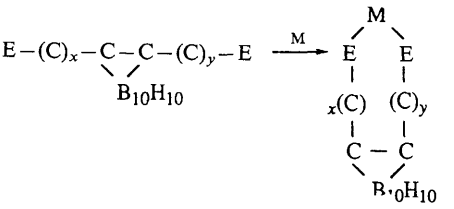
Attempts have been made to determine the three-dimensional structure of the heterocyclic ligands in solutions of the complexes and to correlate the composition and structure of the complexes with the nature of the substituents in the ring.[118]

1,3,2,5-Dioxaboraphosphorinones form complexes with platinum(II) chloride (composition 2:1). Conclusions on the structure of complexes in the solutions have been made from ^{1}H- and ^{31}P-NMR and i.r. spectra in the longwave range and they have been compared with data on the free ligands. The configuration of the central ion differs depending on the substituent in the 4,6-position of the heterocycle.[119]



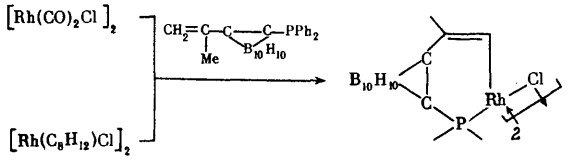
These heterocycles form 1:1 complexes with palladium(II) chloride even in excess of ligand.

Hetero-substituted carboranes are very interesting types of ligands or chelates.[120] The phosphorylated carboranes and their analogues are systematically used as ligands, and phosphorus-containing or such functional groups as for example isopropenyl may be the donor centres involved in the formation of coordination bonds.[115,116,121]



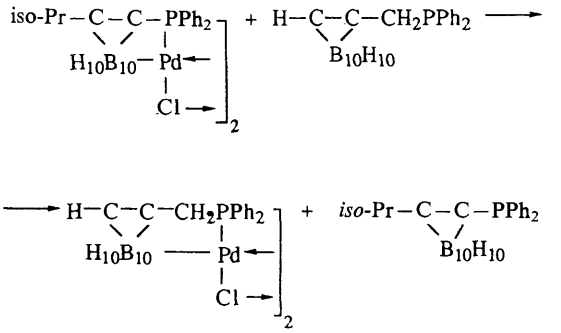
(C) = CH_2, CH_2CH_2, CH=CH etc.
|
Me

$x, y = 0, 1, 2$; E = PR_2, AsR_2, SH; M = Metal

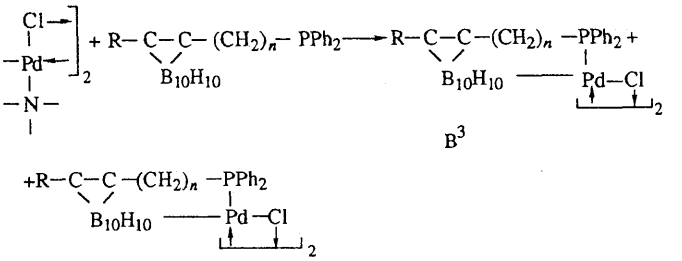


C_8H_{12} = 1.5-cylooctadiene

The metal complexes of phosphorylated carboranes possess the ability to exchange ligands with the involvement of only P-donor molecules. In this case a boron–metal bond is disrupted and formed.[122]



This transition may be attributed to the high stability of the 5-membered ring in comparison with the 4-membered metallo ring. On metallisation of the phorphorylated *o*-carboranes two isomeric products may be formed owing to the formation of the B–Pd bond in a different position of the *o*-carborane.[123]



B^3

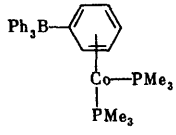
B^4

By using coordination compounds of phosphorus and boron for the synthesis of PBS it is possible to obtain most unusual and unexpected structures in which these atoms are linked by bonds of atypical valency or via metal atoms. For example a unique structure has been obtained on interaction of the triethylphosphine complex of cobalt with sodium tetraphenylborate.[124]

$$Co(PMe_3)_3Br + NaBPh_4 \longrightarrow Co(PMe_3)_4BPh_4 +$$

$$+ \; Co(PMe_3)_2BPh_4 + NaBr.$$

An X-ray diffraction study of the cobalt complex with two phosphine ligands showed the unusual structure of this compound.



Methods have been systematically developed to obtain and study the properties of the $P_x-M-(B_yH_z)$ type of metallo boron hydride complexes where P is the phosphorus-containing ligand, and M = Pt, Os, and Rh, and (B_yH_z) are the boron hydrides, B_6H_9, B_8H_{11}, $B_{10}H_{11}$, $B_{16}H_{15}$ and B_9H_{10}, etc.[125–131] These coordination compounds are formed on interaction of the metal complexes with the anions of the corresponding boron hydrides, for example:[129]

$$[RuCl_2(PPh_3)_3] + [B_{10}H_{10}]^{2-} + 2EtOH \longrightarrow$$

$$\longrightarrow [(PPh_3)_2RuB_{10}H_8(EtOH)_2] + PPh_3 + 2Cl^- + 2H_2.$$

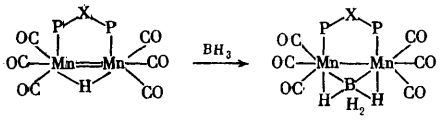
In this type of compound the P atom is linked with the borohydride fragment via a metal atom.

Complexes with a more complicated structure may be obtained in which the substituents are bound in the phosphorus-containing ligand with the borohydride fragment.[129–131]

$$[OsCl_2(PPh_3)_3] + [B_{10}H_{10}]^{2-} + 2EtOH \longrightarrow$$

$$\longrightarrow [(PPh_3)(Ph_2PC_6H_4)OsB_{10}H_7(OEt)_2].$$

The interaction of unsaturated manganese dihydrides containing phosphine ligands with B, Si and Sn hydrides has been studied.[132] When a borane was used, a complex in which the hydride anion enters the inner coordination sphere was obtained.

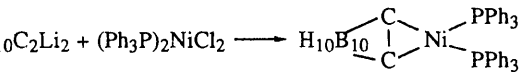


P—X—P = $Ph_2PCH_2PPh_2$, $(EtO)_2PCH_2P(OEt)_2$

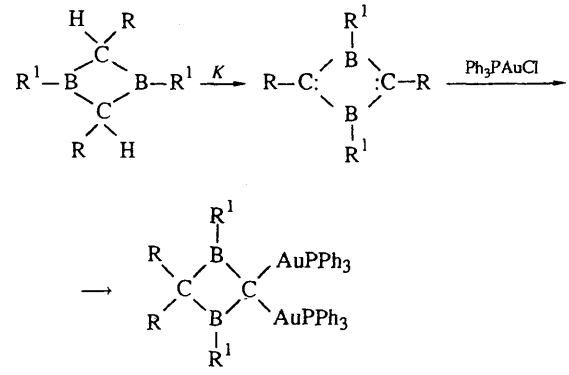
Closo-complexes of the carboranes have been obtained by the interaction of rhodium triphenylphosphine complexes with C-substituted nido-carborane-anions ($C_2B_9H_{12}$).[133,134]

The dilithium derivative of *o*-carborane reacts with the *bis*-(triphenylphosphine)complex of nickel dichloride, expressing the properties of a chelate ligand.[135]

$$o\text{-}B_{10}H_{10}C_2Li_2 + (Ph_3P)_2NiCl_2 \longrightarrow$$

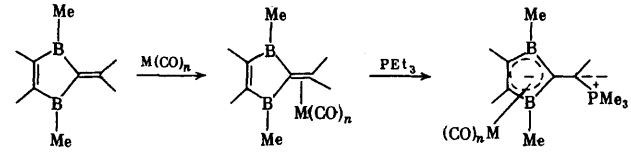


On treatment with metallic potassium 1,2-dihydro-1,3-diboretane gives rise to a dianion, which forms a binuclear complex with the gold triphenylphosphinechloride complex. During complex formation migration of the *tert*-butyl or silyl group in the dianion occurs.[136]



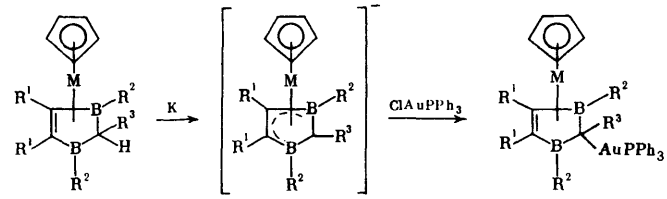
$R^1 = NMe_2$, $N(Pr\text{-}iso)_2$; R = *tert*-Bu, $SiMe_3$.

Coordination compounds containing the phospha- and bora-groups may be obtained also by phosphorylation of organoboron compound complexes with metals.[137,138]



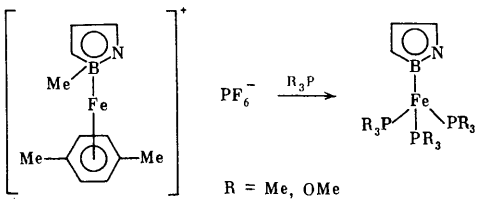
M = Cr, Mo

One example may be given in which on interaction of two complexes, one containing the phosphine ligand and the other with a boron-containing ligand, a third binuclear complex is formed which contains P and B atoms and two different metals.[138]



M = Co, $R^1 = R^2 = Me$, $R^3 = H$; M = Rh, $R^1 = R^2 = Et$, $R^3 = Me$.

The exchange of ligands in the following complex is yet another method used to obtain coordination compounds of PBC.[139]



Most of the above-mentioned coordination compounds containing phosphorylated carborane structures in the ligand have been obtained essentially by an exchange reaction of the ligands at the central ion.

Thus the information presented shows that a large number of quite accessible methods are available to obtain phosphorus-boron-containing compounds leading to the formation of the most diverse cyclic and acyclic structures in which the heteroatoms are bound in different ways and with varied properties which are often dependent on the interaction of the phosphorus-boron-containing functional groups. The nature of these interactions is dependent mainly on the coordination of the heteroatoms and the nature of the fragment, which separates the heteroatoms. When this fragment is a hydrocarbon, for compounds with three-coordinate phosphorus and boron atoms stabilising donor-acceptor interactions through space are most often found, i.e. intermolecular when the heteroatoms are in an α-arrangement and intramolecular when they are in the β- or γ-position, provided that this is not hindered by the rigidity of the binding fragment or the strong *p*-donor substituents at the boron atom. Such interactions reduce the activity of the unshared electron pair of the phosphorus and the vacant orbital of boron, but nevertheless these compounds have a tendency to form very stable betaines. The oxygen atom separating the phosphorus and boron atoms does not hinder the formation of betaine structures, whereas as a result of the partial π-binding with the boron atom the nitrogen atom hinders the donor-acceptor interactions with phosphorus. Even for the betaines the structures with a positive charge on the nitrogen atom and not on the phosphorus atom make a large contribution. Strong donor-acceptor interactions transferring through the system of bonds and stabilising the compounds are also found for the cyclic compounds containing the C–O polar fragment between the heteroatoms. The mutual effect of phosphorus- and boron-containing groups not only changes their reactivity in normal reactions of organophosphorus compounds or organoboron compounds but also in a number of cases leads to a change in their direction. Furthermore processes may occur in which both heteroatoms are involved and in which coordination compounds with unusual bonds are formed, etc. This suggests that this class of compounds has specific characteristics and may be regarded as an independent section of hetero-organic chemistry.

References

1. D Corbridge *Phosphorus* (Translated into Russian), Mir, Moscow, 1982, p. 680
2. G Wilkinson (Editor) *Comprehensive Organometallic Chemistry*, Oxford–New York–Toronto, 1982, Vol. 1, pp. 6–7
3. O A Erastov, G N Nikonov *Funktsional'nozameshchennye Fosfiny i ikh Proizvodnye* (Functionally Substituted Phosphines and their Derivatives), Nauka, Moscow, 1986, 326 pp.
4. B A Arbuzov, G N Nikonov *Rev. Heteroatom Chem.*, 1990, **3** 1
5. O A Erastov, G N Nikonov *Usp. Khim.*, 1984, **53**(4) [English translation in *Russ. Chem. Rev.*, 1984(4)]
6. V M Mikhailov *Khimiya Borovodorodov* (Chemistry of the Boron Hydrides), Nauka, Moscow, 1967, 519 pp.
7. B A Arbuzov, N A Polezhaeva, R P Arshinova *Chem. Rev.*, 1984, **6** 2 (Edited by M E Vol'pin)
8. P Kolle, H Noth, R T Paine *Chem. Ber.*, 1986, **119**(8) 2681
9. A M Arif, A H Cowley, M Pakulski, et al. *J. Chem. Soc., Chem. Commun.*, 1986, (11) 889
10. A H Cowley *Phosphorus Sulfur*, 1987, **30**(1/2) 129
11. A M Arif, J E Boggs, A H Cowley, et al. *J. Am. Chem. Soc.*, 1986, **108**(19) 6083
12. R A Bartlett, X Feng, P P Power *J. Am. Chem. Soc.*, 1986, **108**(21) 6817
13. R A Bartlett, X Feng, M M Olmstead, et al. *Phosphorus Sulfur*, 1987, **30**(1/2) 245
14. B Carriques, C Couret, J Escudie, et al. *Can. J. Chem.*, 1987, **65**(6) 1230
15. R A Bartlett, H V R Dias, X Feng, et al. *J. Am. Chem. Soc.*, 1989, **111**(4) 1306
16. J Rathke, R Schaffer *Inorg. Chem.*, 1972, **3**(5) 1150
17. D Seyfert *Angew. Chem.*, 1960, **72**(1) 6
18. D Purdela, R Vylchanu *Khimiya Organicheskikh Soedinenii Fosfora* (Chemistry of Organophosphorus Compounds), Khimiya, Moscow, 1972, p. 231
19. W Siebert *Z. Naturforsch*, 1976, **25**(3) 314
20. E Fluck, H Bayha, G Heckmann *Z. Anorg. Allg. Chem.*, 1976, **421**(1) 1
21. D R Mathiason, N E Miller *Inorg. Chem.*, 1968, **7**(4) 700
22. D Seyfert, S O Grim *J. Am. Chem. Soc.*,1961, **83**(7) 1613
23. J Svara, E Fluck *Phosphorus Sulfur*, 1985, **25**(2) 129
24. R Koster, B Rickborn *J. Am. Chem. Soc.*, 1967, **89**(11) 2782
25. G Gunter *Diss. Doctorgrad. Naturwiss. Fok. Fridrich-Alexander Univ. Erlangen-Numberd, 1985, 121 pp.*
26. H Schmidbaur, G Muller, G Blaschke *Chem. Ber.*, 1980, **113**(4) 1480
27. H Schmidbaur, G Muller, B Milewsky-Mahria, et al. *Chem. Ber.*, 1980, **113**(7) 2575
28. H J Bestmann, H Suhs, T Roder *Angew. Chem.*, 1981, **93**(12) 1098
29. H J Bestmann, T Roder *Angew. Chem.*, 1983, **95**(10) 812
30. H Schmidbaur *Acc. Chem. Res.*, 1975, **8** 62
31. M E Gurskii, D G Perschin, B M Michailov *J. Organomet. Chem.*, 1984, **250**(1) 17
32. M V Sergeeva, A I Yanovskii, Yu T Struchkov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, (11) 2483
33. R Koster, G Seidel, G Muller, et al. *Chem. Ber.*, 1988, **121**(8) 1381
34. H J Bestmann, T Arenz *Angew. Chem.*, 1984, **96**(5) 363
35. D S Matteson, D Majumdar *Organometallics*, 1983, **2**(2) 230
36. H J Bestmann, T Arenz *Angew. Chem.*, 1986, **98**(6) 571
37. H J Bestmann, T Arenz *Tetrahedron lett.*, 1986, **27**(18) 1995
38. E Meller Normann *J. Organomet. Chem.*, 1984, **269**(2) 123
39. J C Driscell, D W Grisley, J V Pustinger, et al. *J. Org. Chem.*, 1964, **29**(8) 2427
40. H Schmidbaur, H J Fuller, G Muller, et al. *Chem. Ber.*, 1979, **112** 1448

41. R Appel, F Vogt *Chem. Ber.*, 1962, **95**(9) 2225
42. M F Hawthorne *J. Am. Chem. Soc.*, 1961, **83**(2) 367
43. G Sub-Fink *Chem. Ber.*, 1986, **119**(7) 2393
44. V A Gilyarov, E T Matrosov *XI Int. Conf. on Phosphorus Chem. Abstr. of Posters*, Tallinn, 1989, p. 1–87
45. H Noth, D Reiner, W Storch *Chem. Ber.*, 1973, **106**(5) 1508
46. G Muckle, H Noth, W Storch *Chem. Ber.*, 1976, **109**(7) 2572
47. W Storch, W Jackstress, H Noth, et al. *Angew. Chem.*, 1977, **89**(7) 494
48. H Noth, W Storch *Chem. Ber.*, 1977, **110**(7) 2607
49. W Storch *III Intern. Meeting Boron Chem. Ettal*, July, 1976
50. H Noth, W Storch *Chem. Ber.*, 1984, **117**(6) 2140
51. W Maringgele, A Meller, H Noth, et al. *Z. Naturforsch*, 1978, **33**(6) 673
52. B-L Li, R H Neilson *Inorg. Chem.*, 1986, **25**(3) 361
53. D E J Arnold, E A V Ebsworth, G W H Rankin *J. Chem. Soc., Dalton Trans.*, 1976, (9) 823
54. H W Roesky *Chem. Ber.*, 1972, **105**(5) 1726
55. P Kolle, H Noth, R T Paine *Chem. Ber.*, 1989, **122**(3) 423
56. E Niecke, W Bitter *Angew. Chem.*, 1975, **87**(1) 34
57. W Jacksties, H Noth, W Storch *Chem. Ber.*, 1985, **118**(5) 2030
58. K Barlos, H Noth, B Wrackmeyer, et al. *J. Chem. Soc., Dalton Trans.*, 1979, (3) 801
59. H Noth, A Brandl *Chem. Ber.*, 1988, **121**(7) 1321
60. A Brandl, P Kolle, H Noth *Chem. Ber.*, 1989, **122**(3) 419
61. P Paetzold, C von Plotho, E Niecke, et al. *Chem. Ber.*, 1983, **116**(9) 1678
62. D Gudat, E Niecke, M Nieger, et al. *Chem. Ber.*, 1988, **121**(3) 565
63. C Malavaud, T N G M'Pondo, L Lopez, et al. *Can. J. Chem.*, 1984, **62** 43
64. B-L Li, P Mukherjee, R H Neilson *Inorg. Chem.*, 1989, **28**(3) 605
65. R Koster *Methoden der Organischen Chemie* (Edited by R Koster) Thieme, Stuttgard, 1982, No. XIII/3a, pp. 494, 509
66. R Koster, L Sunoradzki *Chem. Ber.*, 1984, **117**(9) 2850
67. R Koster, W Schubler, L Sunoradzki *Chem. Ber.*, 1987, **120**(7) 1105
68. R Koster, Tsay Yi-Hung, L Sunoradzki *Chem. Ber.*, 1987, **120**(7) 1117
69. A B Burg, J S Basi *J. Am. Chem. Soc.*, 1969, **91**(8) 1937
70. A B Burg, W E McKee *J. Am. Chem. Soc.*, 1951, **73**(10) 4590
71. J L Vidal, G E Ryschkewitsh *J. Inorg. Nucl. Chem.*, 1976, **38**(11) 1937
72. S K Xi, H Schmidt, C Lensink, et al. *J. Inorg. Nucl. Chem.*, 1990, **29**(12) 2214
73. H Noth, W Regnet, H Rihl, et al. *Chem. Ber.*, 1971, **104**(3) 722
74. M J Braun, M G Champelier *Compt. Rend. Acad. Sci. Paris*, 1965, **260**(1) 218
75. H Normant, J Braun *Compt. Rend. Acad. Sci. Paris*, 1959, **248**(4) 826
76. P Binger, R Koster *J. Organomet. Chem.*, 1974, **73**(2) 205
77. H O Berger, H Noth *Z. Naturforsch*, 1975, **30**(4) 641
78. H O Berger, H Noth *J. Organomet. Chem.*, 1983, **250**(2) 33
79. R Koster, L A Hagelee *Synthesis*, 1976, (2) 118
80. L A Hagelee, R Koster *Synth. React. Inorg. Metal-Org. Chem.*, 1977, **7** 53
81. A S Balueva, O A Erastov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, (1) 163
82. S G Vul'fson, N N Sarvarova, A S Balueva, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, (1) 1445
83. A S Balueva, Yu Ya Efremov, V M Nekhoroshkov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, (11) 2793
84. A S Balueva, O A Erastov, T A Zyablikova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, (2) 975
85. L V Ermolaeva, A S Balueva, O A Erastov, et al. *Zh. Obshch. Khim.*, 1990, **60**(4) 755
86. T V Troepol'skaya, L V Ermolaeva, G A Vagina, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, (1) 24
87. G A Vagina, T V Troepol'skaya, A S Balueva, et al. *J. Heyrovsky Centennual Congress on Polarography. Prague, Chechoslovakia, Aug. 20–25th 1990, Proceedings II, Th. 109*
88. A S Balueva, A A Karasik, G N Nikonov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, (9) 2147
89. A S Balueva, G N Nikonov, N N Sarvarova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, (11) 2613
90. R M Kamalov, G N Nikonov, A S Balueva, et al., Authors' Certificate USSR, Application No. 484378/04 from 28.06.1990 1990
91. A S Balueva, G N Nikonov, R M Kamalov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, (11)
92. B A Arbuzov, G N Nikonov, A S Balueva, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, (11)
93. B A Arbuzov, P M Kamalov, G N Nikonov, et al. *Tetrahedron Lett.*, 1991 (in press)
94. A M Torgomyan, A S Pogosyan, M Zh Ovakimyan, et al. *Arm. Khim. Zh.*, 1980, **33**(5) 408
95. G Wittig, H Matzura *Annalen*, 1970, **732**(2) 97
96. G Wittig, E Benz *Chem. Ber.*, 1959, **92**(9) 1999
97. E G Neganova, R V Brunov, Yu A Veits, et al. *Zh. Obshch. Khim.*, 1988, **98**(1) 226
98. Yu A Veits, E G Neganova, V L Foss *Zh. Obshch. Khim.*, 1986, **56**(3) 715
99. Yu A Veits, E G Neganova, N A Borisenko, et al. *Dokl. Akad. Nauk SSSR*, **292**(5) 1131
100. E G Neganova, Yu A Veits, A A Borisenko *XI. Int. Conference on Phosphorus Chemistry. Tallinn. USSR, July 3–7*, 1989. Abstr. of Posters, Vol. 1, No. 1–27
101. B A Arbuzov, G N Nikonov, O A Erastov, et al. *Izv. Akad. Nauk SSSR*, 1990, (5) 1120
102. M Pailer, H Huemer *Monatch. Chem.*, 1964, **95**(2/3) 73
103. G W Parshall *Inorg. Chem.*, 1965, **4**(1) 52
104. A S Balueva, G N Nikonov, S G Vul'fson, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, (1) 477
105. A S Balueva, S R Prokhorova, G N Nikonov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, (12)
106. C Charrier, W Choclkiewicz, P Cadiot *Bull. Soc. Chim. Fr.*, 1966, **3** 1002
107. H J Bestmann, H Behl, M Bremer *Angew. Chem.*, 1989, **101**(9) 1303
108. H H Karsch, G Hanika, B Huber, et al. *J. Chem. Soc., Chem. Commun.*, 1989, (6) 373
109. G B Butler, G L Statton *J. Am. Chem. Soc.*, 1964, **86**(22) 5045
110. Z Benmaarouf-Khallaayoun, M Baboulene, V Speziale *Synth. Commun.*, 1985, **15**(3) 233
111. Z Benmaarouf-Khallaayoun, M Baboulene, V Speziale *Phosphorus Sulfur*, 1988, **36**(3–4) 181
112. Z Benmaarouf-Khallaayoung, M Baboulene, V Speziale *J. Organomet. Chem.*, 1986, **306**(3) 283
113. Z Benmaarouf-Khallaayoung, M Baboulene, V Speziale *J. Organomet. Chem.*, 1985, **289**(3) 309
114. R Contreras *Tetrahedron Lett.*, 1981, (22) 3953

115. L I Zakharkin, A V Kazantsev, M G Meiramov *Zh. Obshch. Khim.*, 1984, **54**(7) 1536
116. L I Zakharkin, K M Uyzbaev, A V Kazantsev, et al., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, (9) 2134
117. A A Karasik, G N Nikonov, B A Arbuzov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, (9) 2134
118. B A Arbuzov, G N Nikonov, A A Karasik, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, (4) 906
119. A A Karasik, G N Nikonov, B A Arbuzov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, (12)
120. V N Kalinin, A V Usatov, L I Zakharkin *Metallorg. Khim.*, 1989, **2**(2) 54 [English translation in *Organomet. Chem. USSR*, 1989(2)]
121. V N Kalinin, A V Usatov, N I Kobel'kova *Zh. Obshch. Khim.*, 1985, **55**(8) 1874
122. A V Ryabov, A V Usatov, V N Kalinin, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, (5) 1212
123. A V Ryabov, A V Usatov, V N Kalinin, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, (12) 2790
124. L C A Carvalho, M Partiguenave, J Dartiguenave, et al. *J. Am. Chem. Soc.*, 1984, **106**(22) 6848
125. J Bould, N N Greenwood, J D Kennedy *J. Chem. Soc., Dalton Trans.*, 1984, (11) 2477
126. J E Crook, N N Greenwood, J D Kennedy *J. Chem. Soc., Dalton Trans.*, 1984, (11) 2487
127. X L R Fontaine, H Fowkes, N N Greenwood, et al. *J. Chem. Soc., Chem. Commun.*, 1985, (17) 1165
128. M A Beckett, N N Greenwood, J D Kennedy *J. Chem. Soc., Chem. Commun.*, 1986, (7) 556
129. M Elrington, N N Greenwood, J D Kennedy, et al. *J. Chem. Soc., Dalton Trans.*, 1986, (10) 2277
130. R Ahmad, J E Crook, N N Greenwood, et al. *J. Chem. Soc., Dalton Trans.*, 1986, (11) 2433
131. G Ferguson, M C Jennings, A J Lengh, et al. *J. Chem. Soc., Chem. Commun.*, 1990, (12) 891
132. R Carreno, V Riera, M A Ruiz *J. Chem. Soc., Chem. Commun.*, 1990, (1) 15
133. R T Baker, M S Delaney, R E King, et al. *J. Am. Chem. Soc.*, 1984, **106**(10) 2965
134. J D Hewes, M Thompson, M F Hawthorne *Organometallics*, 1985, **4**(1) 13
135. A A Sayler, H Beall, J F Sieckhaus *J. Am. Chem. Soc.*, 1973, **95**(17) 5790
136. P Hornbach, M Hildenbrand, H Pritzkow, et al. *Angew. Chem.*, 1986, **98**(12) 1121
137. V Schafer, H Pritzkow, W Siebert *Chem. Ber.*, 1989, **122**(3) 401
138. K Geilich, K Stumpt, H Pritzkow, et al. *Chem. Ber.*, 1987, **120**(6) 911
139. G Schmid, G Barbenheim *Chem. Ber.*, 1987, **120**(3) 401

Translated from *Uspekhi Khimii* 61 647–667 (1992)

U.D.C. 678.86:546.27

Effect of carborane groups and the structure of their surrounding organic residues on the reactivity of monomers and properties of polymers

N I Bekasova, N G Komarova

Nesmeyanov Institute of Organometal Compounds, Russian Academy of Sciences, Moscow

ABSTRACT. The results of studies on carborane-containing polymers concerning the effect of carborane rings and the structure of the organic residues adjacent to carborane groups on the reactivity of monomers and the properties of the polymers obtained have been correlated.

The bibliography includes 109 references.

Contents

I. Introduction 352
II. Effect of carborane groups on the reactivity of monomers 352
III. Effect of carborane groups on the properties of carborane-containing polymers 354
IV. Effect of the configuration of carborane groups in a macromolecule and the structure of the residues directly bonded to them on the properties of carborane-containing polymers 358

I. Introduction

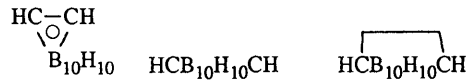
The first reports on the synthesis and properties of carborane-containing polymers were published in 1963.[1,2] Studies on the synthesis and research into the properties of carborane-containing polymers are undergoing rapid development at the present time. These polymers have attracted the attention of research workers because they have a whole series of interesting and valuable properties, such as a combination of high thermal stability and ready solubility. Many of these unusual polymers are capable of withstanding extremely severe conditions, under which normal organic polymers are almost completely degraded.

Carborane-containing polymers are obtained by both polycondensation and polymerisation. Polymers with different structures — polyethers, polycarboranylenes, polyamides, polyphenylenes, polyurethanes, polysiloxanes, polyazoles, and polyphosphazenes, etc. — have been reported.[3–14]

Some recently published reviews[15–18] are concerned with a correlation of the results on the synthesis and research into the properties of carborane-containing polymers.

The chemical structure of the monomer unit of a polymer is known to be one of the main factors governing its properties. Therefore, a study of the dependence of the properties of polymers on the structure of the initial components has both theoretical and practical value, since it makes it possible to carry out the directed synthesis of polymers with predetermined properties. The specific characteristics of icosahedral carborane groups are a negative inductive effect and steric hindrance, which have a considerable effect on the reactivity of monomers and the properties of the polymers obtained.

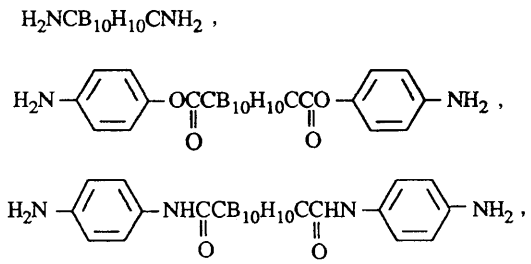
In this review an attempt is made to correlate the theoretical and experimental material on the synthesis and research into the properties of carborane-containing polymers in relation to the specific characteristics of carborane groups. The review covers polymers obtained from the isomeric carboranes which are usually depicted as follows:[19]



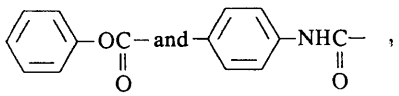
o-carborane *m*-carborane *p*-carborane .

II. Effect of carborane groups on the reactivity of monomers

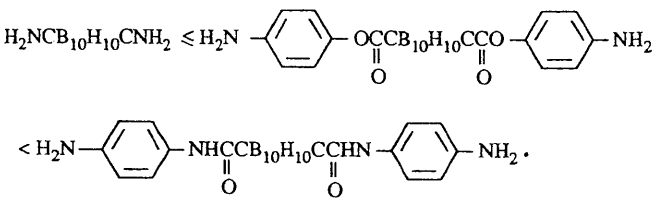
The presence of bulky carborane groups very frequently makes the synthesis of carborane-containing polymers difficult to carry out. However, the reason for the difficulty of synthesis does not arise solely from steric inhibition of polycondensation by the carborane groups (the effective van der Waals radius is equal to 4 Å) but also from the effect of the electron-withdrawing nature of these groups on functional groups in the monomers. Thus, for example, it was established from the kinetic data of acylation of aniline with *m*- and *p*-carboranedicarboxylic acid dichlorides in different solvents that *m*-carboranedicarboxylic acid dichloride is 2–3 times more active than the dichloride of *p*-carboranedicarboxylic acid.[20] This is probably due to the fact that the *p*-carborane group is a weaker electron acceptor than *m*-carborane. In a study of relative reactivity in the acylation of three *m*-carborane-containing diamines with the following structure:



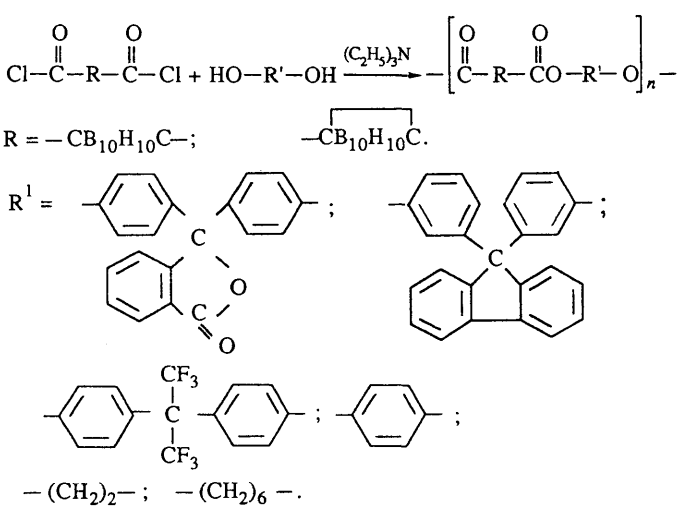
it was shown that introduction of the residues:



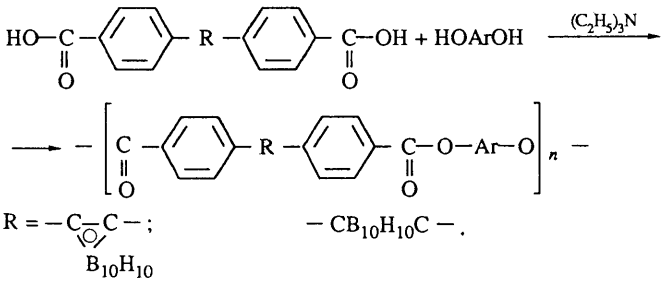
between the amino group and the *m*-carborane cage results in a marked increase in reactivity of the diamines in the following series:[21,22]



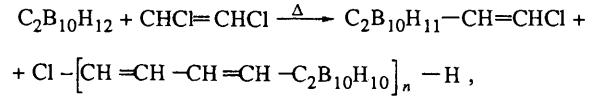
It was established, moreover, that polyesterification of *o*-carborane-containing diols occurs much more slowly than polyesterification of organic diols.[23] If an *o*-carborane group is present in both the diol and dicarboxylic acid, polyesterification occurs at such a low rate that low-molecular-weight compounds are formed.[24,25] However, with a correct choice of the initial reactants and also the synthesis conditions, which made it possible to reduce the steric inhibition of polycondensation and increase the rate of reaction, it proved possible to obtain high-molecular-weight polyesters. For example, if the polycondensation of dichlorides of *m*- and *p*-carboranecarboxylic acids with different diols is carried out in solution in the presence of a catalyst, polyesters with a molecular weight of 20 000 or more are formed:[26–28]



Starting from 1,2- and 1,7-bis(dicarboxyphenyl)carboranes and different dihydric phenols, high-temperature polycondensation in a solution of chlorinated biphenyl at 220 °C or acceptor-catalyst polycondensation in acetone solution gave *o*- and *m*-carborane-containing polyarylates with a molecular weight ranging from 22 000 to 132 000:[29,30]

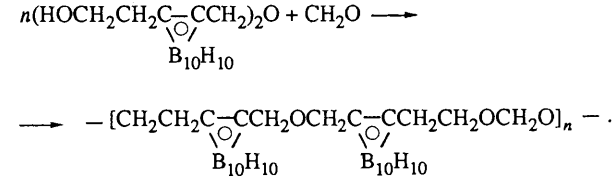


The variation in electron-withdrawing capacity of the groups in the series *o*- > *m*- > *p*-carboranes has an effect on their reactivity towards the addition of 1,2-dichloroethylene.[31] In a study of the kinetics and mechanism of high-temperature condensation of *o*-, *m*-, and *p*-carboranes with 1,2-dichloroethylene according to the reaction:



it was established that *o*- and *m*-carboranes exhibit almost the same reactivity in reactions with 1,2-dichloroethylene while *p*-carborane reacts 1.5 times more slowly than *o*-carborane.

The steric hindrance due to the bulky carborane groups has a very considerable effect on the formation of polyformals.[1] Thus, bis(hydroxymethyl-1-*o*-carboranylmethyl) ether does not react with formaldehyde. When bis(hydroxyethyl-1-*o*-carboranylmethyl) ether is reacted with formaldehyde, an oligomer with a molecular weight of 4400 is obtained:

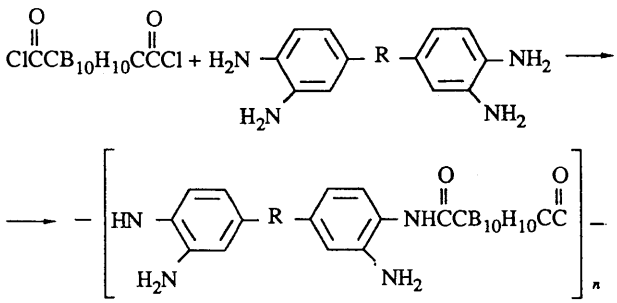


It has been suggested that in order to form polymers it is necessary for the distance between the carborane groups located sequentially to be not less than five carbon atoms at the very least.

The steric hindrance due to a carborane group has a considerable effect on the formation of high-molecular-weight poly(aminoamides).

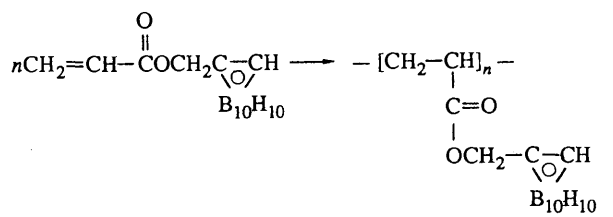
Normally polycondensation of aromatic acid dichlorides with different aromatic tetraamines results in the formation of cross-linked polymers, since the difference between the reactivities of the amino groups at the *ortho* position relative to each other does not change very much after one of them has reacted. When an aromatic acid dichloride is replaced by *m*- or *p*-carboranedicarboxylic acid dichloride, the difference in reactivity between the amino groups at the *ortho* position relative to each other increases after one of them has reacted as a consequence of the steric hindrance caused by the carborane residues. It was therefore possible under certain

conditions to obtain high-molecular-weight polyaminoamides according to the following scheme:[32–35]



R = —O—; —CH_2—; —SO_2—; —$C(CH_3)_2$—; bond.

A polymerisation process is used less frequently than polycondensation to obtain carborane-containing polymers. Not many studies devoted to the homopolymerisation of alkenylcarboranes have been published. The difficulty in conducting this type of synthesis is due to steric hindrance caused by the bulky carborane groups and also the electron-withdrawing nature of the groups, which is responsible for a decrease in electron density on the double bond and hence a decrease in its reactivity. The polymerisation of monomers in which the carborane group is situated some distance from the double bond occurs more readily. For example, 1-acrylyloxymethylene-*o*-carborane readily polymerises in bulk in the presence of 2% benzoyl peroxide at 60 °C:[36]



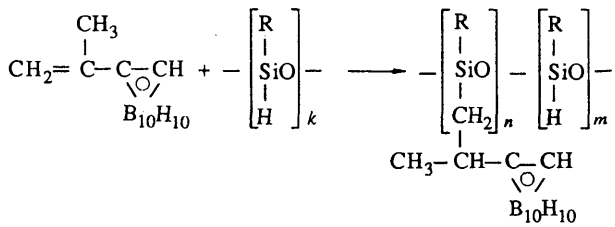
Since the homopolymerisation of carborane monomers occurs with difficulty, there is particular interest in the copolymerisation of carborane-containing compounds with vinyl monomers, making it possible to impart valuable new properties to known polymers through the introduction of carborane cages into their structure. This usually raises the temperature at which polymers start to decompose and increases the yield of carbon residue.

With the aim of modifying low-density polyethylene, the radical copolymerisation of ethylene with isopropenyl-*o*-carborane at a pressure of 1400 kg cm^{-2} and temperature of 160 °C was studied.[37] It was established from the IR spectroscopic data that the rate of copolymerisation and the molecular weight of the polymers decrease rapidly as the content of the *o*-carborane derivative in the reaction mixture increases from 1 to 40 mol%.

A study has been made of the effect of the structure of unsaturated *m*- and *p*-carborane-containing polyesters on their ability to undergo bulk, solution, and emulsion copolymerisation with styrene, acrylonitrile, and 1,1,2-trichloro-1,3-butadiene in the presence of radical and ionic initiators on exposure to γ-radiation or high pressure.[38,39] It was established that the introduction of electron-withdrawing *m*-carborane groups into unsaturated polyesters reduces their reactivity, as a result of which unsaturated polyester-*m*-carboranes in which there is one carborane cage for each unsaturated bond are incapable of undergoing thermochemical cross-linking and only form cross-links on exposure to γ-radiation and high pressure.

In contrast to *m*-carborane-containing polyesters, all polyesters of *p*-carboranedicarboxylic acid undergo copolymerisation with styrene, which evidently may be due to the weaker electron-withdrawing properties of the *p*-carborane cage, having virtually no effect on the reactivity of unsaturated bonds.

Information in the literature about the preparation of carborane-siloxane polymers by polymerisation and copolymerisation methods is sparse. Migration copolymerisation of isopropenyl-*o*-carborane with polyalkylhydroxysiloxanes gave polysiloxanes containing *o*-carborane cages in the side chain.[40,41]



R = CH_3; C_2H_5, C_6H_5; k = *n* + *m*.

Studies showed that without a catalyst there is virtually no reaction below 200 °C and even at higher temperatures the rates of copolymerisation remained low, which may be due to the electron-deficient nature of the carborane cage, which deactivates the adjacent unsaturated bond, and to steric hindrance.

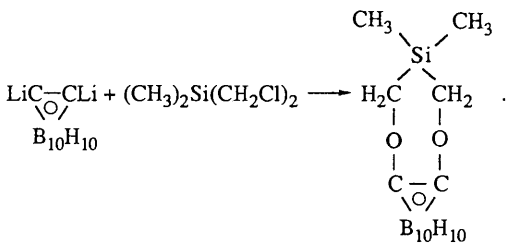
III. Effect of carborane groups on the properties of carborane-containing polymers

In 1963 Grafstein and Dvorak,[42] while attempting to carry out the thermal dehydrodimerisation and dehydropolymerisation of *o*-carborane, found that at 465–500 °C *o*-carborane is isomerised to *m*-carborane, while in 1964 Papetti and Heying,[43] on heating *o*-carborane at 617 °C, obtained a third isomer—*p*-carborane. In neither case were dehydropolymers detected. There are considerable differences in the chemical and phyiscal properties of derivatives of these isomers, which can be classified according to the different configuration of the carbon atoms in the *o*-, *m*-, and *p*-carborane skeleton, resulting in a decrease in electron-withdrawing properties in the series *o*- > *m*- > *p*-isomer,[44,45] and an increase in thermal stability: *o*- < *m*- < *p*-carborane isomer.[46] Moreover, in the series *o*- > *m*- > *p*-carborane isomer, there is a decrease in acidity of the hydrogen atom in the CH group,[47] ease of electrophilic, radical, and exchange halogenation of the B—H bond,[48,49] rate of nucleophilic substitution of the halogen atoms in halogen derivatives of the carborane by other atoms and groups compared to halogen derivatives of benzene and ferrocene.[50] The electron affinity of the carborane system decreases in the same series of isomers as does the ease of cleavage of a C_{carb}—C bond in carborane-containing aldehydes, ketones, acids, and alcohols by nucleophilic reagents. Therefore *o*-carborane derivatives are reduced much more easily than the other carborane isomers, and in the same series the stability towards bases[49,55] and oxidising agents[56] increases, and the volatility of the compounds and in the majority of cases the melting point[19] also increase.

This series of variation in the physicochemical propeties of *o*-, *m*-, and *p*-carboranes and their derivatives is related to the more uniform distribution of electron density in the *p*-carborane cage (all ten boron atoms are equivalent) compared to the *o*- and *m*-carborane cages.

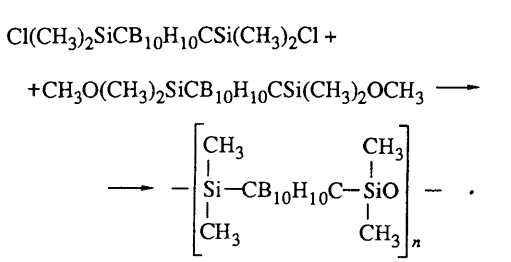
Isomerism of the carborane cage has a considerable effect on the preparation and properties of polymers based on different isomeric derivatives of carboranes.

It follows from a review of the considerable number of studies on the synthesis and research into the properties of carborane-containing polymers that the *m*- and *p*-carborane isomers have a greater tendency to form polymers than the *o*-isomer, since during the development of methods for the synthesis of polymers with *o*-carborane cages in the chain, research workers have frequently encountered steric problems. One of these is typically the tendency of C,C′-difunctional *o*-carborane derivatives to form *exo*-polyhedral rings. This evidently occurs as a result of the adjacent configuration of the carbon atoms in the *o*-carborane cage. The bond between them, with a length equal to that of a single covalent C–C bond (1.64–1.67 Å), is longer than the single covalent C–C bond of alkanes (1.54 Å), thus assisting the formation of *exo*-rings.[57–59] Therefore, the first attempts to synthesise silicon-*o*-carborane-containing polymers with a linear structure were unsuccesful because of the considerable tendency of the initial *o*-carborane-siloxane derivatives to form stable cyclic systems. For example, reaction of *o*-carboranedilithium with dimethyldichloromethylsilane gave a cyclic product instead of the expected polymer:[60]



The lack of success in attempts to synthesise silyl-*o*-carboane with a linear structure stimulated research workers to consider *m*-carborane systems, in which the nonadjacent configuration of the carbon atoms excludes the possibility of exocyclic structures being formed.

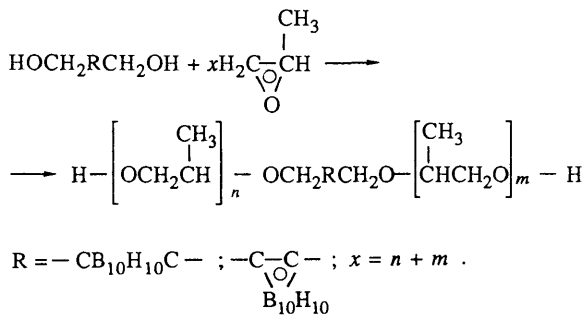
Thus, polycondensation of *m*-carborane-containing chlorosilanes and alkoxysilanes in the presence of a catalyst—ferrous chloride—gave elastomeric *m*-carborane-containing polysiloxanes,[19,61–65] the synthesis of which from the practical point of view may be regarded as an important advance in the development of heat-resistant carborane elastomers.



These polymers (trade name "Dexsil") consist of dialkyl- or diaryl-siloxane units linked by *m*-carborane groups and, in addition to the method already indicated, they are obtained by polycondensation of *m*-carborane-containing disilanol with an active silane such as bis(*N*,*N*-dimethylcarbamato)dimethylsilane or bis(ureidosilanes) or bis(*N*,*N*-dimethylamino)dimethylsilane[11,16,63,64] or directly from *m*-carborane.[65]

There have been reports on the synthesis of "Dexsil" polysiloxanes containing *p*-carborane groups.[66,67] These polymers are elastic materials but more rigid at low temperatures than the corresponding *m*-carborane-containing polysiloxanes.

In the migration copolymerisation of 1,2-bis(hydroxymethyl)-*o*-carborane with epoxypropyltriethoxysilane[68] and 1,2- or 1,7-bis-(hydroxymethyl)-*m*-carborane with propylene oxide[69,70] it was shown that the rate of reaction of propylene oxide with 1,2-bis(hydroxymethyl)-*o*-carborane is higher than with 1,7-bis(hydroxymethyl)-*m*-carborane.

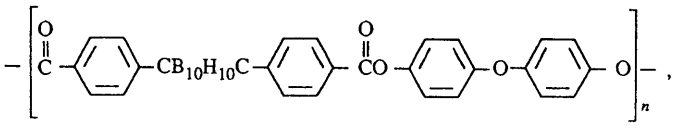


The more pronounced electron-withdrawing nature of the *o*-carborane cage evidently gives rise to a greater proton mobility of the hydrogen atoms of the hydroxyl group and hence assists a higher rate of reaction.

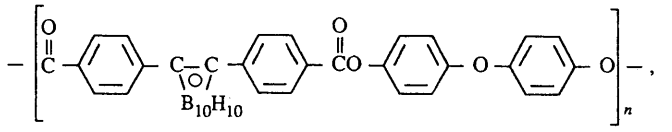
Korshak et al.[4] described the preparation of *o*-, *m*-, and *p*-carborane-containing esters of cellulose by acylating the latter with *o*-, *m*-, and *p*-carboranecarboxylic acid chlorides in toluene in the presence of pyridine at 110 °C. It was established that under these conditions the carborane cage decomposes in *o*- and *m*-carborane-carboxylic acid chlorides to the anion of dicarbaundecaborane while only a small degree of acylation of cellulose occurs (about 2 wt.% boron is introduced). *p*-Carboranecarboxylic acid chloride reacts with cellulose to form a *p*-carborane-containing cellulose ester with about 40 wt.% boron content and which does not dissolve in either organic solvents or in a cuprammonium complex or in cadoxene (a complex between ethylenediamine and cadmium hydroxide). On heating in an inert medium under isothermal conditions at 300 °C for 2 h the "char" residues of *o*-, *m*-, and *p*-carborane-containing cellulose at 48, 39, and 38% of the initial weight respectively. The "char" residue of the initial cellulose under these conditions does not exceed 22 wt.%.

The effect of the isomerism of the carborane cage on the molecular mobility of macromolecules has been demonstrated in two studies.[71,72] It was established that the vibrations of the *o*-carborane cage in polyarylates are more difficult compared to the *m*-isomer because of the greater conjugation of the *o*-carborane residue with the automatic rings and also because of steric effects. This characteristic affects the relaxation processes in carborane-containing

polyesters, and the results of studies on these using different methods suggest that there is an increase in rigidity of the macrochain and an increase in softening point on changing from *m*- to *o*-carborane-containing polyesters, as for example:



$T_{soft} = 240-260$ °C



$T_{soft} = 260-280$ °C.

An essentially ionic form of electrical conductivity is characteristic of carborane-containing polyesters, and the electrical conductivity of *o*-carborane-containing polyesters is higher than those values for the corresponding polyesters with *m*-carborane residues by a factor of 10^1-10^2.[73] All of the polyesters synthesised from bis(hydroxymethyl)-*m*-carborane have a softening point that is lower than that of the corresponding polyesters obtained from bis(hydroxymethyl)-*o*-carborane.[74]

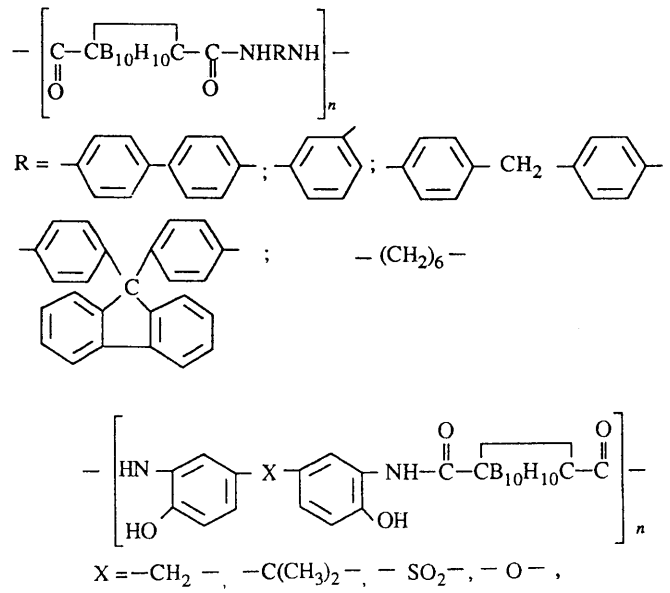
In a study of the properties of solutions of polyarylates obtained by acceptor-catalytic and high-temperature polycondensation from 1,2- and 1,7-(4-carboxyphenyl)carboranes and dihydric phenols such as 4,4′-dihydroxydiphenyl oxide, 4,4′-dihydroxydipyhenyl-2,2-propane, 9,9-bis(4-hydroxyphenyl)fluorene, and 9,9-bis(4-hydroxyphenyl)-10-anthrone, it was established that with similar molecular weight values, polyarylates with 1,7-diphenyl-*m*-carborane residues in the chain have a considerably higher intrinsic viscosity than polymers with 1,2-diphenyl-*o*-carborane residues.[75] The authors were able to conclude from this that polyarylates based on 1,2-bis-(4-carboxy-phenyl)-*o*-carborane are in the form of more compact macromolecular bundles in solution, which can be attributed to both steric factors and to a greater effect from the dipole moment for polyarylates with *o*-carborane groups.

It was established that polyarylates obtained by reaction of *p*-carboranedicarboxylic acid dichlorides with different bisphenols have a softening point that is 40–100 °C higher than that of the corresponding polyarylates of *m*-carboranedicarboxylic acid. However, the "char" residue of *p*-carborane-containing polyarylates at 800 °C is less by 10–20 wt.% than the "char" residue of *m*-carborane-containing polyarylates at the same temperature.[26-28]

In a study of the thermal stability of polyarylates with 1,2- and 1,7-diphenylcarborane residues in the chain in air and in an inert atmosphere under both dynamic and isothermal conditions, it was established thermogravimetrically that carborane-containing polyarylates have a decomposition temperature that is 20–60 °C higher than that of conventional polyarylates.[76] The authors note that all the *o*- and *m*-carborane-containing polyarylates are characterised by a high "char" residue (50–90% of the initial weight of the polymer) when they are heated in air to 900 °C, whereas conventional polyarylates (such as polyarylate D-9) are completely combusted at 650–700 °C. In an inert atmosphere the weight of polyarylates of 1,2- and 1,7-bis(4-carboxylphenyl)-carboranes starts to change at the same temperatures as in air, but their "char" residue after thermal degradation is even higher than on heating in air. On the basis on this the authors assumed that the "char" residue formed on heating *o*-and *m*-carborane-containing polyarylates results not only from oxidation but is generally typical of the thermal degradation of polyarylates of this structure.[76,77]

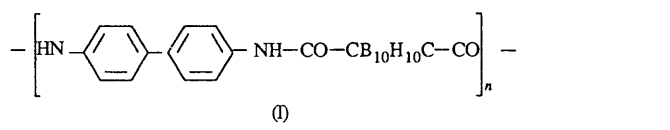
The majority of the *o*- and *m*-carborane-containing polyamides that have been reported are amorphous polymers that are readily soluble in organic solvents, whereas *p*-carborane-containing polyamides have a crystalline structure and an inferior solubility in organic solvents. This is due to the more ordered structure of *p*-carborane-containing polyamides as well as the nonpolar nature of the *p*-carborane cage.[76]

In contrast to infusible *m*-carborane-containing polyamides and poly(hydroxyamides), *p*-carborane-containing polyamides and poly(hydroxyamides) with the following structure:

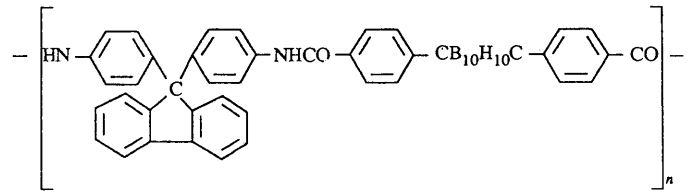


soften at 250–460 °C and 220–270 °C respectively.

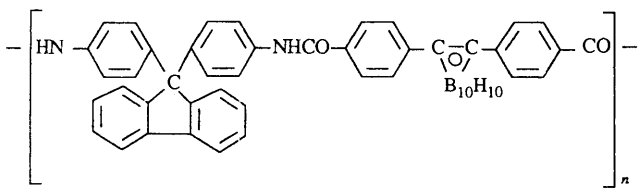
In a review article by Korshak et al.[79] detailed consideration is given to questions concerning the degradation of *o*-, *m*-, and *p*-carborane-containing polyamides with the following structure (under vacuum, in an atmosphere of oxygen, and water vapour at 200–800 °C):



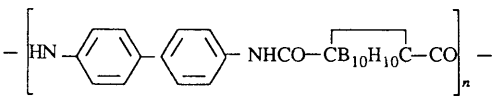
(I)



(II)



(III)



(IV)

It was demonstrated in the review that isomerism of the carborane cage has a considerable effect on the stability of polyamides. It transpired that the *p*-carborane-containing polyamide (IV) has inferior thermal stability compared to polyamides containing *m*- and *o*-carborane residues. Moreover, while the main degradation route in *o*- and *m*-carborane-containing polyamides is decomposition of the *o*- and *m*-carborane residues with evolution of hydrogen, whereby the amide groups become stable towards homolytic and heterolytic cleavage reactions, in *p*-carborane-containing polyamides cleavage of the NH—CO bond mainly occurs, and the principal gaseous degradation product is carbon dioxide.

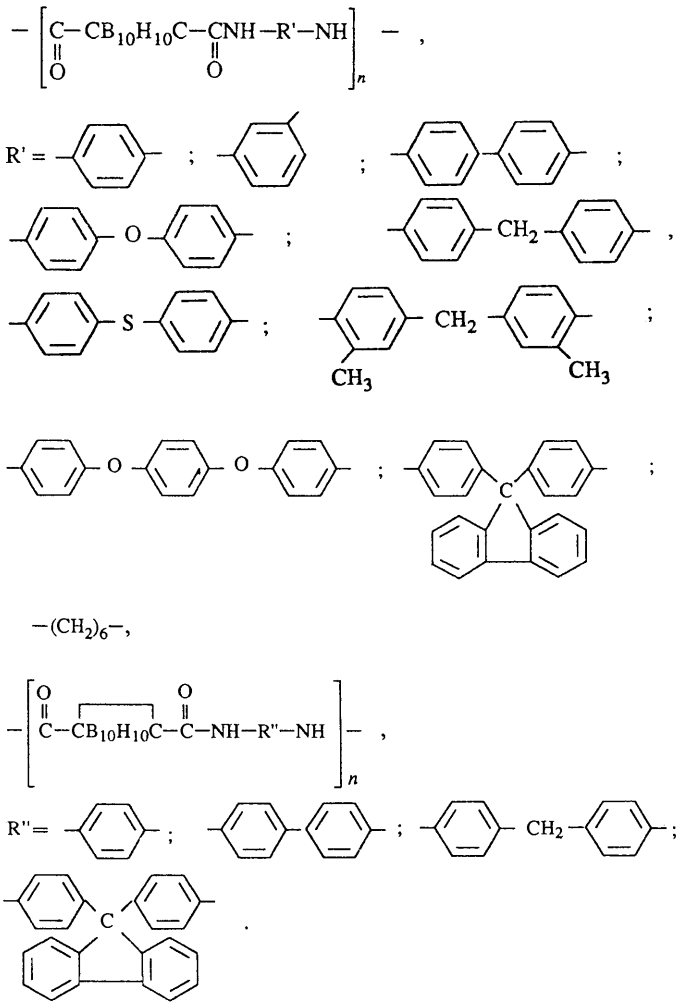
On degration in an atmosphere of saturated water vapour *o*- and *m*-carborane residues undergo more substantial decomposition, as is suggested by the increase in quantities of hydrogen and methane in the hydrolysis products, compared to degradation under vacuum. The degradation of the *p*-carborane-containing polyamide is similar to that of aromatic polyamides, i.e., the presence of excess moisture gives rise to more substantial hydrolysis of the amide groups.

During thermooxidative degradation a decisive factor is the oxidative stability of the carborane cage and, as is suggested by the experimental findings, this is virtually the same for all the isomers.

However, on comparing the degree and rate of degradation of polyamides containing *p*-carborane (IV) and *m*-carborane (I) residues in an atmosphere of oxygen, it should be noted that decomposition of *m*-carborane residues occurs to a much greater extent. Hence the degree of stability of the carborane isomers towards oxygen is not the only factor that governs the oxidation of carborane-containing polyamides, and, like thermal degradation, the electron-withdrawing properties of the carborane cage play a significant role. Although the oxidative stabilities of the *m*- and *p*-isomers of carborane are similar in magnitude, decomposition of the carborane cage and stabilisation of the amide groups occur to a greater extent in the thermal oxidation of the *m*-carborane-containing polyamide (I).

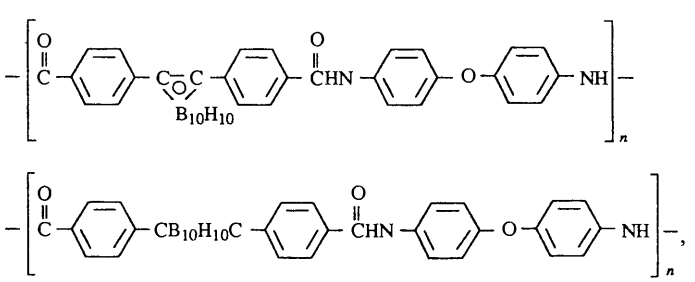
The antifrictional properties of *m*-carborane-containing polyamide (I) and its *p*- analogue (IV) have been studied over the temperature range 250—450 °C.[80] From the results obtained by Korshak et al.[80] concluded that the hydrogen which is formed in considerable quantities during decomposition of *m*-carborane-containing polyamides produces a reducing medium between the frictional surfaces, resulting in inhibition of the oxidative processes that occur at high temperatures. This is to a considerable degree responsible for the improvement in lubricating properties of antifrictional plastics based on *m*-carborane-containing polyamides compared to *p*-carborane-containing polyamides (in which the evolution of hydrogen occurs to a lesser degree over the studied temperature range) and in comparison with polyamides that do not contain carborane residues (which evolve virtually no hydrogen at these temperatures).

Isomerism of the carborane cage has an effect on the chemical stability of known carborane-containing polyamides. Thus, *m*- and *p*-carborane-containing polyamides with the following structure are stable towards boiling water and 40% sulphuric acid:



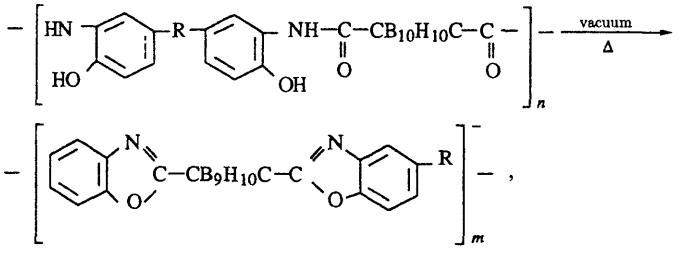
However, on heating in a 40% aqueous alkali solution only alkaline hydrolysis of the macromolecules occurs in *p*-carborane-containing polyamides while in polyamides with *m*-carborane residues decomposition of the *m*-carborane groups occurs together with alkaline hydrolysis.

The molecular mobility properties of carborane-containing polyamides with the following structure:



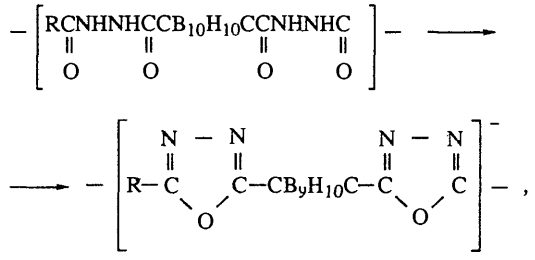
and an investigation of the effect of their structure on electrophysical properties were the subject of a study by Voishchev et al.[81] It was shown that replacement of the *o*-carborane cage by a *m*-carborane cage resulted in a decrease in rigidity of the macromolecules.

The isomerism of carboranes has a considerable effect on the formation of polyheterocycles.[12,15,82–88] Thus, according to the data of differential IR spectroscopy, the cyclohydration of *m*-carborane-containing poly(hydroxyamides) is always accompanied by partial conversion of the *m*-carborane groups to dicarbaundecarborate residues:



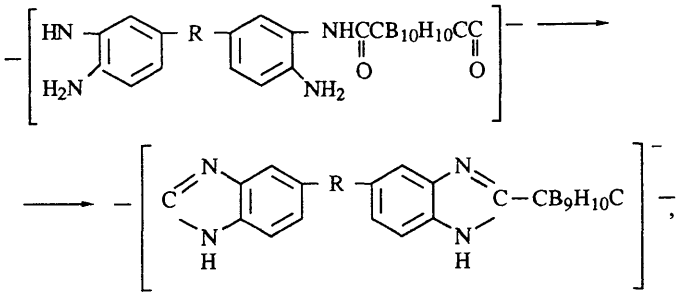
R = —CH_2—, —O—, —SO_2—, —$C(CH_3)_2$—.

The conversion of *m*-carborane groups to dicarbaundecarborate residues also occurs to a greater or lesser extent in the formation of *m*-carborane-containing poly(oxadiazoles):



R = arylene, alkylene;

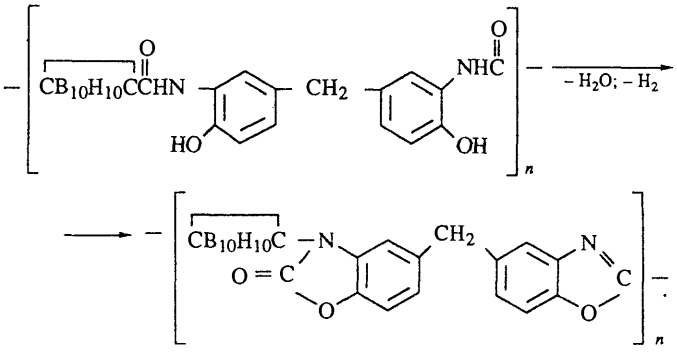
and poly(benzimidazoles):



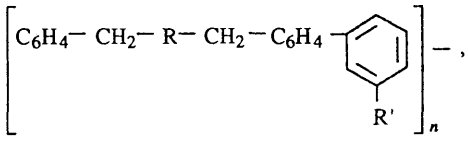
R = —O—, —CH_2—, —SO_2—,

and, according to the authors, apparently takes place via the amide bond.

Since *p*-carborane residues are the most stable of the carborane isomers towards a basic compound, the conversion of *p*-carborane-containing poly(aminoamides) and polyhydrazides to the corresponding polyheterocycles occurs smoothly, without decomposition of the *p*-carborane residues. However, in this case Korshak et al.[88] recorded the conversion of a hydroxyamide structure to a benzoxazole group, which had not been observed previously in polymers:[89]



It follows from the examples given above that the properties of the polymers depend on which of the carborane isomers is present in them. However, in some cases isomerism of carborane has virtually no effect on the properties of the polymers. Thus, in a study of the properties of *o*-, *m*-, and *p*-carborane-containing polyphenylenes with the following structure:

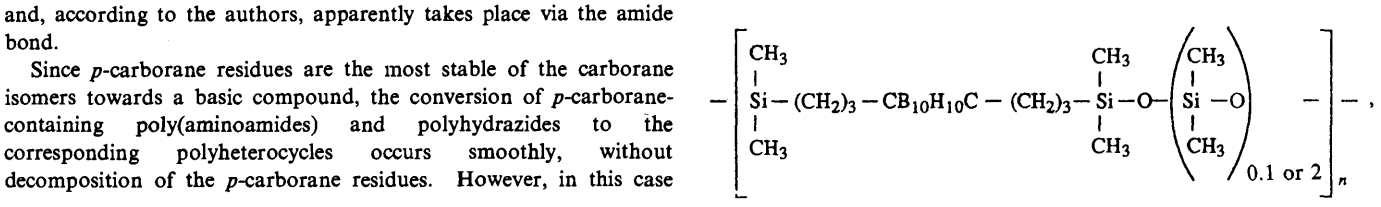


where R = *o*-, *m*-, or *p*-carboranylene and R′ = phenyl, benzyl-*o*-, benzyl-*m*-, or benzyl-*p*-carbonyl, it was established that the solubility of the oligophenylenes synthesised and the thermal stability of the polyphenylenes hardly depend at all on which of the carborane isomers are used to prepare them.[90–93]

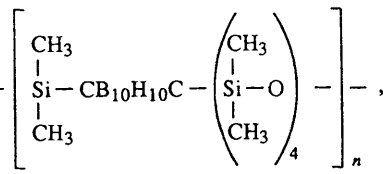
IV. Effect of the configuration of carborane groups in a macromolecule and the structure of the residues directly bonded to them on the properties of carborane-containing polymers

The properties of carborane-containing polymers are dependent on the configuration of the carborane groups in the side chain or main chain of macromolecules and also on the structure of the residues that are adjacent to the carborane groups.

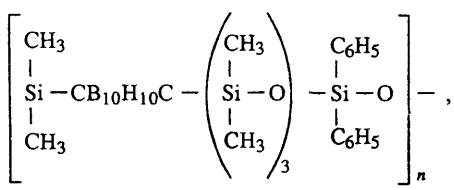
It was established that there is some correlation between the structure of *m*-carborane-containing siloxanes and their properties.[19,94] For example, the thermal stability and oxidative stability decrease with an increase in siloxane groups not bonded to the carborane. Thus, polymers of the type:



are susceptible to thermal oxidation even at 240 °C (in an atmosphere of nitrogen they are stable up to 350 °C).[95] At the same time a characteristic feature of all Dexsil polymers (in which the Si atom is bonded directly to the *m*-carborane residue) is their high thermal stability and resistance to oxidative attack at 300–500 °C.[94,96] This effect is attributed to the result of the inductive stabilisation of the silyl groups through the neighbouring electron-withdrawing *m*-carboranyl groups. Partial replacement of the methyl groups in Dexsil polymers by phenyl groups results in an increase in oxidative stability of the polymers. For example, Dexsil-400:



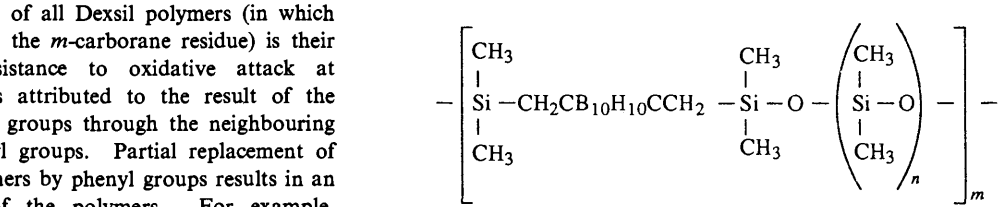
is oxidised at 325 °C, while a polymer with the structure:



is only oxidised at 370 °C.[94]

The presence of trifluoropropyl groups in the Dexsil skeleton imparts the greatest stability to the polymers and stability towards solvents. It was shown that with an increase in the number of siloxane units located between two carborane groups in Dexsil polymers, the softening point of the polymers decreases but the stability towards thermooxidative degradation changes only slightly and remains high (310–340 °C).[96] A feature that distinguishes the thermal degradation of poly(*m*-carboranylene-siloxanes) from that of conventional polysiloxanes is the small content of cyclic oligosiloxanes in the decomposition products.[97] Szekely and Blazgo[97] assume that the large size of the *m*-carborane group inhibits the formation of a helical macromolecular shape and hence decyclopolymerisation of *m*-carborane-containing polysiloxanes is made difficult. It has also been noted that, in contrast to conventional polysiloxanes, Dexsil polymers readily undergo cleavage of the $Si-C_{carb}$ bond by the action of nucleophilic and electrophilic reagents.

It was shown by Kalinin et al.[98] that the presence of methylene bridges between the carborane cage and silicon atom reduces the electron-withdrawing effect of the carborane cage on the silicon atoms, as a result of which the $Si-CH_2-C_{carb}$ system of bonds becomes less polar and hence more stable towards nucleophilic and electrophilic reagents. This is in contrast to the $Si-C_{carb}$ bond, which under identical conditions readily undergoes cleavage with elimination of *m*-carborane. Therefore, the synthesis of poly(*m*-carboranylene-organosiloxanes) was carried out in order to increase the chemical stability of *m*-carborane-containing polysiloxanes.[99] The molecular weight of the resulting polysiloxanes was equal to 171 000–400 000.



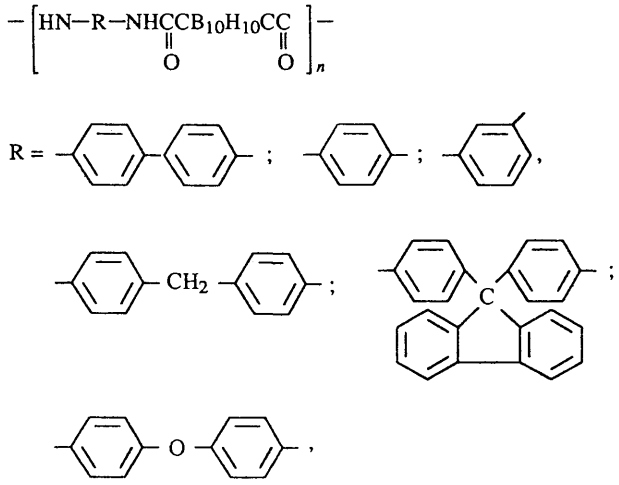
n = 2, 3, 5, 10, 80.

It was established that in terms of thermal stability polyorganosiloxanes with 1,7-bis(dimethylsilylmethyl)-*m*-carborane units are not inferior to similar polymers with 1,7-bis(dimethylsilyl)-*m*-carborane units and they have greater chemical stability than the latter. By changing the length of the organosiloxane block between carborane groups it is possible to vary the physicomechanical properties of the polymers over a wide range.

The properties of carborane-containing polyesters are very markedly dependent on the chemical structure of the organic residues located between the carborane groups. Aliphatic *m*- and *o*-carborane-containing polyesters obtained by reaction between carborane-containing diols and aliphatic dicarboxylic acids are generally low-molecular-weight viscous liquids or brittle materials with softening points at about 100 °C.[3,23,24,100] They are polydisperse[101] and soluble in aromatic hydrocarbons, chlorohydrocarbons, and acetone, and insoluble in aliphatic hydrocarbons, alcohols, and water; and they have an amorphous structure. Replacement of the methylene groups in aliphatic polyesters by CF_2 groups causes a lowering in softening point of these polymers.[3,23,24,100]

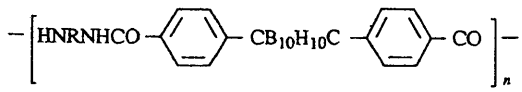
Polyesters synthesised by polycondensation of bis(hydroxymethyl)-*o*-carborane or bis(hydroxymethyl)-*m*-carborane with aromatic dicarboxylic acid dichlorides have greater thermal stability and are less soluble than polyesters obtained from the same diols and aliphatic dicarboxylic acids.[74,101,102] For example, the polyester derived from terephthaloyl dichloride and bis(hydroxymethyl)-*o*-carborane has a softening point of 204 °C,[74] while the softening points of polyesters derived from bis(hydroxymethyl)-*o*-carborane and aliphatic dicarboxylic acids do not exceed 100 °C.[3,23,24,100]

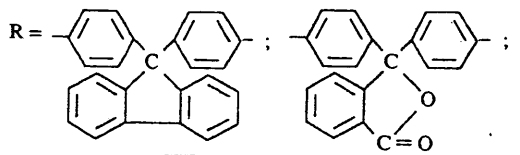
All aromatic *m*-carborane-containing polyamides with the following structure:

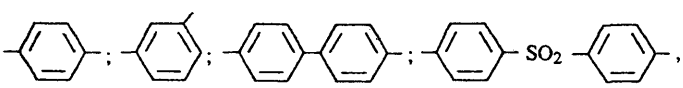


in which the NH—CO bond is adjacent to the carborane group are infusible products.

Polyamides with the structure:



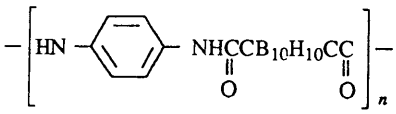




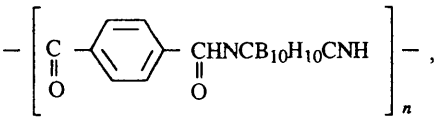
in which the NH—CO bond is separated from the *m*-carborane group by phenylene residues soften over a temperature range of 280—390 °C.

In a study of the thermal degradation of these polyamides over a temperature range of 200—300 °C it was established that the introduction of phenylene residues between the *m*-carborane cage and the NH—CO bond increases the temperature at which degradation of the *m*-carborane groups starts by approximately 100 °C. At the same time the stability of the NH—CO bond towards heterolytic and homolytic cleavage reactions decreases.[103]

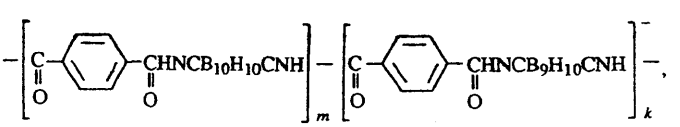
The thermal stability of *m*-carborane-containing polyamides depends to a considerable extent on the manner in which the NH—CO bond is joined to the *m*-carborane group. Thus, a polyamide with the structure:



with a molecular weight of 42000 is stable on heating in air to 230 °C, according to the data of thermogravimetric analysis and IR spectroscopy, while in a polyamide with the structure:

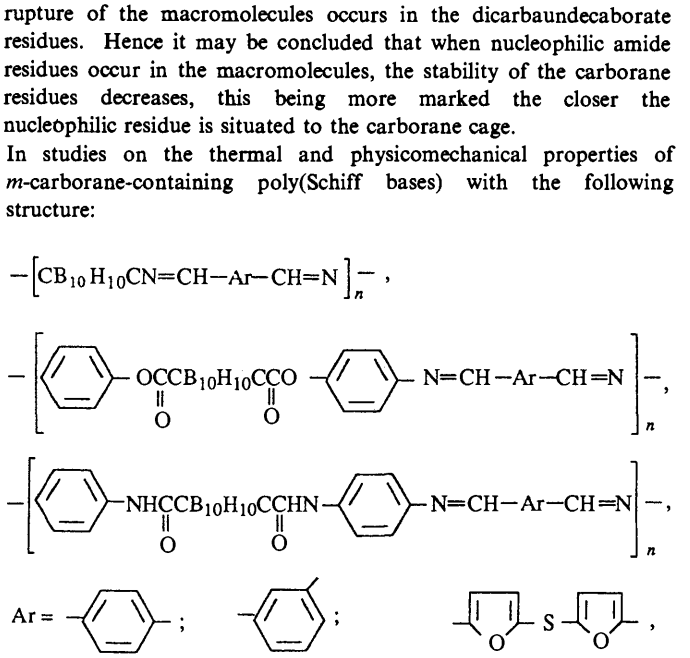


the *m*-carborane residue proved very unstable. Even at 20 °C while this polyamide was being formed, the *m*-carborane groups were partially converted to dicarbaundecaborate groups, according to the IR spectroscopic data. At the same time heterounit polyamides with the following structure were formed:

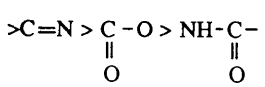


which slowly decomposed on standing. Since carbon dioxide or monoxide are not formed during the degradation of this polymer at room temperature, Korshak et al.[103] maintain that in this case rupture of the macromolecules occurs in the dicarbaundecaborate residues. Hence it may be concluded that when nucleophilic amide residues occur in the macromolecules, the stability of the carborane residues decreases, this being more marked the closer the nucleophilic residue is situated to the carborane cage.

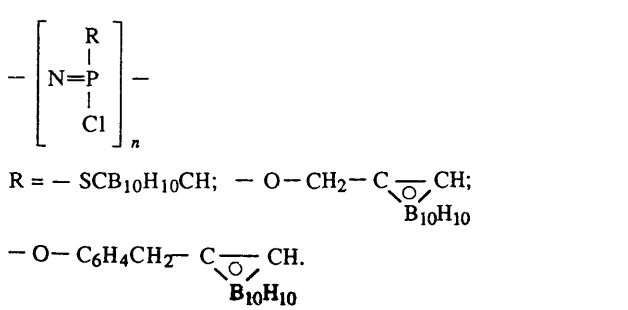
In studies on the thermal and physicomechanical properties of *m*-carborane-containing poly(Schiff bases) with the following structure:



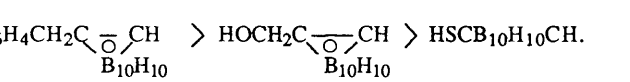
it was established that the chemical and thermal stability in air of these polymers depends on the structure of the organic residues that are adjacent to the *m*-carborane cage and it decreases in the following series:[104,105]



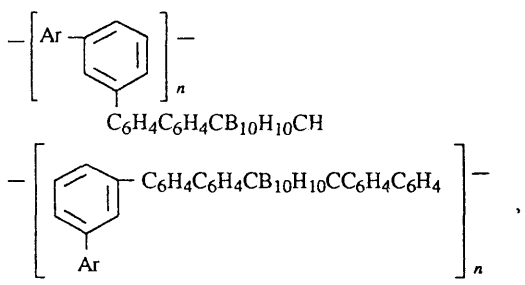
Polymer-like conversions of polydichlorophosphazene with different carborane-containing nucleophiles are used to synthesise the following carborane-containing polyphosphazenes:



Korshak et al. demonstrated that the carborane reagents studied can be arranged in the following series with respect to their favourable effect on the thermal and hydrolytic stability of polyphosphazenes:



Polyphenylenes with the following structure:



containing *o*-, *m*-, and *p*-carborane residues solely in the side chain or solely in the main chain of the macromolecules have been prepared and studied.[90,107–109] Korshak et al. note that the introduction of carborane residues into the side chain of polyphenylenes results in an improvement in their thermal stability but this effect is weaker than in polyphenylenes containing carborane groups in the main macromolecular chain.

Thus, it may be concluded from the above that the properties of carborane-containing monomers and polymers are affected not only by isomerism of the carborane but also by the configuration and structure of the organic residues adjacent to a carborane group.

References

1. J Green, N Mayes, A P Kotloby *J. Polym. Sci., Polym. Lett.*, 1964, **2**(1) 109
2. US P. 3 109 031
3. A F Zhigach, M V Sobolevskii, I G Sarishvili, B A Akimov *Plast. Massy*, 1965, (5) 20
4. V V Korshak, N I Bekasova, L G Komarova, et al. *Vysokomol. Soedin., Ser. A*, 1974, **26**(1) 43
5. L I Zakharkin, I V Pisareva *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, (5) 1158
6. V V Korshak, N I Bekasova, L G Komarova, G A Kats *Vysokomol. Soedin., Ser. A*, 1984, **26**(1) 48
7. V V Korshak, N I Bekasova, L G Komarova *Vysokomol. Soedin., Ser. A*, 1982, **24**(11) 2424
8. V V Korshak, A F Zhigach, M V Sobolevskii, et al. *Plast. Massy*, 1968, (7) 48
9. Z M Frolova, I G Sarishvili, M V Sobolevskii, et al. *Plast. Massy*, 1976, (2) 35
10. USSR P. 296 789; *Byull. Izobret.*, 1971, (9) 86
11. E Hodoya, I H Kawakami, P W Kopf, et al. *J. Polym. Sci., Polym. Chem. Ed.*, 1977, **15**(9) 2229
12. V V Korshak, V V Vagin, A A Izyneev, N I Bekasova *Vysokomol. Soedin., Ser. A*, 1975, **17**(9) 1894
13. H R Allcock, A G Scopelianos, R R Whittle, N M Tollefson *J. Am. Chem. Soc.*, 1983, **105**(5) 1316
14. L L Fewell, R J Basi, J A Parker *J. Appl. Polym. Sci.*, 1983, **28**(11) 2659
15. N I Bekasova *Usp. Khim.*, 1984, **53**(1) 107 [English translation in *Russ. Chem. Rev.*, 1984(1)]
16. E N Peters *Ind. Eng. Chem. Prod. Res. Dev.*, 1984, **23**(1) 28
17. V V Korshak (Editor) *Uspekhi v Oblasti Sinteza Elementoorganicheskikh Polimerov* (Progress in the Synthesis of Organoelemental Polymers), Nauka, Moscow, 1988, p. 60
18. O A Mel'nik, A A Sakharova, T M Frunze *Usp. Khim.*, 1988, **57**(9) 1529 [English translation in *Russ. Chem. Rev.*, 1988(9)]
19. R N Grimes *Carboranes* Academic Press, New York–London, 1970, p. 183
20. N K Vorob'ev, L I Smirnova, E A Chizhova *Izv. Vuzov. Khim. Teckhnol.*, 1971, **14**(6) 955
21. N K Vorob'ev, E A Chizhova, N I Bekasova, et al. *Voprosy Kinetiki i Kataliza: Mezhvuzovskii Sbornik* (Problems in Kinetics and Catalysis: Symposium of Schools of Higher Education), Izd. MKhTI, Ivanovo, 1976, No. 3, p. 9
22. N I Bekasova, L G Komarova, N G Komarova, et al. *Zh. Obshch. Khim.*, 1991, **61** 2224
23. R A Svitsin, A F Zhigach, I G Sarishvili, et al. *Plast Massy*, 1965, (8) 18
24. J Green, N Mayes, M S Cohen *J. Polym. Sci., General Papers*, 1964, **2(7) 3113**
25. US P. 3 258 479
26. V V Korshak, N I Bekasova, L G Komarova *Vysokomol. Soedin., Ser. A*, 1970, **12**(8) 1866
27. V V Korshak, N I Bekasova, L G Komarova *J. Polym. Sci., Polym. Chem. Ed.*, 1970, **8**(9) 2351
28. V V Korshak, N I Bekasova, L G Komarova, S V Parashina *Vysokomol. Soedin., Ser. B*, 1973, **15**(10) 771
29. V V Korshak, S V Vinogradova, A I Kalachev, et al. *Vysokomol. Soedin., Ser. A*, 1971, **13**(4) 848
30. V V Korshak, S V Vinogradova, A I Kalachev, et al. *Vysokomol. Soedin., Ser. A*, 1972, **14**(6) 1306
31. M V Seregina, Yu A Kabachii, P M Valetskii, et al. *Vysokomol. Soedin., Ser. B*, 1991, **33**(2) 105
32. V V Korshak, N I Bekasova, V V Vagin, A A Izyneev *Vysokomol. Soedin., Ser. B*, 1973, **15**(1) 6
33. V V Korshak, N I Bekasova, V V Vagin, A A Izyneev *Dokl. Akad. Nauk SSSR*, 1973, **210**(1) 110; **212**(3) 638
34. V V Korshak, N I Bekasova, V V Vagin, A A Izyneev *Vysokomol. Soedin., Ser. A*, 1974, **16**(4) 718
35. V V Korshak, N I Bekasova, L G Komarova, et al. *Sintez i Issledovanie p-Karboransoderzhashchikh Lineinykh Polyaminoamides* [Synthesis and Study of *p*-Carborane-containing Linear Poly(aminoamides)], Moscow, 1975, p. 11; Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), Moscow, 1975, No. 1688
36. J Green, N Mayes, M S Cohen *J. Polym. Sci., General Papers*, 1965, **3**(9) 3275
37. O A Mel'nik, A A Sakharova, T M Frunze, et al. *Vysokomol. Soedin., Ser. B*, 1984, **26**(5) 373
38. Zh P Vagina, Candidate's Thesis in Chemical Sciences, Institute of Organoelemental Compounds, USSR Academy of Sciences, 1978, p. 133
39. V V Korshak, N I Bekasova, A I Solomatina, et al. *Vysokomol. Soedin., Ser. A*, 1983, **25**(5) 989
40. M V Sobolevskii, A F Zhigach, K P Grinevich, et al. *Plast. Massy*, 1966, (1) 21
41. K P Grinevich, A F Zhigach, I G Sarishvili *Kremniiorganicheskie Soedineniya. Trudy Soveshchaniya* (Organosilicon Compounds. Conference Proceedings), Izd. NIITEKhIM, Moscow, 1966, No. 4, p. 77
42. D Grafstein, J Dvorak *Inorg. Chem.*, 1963, **2**(6) 1128
43. S Papetti, T L Heying *J. Am. Chem. Soc.*, 1964, **86**(11) 2295
44. L I Zakharkin, V N Kalinin, I P Shepilov *Dokl. Akad. Nauk SSSR*, 1967, **174**(3) 606
45. L I Zakharkin, V N Kalinin, L S Podvisotskaya *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, (6) 1297

46. L I Zakharkin, V N Kalinin, T N Balykova, et al. *Zh. Obshch. Khim.*, 1973, **43**(10) 2258
47. E S Petrov, V A Yakovleva, G G Isaeva, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, (8) 1697
48. L I Zakharkin, V N Kalinin *Zh. Obshch. Khim.*, 1966, **36**(12) 2218
49. V N Kalinin, Candidate's Thesis in Chemical Sciences, Institute of Organoelemental Compounds, Moscow, 1967, p. 168
50. L I Zakharkin, V N Kalinin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, (11), 2577
51. V I Stanko, V I Bregadze, A I Klimova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, (2) 421
52. L I Zakharkin, V N Kalinin, A N Snyakin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, (1) 197
53. A V Kazantsev, Candidate's Thesis in Chemical Sciences, Institute of Organoelemental Compounds, Moscow, 1966, p. 171
54. A I L'vov, Candidate's Thesis in Chemical Sciences, Institute of Organoelemental Compounds, Moscow, 1967, p. 122
55. L I Zakharkin, V N Kalinin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, (2) 462
56. L I Zakharkin, V N Kalinin, L S Podvisotskaya *Zh. Obshch. Khim.*, 1966, (10) 1786
57. J A Potenza, W N Lipscomb *J. Am. Chem. Soc.*, 1964, **86**(9) 1874
58. J A Potenza, W N Lipscomb *J. Inorg. Cherm.*, 1964, **3**(12) 1673
59. D Voet, W N Lipscomb *J. Inorg. Chem.*, 1964, **3**(12) 1679
60. T L Heying, J M Ager, S I Clark, et al. *J. Inorg. Chem.*, 1963, **2**(6) 1089
61. S Papetti, B B Schaeffer, A P Grey, T L Heying *J. Polym. Sci., A1*, 1966, **4**(6) 1623
62. US P. 3 388 090
63. D D Stewart, E N Peters, C D Beard, et al. *Macromolecules*, 1979, **12**(3) 373
64. E N Peters, D D Stewart, I I Bohan, et al. *J. Polym. Sci., Polym. Chem. Ed.*, 1977, **15** (4) 973
65. US P. 4 235 987
66. V V Korshak, V A Zamyatina, N I Bekasova *Boroorganicheskie Polimery* (Organoboron Polymers), Nauka, Moscow, 1975, p. 254
67. T L Heying *Progress in Boron Chemistry*, Pergamon Press, Oxford–London, 1970, Vol. 2, p. 119
68. M V Sobolevskii, A F Zhigach, I G Sarishvili, et al. *Plast. Massy*, 1966, (4) 19
69. B A Akimov, A F Zhigach, V V Korshak, et al. *Plast. Massy*, 1966, (7) 21
70. I G Sarishvili, B A Akimov, A F Zhigach, M V Sobolevskii *Plast. Massy*, 1975, (8) 73
71. V S Voishchev, V A Beloglazov, V I Sidorenko, et al. *Vysokomol. Soedin., Ser. B*, 1979, **21**(6) 423
72. P I Ivanov, A I Kalachev, P M Valetskii, et al. *Vysokomol. Soedin., Ser. A*, 1979, **21**(6) 1264
73. V S Voishchev, V A Beloglazov, O V Voishcheva, et al. *Tezisy Dokladov Mezhdunarodnogo Simpoziuma po Makromolekulyarnoi Khimii* (Abstracts of Reports at the International Symposium on Macromolecular Chemistry), Tashkent, 1978, Part 7, p. 128
74. V V Korshak, A F Zhigach, M V Sobolevskii, et al. *Vysokomol. Soedin., Ser. A*, 1970, **12**(12) 2737
75. L V Dubrovina, N F Ivanova, A I Kalachev, et al. *Vysokomol. Soedin., Ser. B*, 1973, **15** 835
76. V G Danilov, V I Stanko, A I Kalachev *Vysokomol. Soedin., Ser. A*, 1971, **13**(10) 2360
77. S R Rafikov, I V Zhuravleva, R S Ayupova, et al. *Dokl. Akad. Nauk SSSR*, 1970, **195**(6) 1351
78. V V Korshak, N I Bekasova, L G Komarova *Vysokomol. Soedin., Ser. A*, 1972, **14**(8) 1761
79. V V Korshak, S-S A Pavlova, P N Gribkova, T N Balykova *Acta Polym.*, 1981, **32**(2) 61
80. V V Korshak, I A Gribova, S-S A Pavlova, et al. *Vysokomol. Soedin., Ser. A*, 1979, **21**(1) 24
81. V S Voishchev, V A Beloglazov, P M Valetskii, V I Sidorenko *Vysokomol. Soedin., Ser. B*, 1981, **23**(2) 123
82. V V Korshak, D P Kunchuliya, N I Bekasova *Vysokomol. Soedin., Ser. A*, 1973, **15**(8) 1731
83. V V Korshak, D P Kunchuliya, N I Bekasova *Vysokomol. Soedin., Ser. A*, 1973, **15**(10) 2195
84. V V Korshak, S V Vinogradova, L A Glivka, et al. *Vysokomol Soedin., Ser. A*, 1973, **15**(7) 1495
85. USSR P. 317 679; *Byull. Izobret.*, 1971, (31) 91
86. V V Korshak, M V Sobolevskii, A F Zhigach, et al. *Vysokomol. Soedin., Ser. B*, 1968, **10**(8) 584
87. M A Surikova, G L Berestneva, V A Khomutov, et al. *Vysokomol. Soedin., Ser. B*, 1977, **19**(8) 597
88. N I Bekasova, V V Korshak, M A Surikova, G M Tseitlin *Vysokomol. Soedin., Ser. A*, 1974, **16**(8) 1723
89. V V Korshak, N I Bekasova, L I Komarova, M A Surikova *Vysokomol. Soedin., Ser. A*, 1988, **30**(2) 116
90. V V Korshak, M M Teplyakov, Ts L Gelashvili, et al. *Vysokomol. Soedin., Ser. A*, 1980, **22**(2) 262
91. V V Korshak, M M Teplyakov, Ts L Gelashvili, et al. *J. Polym. Sci., Polym. Lett.*, 1979, **17**(3) 115
92. M M Teplyakov, I A Khotina, Ts L Gelashvili, V V Korshak *Dokl. Akad. Nauk SSSR*, 1983, **271**(4) 874
93. I V Zhuravleva, N K Vinogradova, Ts L Gelashvili, et al., *Vysokomol. Soedin., Ser. A*, 1984, **26**(1) 22
94. A D Delman, A A Stein, I J Kelly, B B Simms *J. Appl. Polym. Sci.*, 1967, **11**(11) 1979
95. N Mayes, J Green,. M S Cohen *J. Polym. Sci., A1*, 1967, **11**(11) 1979
96. E N Peters *J. Macromol. Sci. C*, 1979, **17** 173
97. T Szekely, M Blazgo *Analytical Pyrolysis of Inorganic Thermostable Polymers. Proceedings of the International Symposium in Hungary*, Budapest, 1977, p. 365; *Chem. Abs.*, 1977, (10) 68829d
98. V N Kalinin, B A Izmailov, A A Kazantsev, et al. *Zh. Obshch. Khim.*, 1981, **51**(4) 859
99. B A Izmailov, V N Kalinin, A A Zhdanov, L I Zakharkin *Vysokomol. Soedin., Ser. A*, 1983, **25**(6) 1253
100. US P. 3 351 616
101. USSR P. 194 314; *Byull. Izobret.*, 1967, (8) 83
102. USSR P. 215 496; *Byull. Izobret.*, 1968, (13) 80
103. V V Korshak, P N Gribkova, L G Komarova, N I Bekasova *Vysokomol. Soedin., Ser. A*, 1972, **14**(7) 1557
104. V V Korshak, N I Bekasova, N G Komarova, et al. *Vysokomol. Soedin., Ser. A*, 1989, **31**(1) 54
105. V V Korshak, N I Bekasova, N G Komarova, et al. *Acta Polym.*, 1989, **40**(7) 439
106. V V Korshak, A I Solomatina, N I Bekasova, et al. *Vysokomol. Soedin., Ser. A*, 1980, **22**(9) 1988
107. USSR P. 704 955; *Byull. Izobret.*, 1979, (47) 107
108. V V Korshak, M M Teplyakov, I A Khotina, et al. *Vysokomol. Soedin., Ser. A*, 1981, **23**(7) 1461
109. USSR P. 717 086; *Byull. Izobret.*, 1980, (7) 128

Translated from *Uspekhi Khimii* **61** 668–685 (1992) U.D.C. 541.632:547.92

Retro-aldol processes in steroid chemistry

M K Dzhafarov
The A N Nesmeyanov Institute of Elementoorganic Compounds, The Russian Academy of Sciences, Moscow

ABSTRACT. This review is devoted to retro-aldol reactions in steroid chemistry. The mechanism of the two-centred inversion of the *C/D* ring junction is discussed, and its application to the synthesis of cardioaglycones [aglycones of cardioglycosides] outlined. Some stereochemical aspects of introducing a functionalised side chain at C_{17} is also examined.

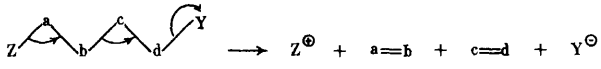
The bibliography contains 56 references.

Contents

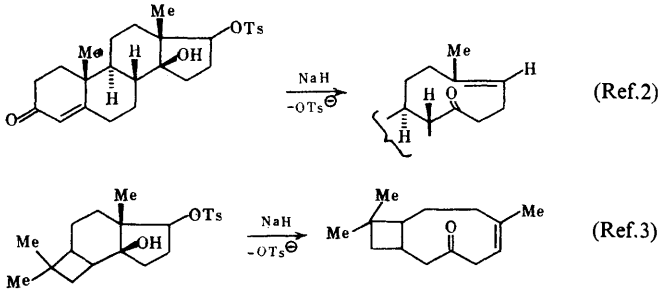
I. Introduction 363
II. Retro-aldol reactions in steroid chemistry 363
III. The two-centred inversion of the *C/D* ring junction and approaches towards the total synthesis of cardiotonic steroids 368

I. Introduction

Hydroxyl and carbonyl groups on the steroid skeleton often determine biological activity as well as provide appropriate functionality for modifying steroidal structures in the search for compounds with physiological activity. Steroidal β-hydroxyketones are potentially interesting in this respect since there is the possibility of structural elaboration via retro-aldol cleavage. The latter cleavage is a fragmentation-type reaction which is initiated by bases or acids. Removal of a proton or anion proceeds more easily if the leaving group is in an anti-parallel configuration (by a Grob-type fragmentation):[1]



The decarboxylation of β-halogeno- and β-hydroxy-glycidic acids exemplifies this type of fragmentation, as also does, among others, the C-cleavage of 1,3-diol monosulphonates:



(Ref.2)

(Ref.3)

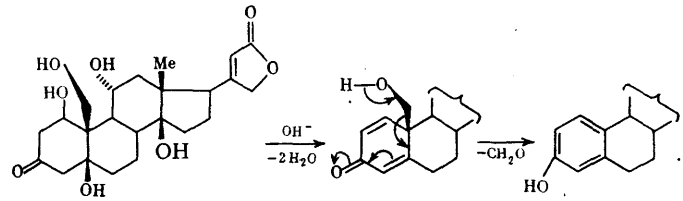
The shift of electron density on keto-enol tautomerism of aldols (−*E* effect in the $\rangle C=O$ group and +*E* effect in the $H-O-C\langle$ group) on treatment with appropriate reagents may be transmitted effectively along a conjugated chain, so that there is the possibility of conjugated retro-aldol processes of a 'remote' type (as is possible with retro-Michael reactions[1]).

Retro-aldol reactions have already been reviewed.[4–6] The present survey is devoted to retro-aldol processes in steroid chemistry and possible applications to the total synthesis of cardiotonic 14β-hydroxy derivatives of estratriene with natural configuration.

II. Retro-aldol reactions in steroid chemistry

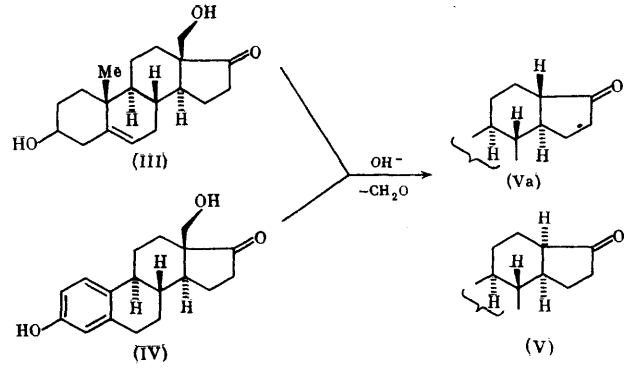
Many reactions of the retro-aldol type are known in steroids which have the basic tetracyclic skeleton (as illustrated in one of the earlier reviews[7]). These can be sub-divided into two categories: 1) retro-aldol cleavage of the side chain and 2) retro-aldol cleavage of the steroid skeleton.

Reactions in the first category have been applied in particular to the synthesis of 18-nor- and 19-nor-steroids, as well as to cleavage of the C_{17} side chain. Thus, the naturally occurring compound (I) is readily converted into the 19-norsteroid (II) via β-elimination of two molecules of water followed by retro-aldol cleavage of formaldehyde.[8] This is the only effective synthetic route to estrone derivatives.



(I) (II)

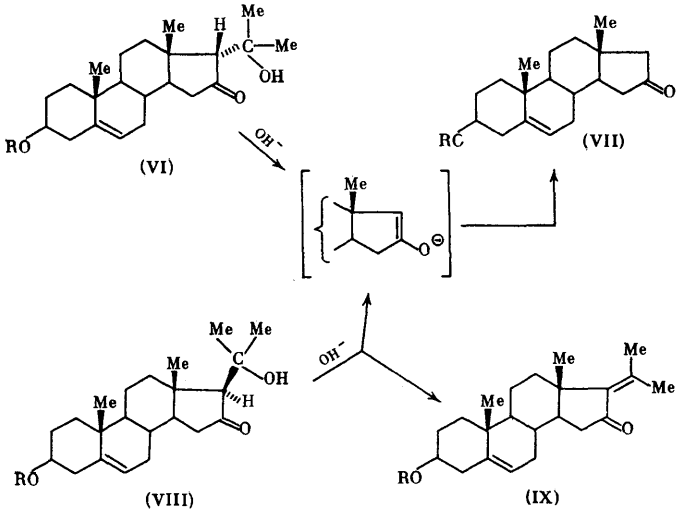
Treatment of 18-hydroxy-17-ketosteroids, (III) and (IV), with base, or pyrolysis of these compounds, also results in retro-aldol cleavage of formaldehyde with the formation of the corresponding 18-norsteroids:[9]



(III) (Va) (IV) (V)

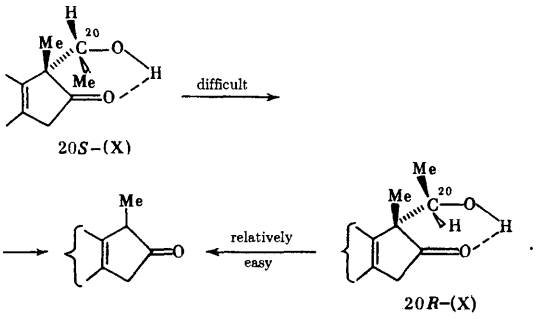
A product (V) with *cis*-fusion at the *C/D* ring junction is formed predominantly. It is possible that the corresponding *trans*-isomer (Va) is formed *in situ*, and then isomerises to the energetically more favourable *cis*-isomer (V) under acid catalysis. Such an isomerisation has, in fact, been observed with *trans*-hydrindan-1-one.[9]

From a stereochemical point of view, it proved interesting to study the behaviour of the C_{17} epimers of 20-methylpregn-5-ene-3β,20-diol-16-one in basic and acidic media. Thus, it has been shown that, even at room temperature in aqueous methanolic K_2CO_3, the 17α-epimer (VI), having a quasi-axial orientation of the side chain, undergoes retro-aldol cleavage of the $C_{17}-C_{20}$ bond to give compound (VII); however, the 17β-epimer (VIII) reacts only on heating with strong base (KOH) to give a mixture of (VII) and the α,β-unsaturated ketone (IX).[10] Under acidic conditions, the reaction proceeds quite differently.† Thus, treatment of hydroxyketone (VIII) with perchloric acid in dioxane fails to undergo retro-aldol cleavage, affording, instead, the α,β-unsaturated ketone (IX) as the only product;[11] however, the 17α-epimer (VI) gives a mixture of (IX) and androst-5-en-3β-ol-16-one (VII).



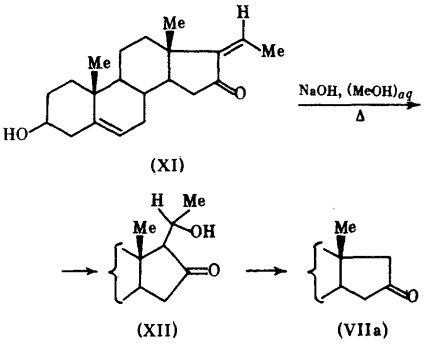
We believe that steric forces may be responsible for the different behaviour of epimers (VI) and (VIII) in basic media. In compound (VI), the approach of the base to the proton at C_{17} is sterically unfavourable as a result of the shielding effect of the angular 18-methyl group. Consequently, the base removes the hydroxylic proton with subsequent retro-aldol cleavage. Evidently, one must also consider the role of stereo-electronic factors. Thus, cleavage of the quasi-axial side-chain at C_{17} in (VI) should proceed more easily than cleavage of the equatorial side-chain in (VIII).[11] On the other hand, as a result of the increased availability of the proton at C_{17} in (VIII), the formation of intramolecular hydrogen bonding between the carbonyl group at C_{16} and the hydroxyl group at C_{20} is more favourable in (VIII) than in (VI), as confirmed by using Dreiding models. This further explains the reluctance of (VIII) to undergo retro-aldol cleavage.

Intramolecular hydrogen bonding may also explain why it is difficult to remove the 17α side-chain of 18-nor-17β-methylpregna-5,13(14)-dien-16-one (X) by retro-aldol cleavage, which only proceeds under forcing conditions (on heating with KOH in methanol):



It is interesting that the formation of a hydrogen-bonded conformer is more likely with the 20*S*-diastereoisomer of (X), having *anti*-oriented methyl groups on C_{17} and C_{20}, than with the 20*R*-diastereoisomer of (X) having the two methyl groups in the *syn*-orientation. Therefore one would anticipate that the 20*S*-diastereoisomer of (X) would be less disposed to undergo retro-aldol cleavage than the 20*R*-isomer. Unfortunately, Akhrem et al.[17] did not establish the absolute configuration at C_{20}. One should also note that the acidity of the OH group of the secondary alcohol (X) is less than that of the tertiary alcohol (VI)—an additional factor which explains the reluctance of (X) to undergo retro-aldol cleavage.[4]

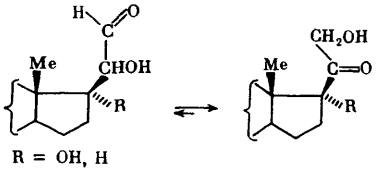
Prolonged heating of pregna-5,17(20)-dien-3β-ol-16-one (XI) in aqueous methanol containing NaOH also leads to 3β-hydroxy-androst-5-en-16-one (VIIa). In this instance, the β-hydroxyketone (XII) is formed initially by Michael addition, and then undergoes retro-aldol cleavage to give the final product (VIIa):[14]



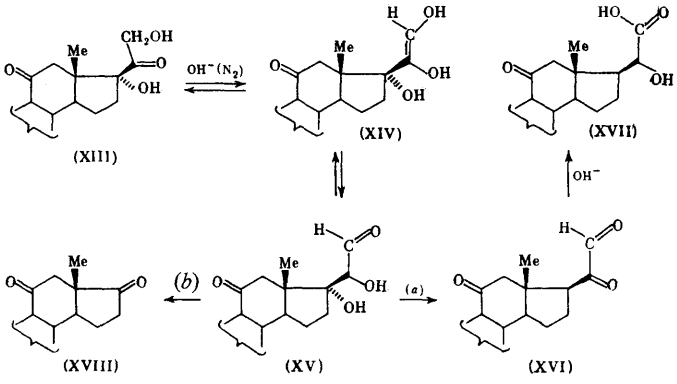
An interesting retro-aldol cleavage has been observed with a corticosteroidal β-hydroketone (XIII). This undergoes a tautomeric shift‡ on treatment with base (in the absence of oxygen) to give the dihydroxyaldehyde (XV), which subsequently cleaves in two ways: a) by initial dehydration to (XVI), followed by benzilic rearrangement to give the acid (XVII); and b) retro-aldol cleavage of the side

† The rate of dehydration of hydroxyketones increases on raising the temperature under acidic conditions.[12]

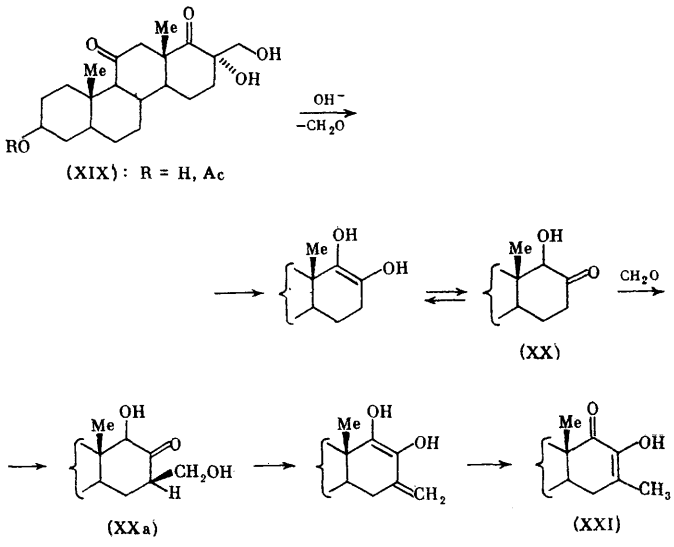
‡ The tautomeric conversion of aldols into the corresponding ketones has been applied to the synthesis of the corticoid side chain:[7]



chain to give the diketone (XVIII).[7,15] Compound (XIII) is also converted to (XVII) in acidic media.

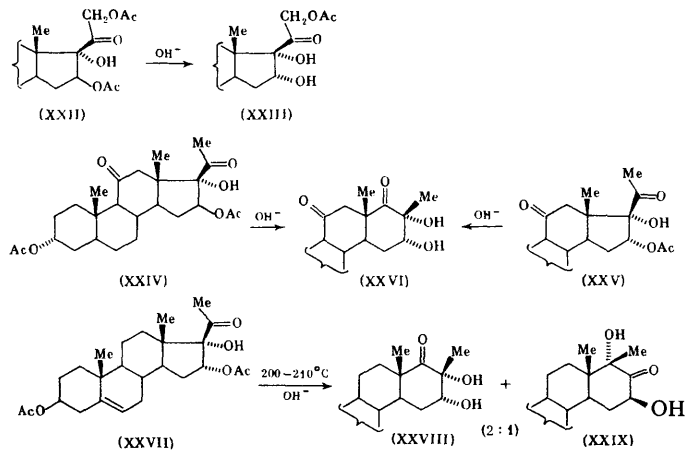


There are also examples of retro-aldol cleavage of formaldehyde from *D*-homosteroids (XIX), followed by its subsequent addition to the resulting ketone (XX). The hydromethyl derivative (XXa) is formed initially, and is then dehydrated to (XXI). This was confirmed by the independent conversion of (XX) into (XXI) on treatment with formaldehyde in basic media.[7]

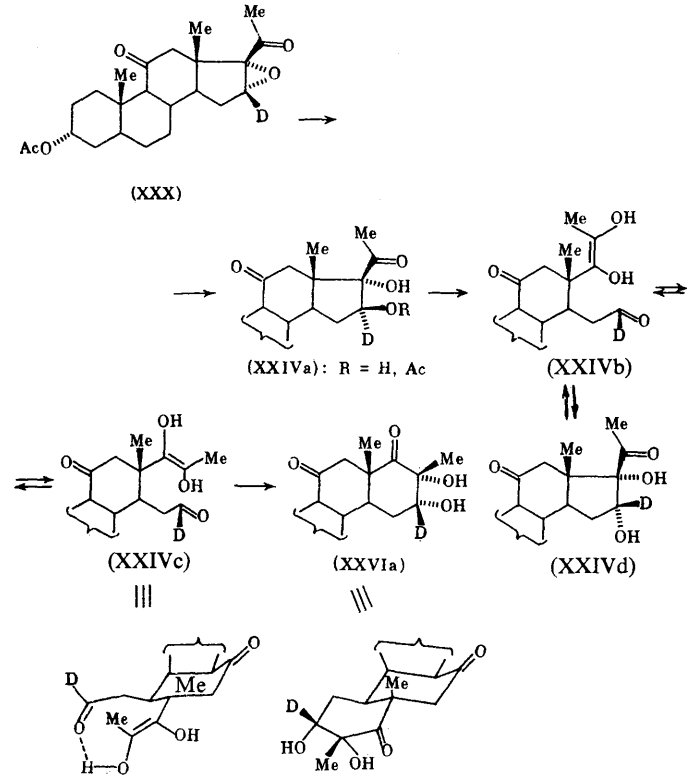


Based on stereochemical considerations, retro-aldol cleavage of the second type (i.e. of the steroid skeleton) may be further subdivided into 1) retro-aldol reactions not involving angular carbon atoms; and 2) retro-aldol reactions involving angular C-atoms (C_5, C_8, C_9, C_{10}, C_{13} and C_{14}).

Those examples in the first category are typified by elimination from C_{16} and C_{17}, but, in principle, retro-aldol cleavage is also possible at C_1, C_2, C_3, C_4, C_6, C_7, C_{11}, C_{12} and C_{15}. Such reactions can also lead to ring expansion or contraction of the skeleton (affording homo- and nor-steroids, respectively). The unusual inversion of configuration at C_{16} on hydrolysis of the 17α-hydroxy-corticosteroid (XXII) to (XXIII) in basic media can also be explained by a retro-aldol mechanism,[16] as also can the conversion of the epimeric 3α,16-diacetoxy-17α-hydroxypregna-11,20-diones, (XXIV) and (XXV), to the same 16α-hydroxy-*D*-homosteroid (XXVI); retro-aldol cleavage of the 11-deoxy-analogues, e.g. (XXVII), which gives a mixture of (XXVIII) and (XXIX), proceeds in a similar way.[17]

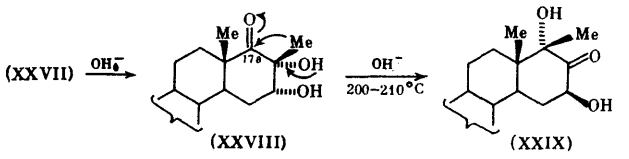


The mechanism of such reactions has been established by labelling experiments.[7]

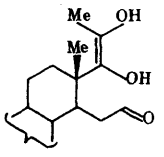


The formation of the *D*-homosteroid (XXVIa) and the epimerisation of (XXIVa) to (XXIVd) can be readily explained by the above scheme. Intramolecular hydrogen bonding in the intermediate 16,17-secosteroid (XXIVc) facilitates retro-aldol cleavage with subsequent formation of the *D*-homosteroid (XXVIa). The 16α-hydroxy and 17β-methyl groups in (XXVIa) are in a pseudoequatorial configuration relative to the *D*-ring (which is thereby stabilised in the boat conformation). The formation of the corresponding chair conformer would have required an unfavourable 1,3-diaxial interaction between the methyl groups at C_{17} and C_{13}.[7]

As has already been shown above, heating compound (XXVII) in basic media affords (XXVIII) as the main product together with (XXIX), in which the methyl group has migrated from C_{17} to C_{17a}.[17] We believe that this occurs as a result of rearrangement of (XXVIII) having a tertiary methyl group at C_{17}:

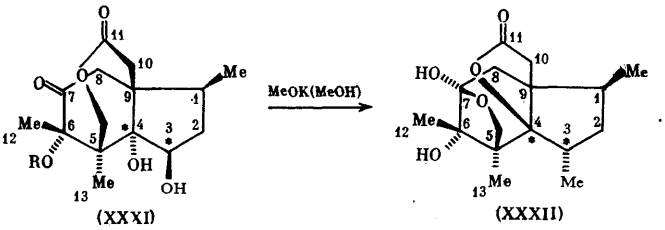


The driving force for this rearrangement is the release of strain energy associated with the 1,3-interaction of the methyl groups in the intermediate secosteroid:

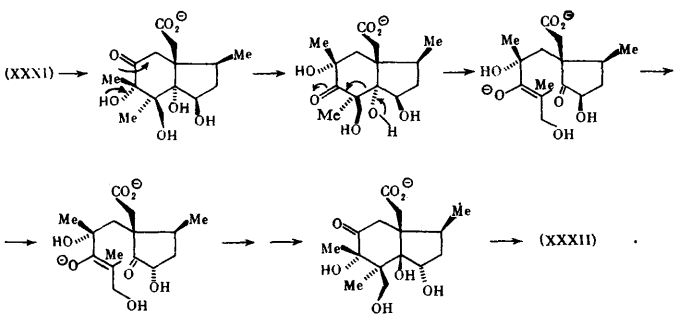


It is worth noting that the migration of the tertiary methyl group usually proceeds more easily under the action of acid. Under these conditions, migration is facilitated by the developing positive charge on the adjacent carbon atom, arising as a result of protonation of the carbonyl oxygen. Akhrem et al., in fact, found that under acidic conditions compound (XXVII) rearranges primarily to give (XXIX), and not (XXVIII).[17]

From X-ray structural analyses and chemical studies, Kouno et al. found that the naturally occurring pseudoanisatin (XXXI), having a complicated substituted hydrindane skeleton, rearranges in the presence of strong base.[18] The product had an unusual configuration at C_3 and C_4, and had been formed by an intramolecular translactonisation to give a stable *peri*-fused γ-lactone ring with simultaneous lactolide ring close involving C_7 and C_5:

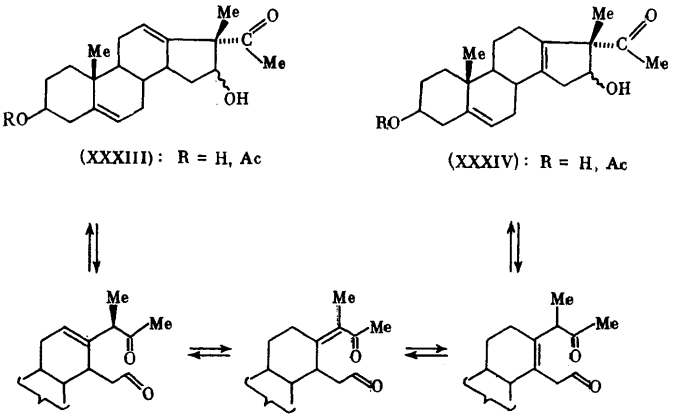


The inversion at C_4 is particularly interesting since, as a result of the reaction, the *trans*-hydrindane ring is converted into the *cis*-form. Barton has proposed a mechanism for this inversion, involving retro-aldol cleavage of the C_4-C_5 bond:[18]



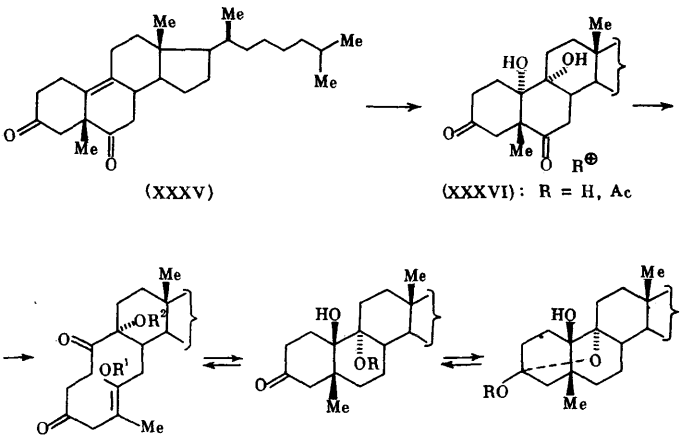
It is considered that the driving force for this rearrangement of pseudoanisatin is the release of strain energy associated with the octahydro-*trans*-indan ring.

In studying the saponification of steroids (XXXIII) and (XXXIV), Herzog et al. discovered that the two compounds were in equilibrium, the double bond shift, $\Delta^{12(13)} \rightleftarrows \Delta^{13(14)}$, being facilitated by a retro-aldol cleavage of the $C_{16}-C_{17}$ bond followed by re-aldolisation.[19]

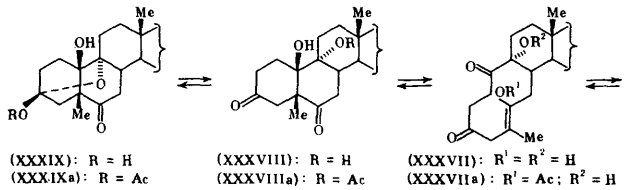


The second sub-category of retro-aldol cleavage, involving the angular carbon atoms, is especially interesting. These reactions lead to isomerisation and a variety of rearrangements.

A study of the dihydroxylation of compound (XXXV) to give (XXXVI) showed that the product subsequently rearranged via retro-aldol cleavage.[20] The *B*-ring of the *cis*-diol (XXVI) is forced into the boat conformation as a result of the steric requirements of the *trans-A/B* fusion. This facilitates retro-aldol isomerisation to give the energetically more favourable *cis-A/B* isomer (XXXVIII) having a chair conformation in ring *B*. This steroid was isolated as the transannular oxido tautomer (XXXIX).



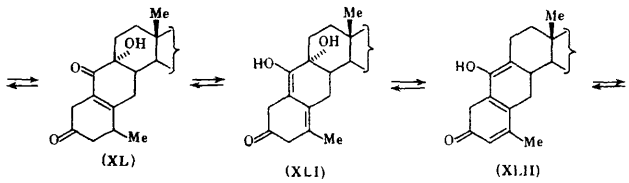
On treatment with base, the oxido compound (XXXIX) rearranges further to give (XL) [presumably via the same intermediate (XXXVII)].[20]



(XXXIX): R = H
(XXXIXa): R = Ac

(XXXVIII): R = H
(XXXVIIIa): R = Ac

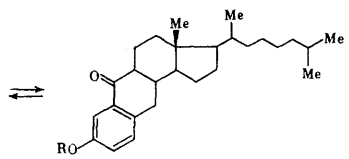
(XXXVII): $R^1 = R^2 = H$
(XXXVIIa): R^1 = Ac; R^2 = H



(XL)

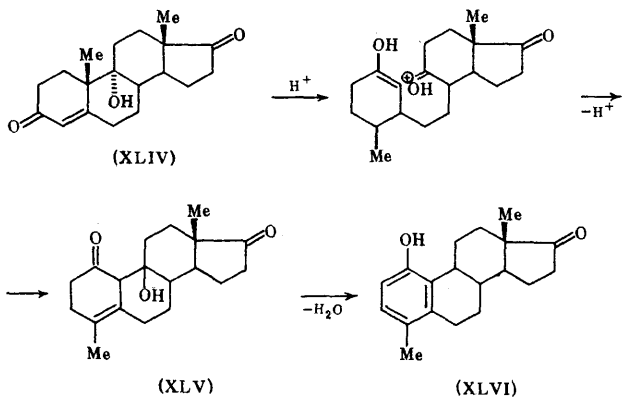
(XLI)

(XLII)



(XLIII): R = H
(XLIIIa): R = Ac

References have also been made to 'remote' retro-aldol reactions, facilitated by conjugation between the keto and hydroxyl group.[21,22] This is exemplified below.

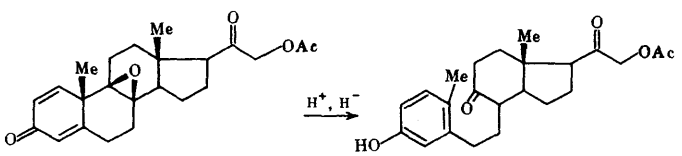


(XLIV)

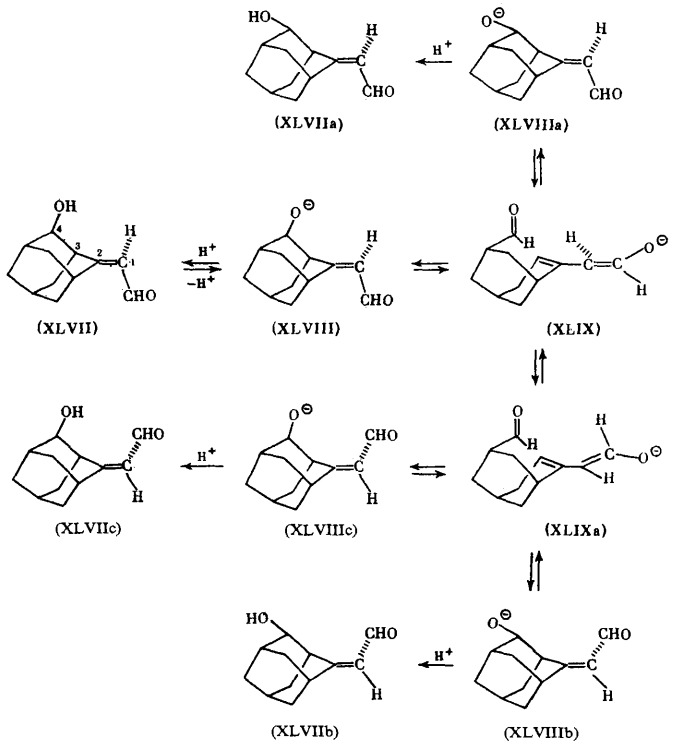
(XLV)

(XLVI)

In such instances, the vinylogous aldol fragment is well disposed to retro-aldol cleavage in acidic media. This is further facilitated by the lack of a labile proton between the functional groups, so that dehydration of the substrate is precluded. However, this is not so in the product (XLV), dehydration of which proceeds readily to give the phenolic ketone (XLVI). Conjugated epoxyketones also undergo such 'remote' retro-aldol cleavage, as illustrated below:[23]



An interesting example of a 'remote' retro-aldol cleavage has been reported in adamantane chemistry. Thus, treatment of (*E*)-(1*R*)-4(a)-hydroxy-2-adamantylideneacetaldehyde (XLVII) with NaH affords anion (XLVIII), which undergoes retro-aldol ring opening to give the isomeric anion (XLIX). The enolate group of the latter is conformationally flexible, so that an equilibrium is established with the stereoisomer (XLIXa). The anions (XLVIIIa–c) are formed by subsequent re-aldolisation, and protonation of the reaction mixture leads to a mixture of all four epimeric hydroxyaldehydes (XLVII, XLVIIa–c) in 33:8:27:32 proportion.[24]



(XLVIIa)

(XLVIIIa)

(XLVII)

(XLVIII)

(XLIX)

(XLVIIc)

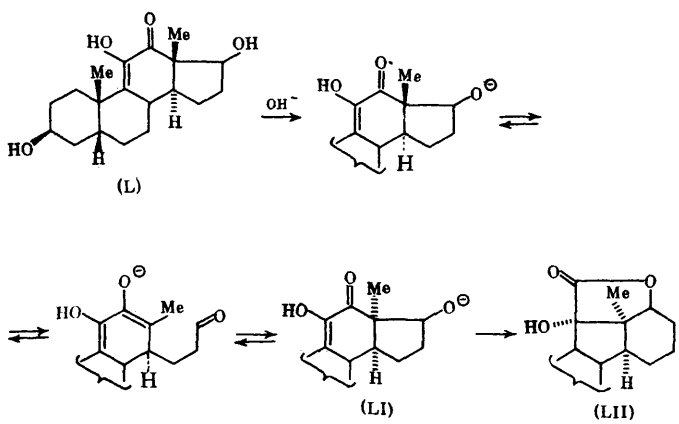
(XLVIIIc)

(XLIXa)

(XLVIIb)

(XLVIIIb)

Retro-aldol reactions may compete with other processes. Thus, the diketone (L), in which benzilic rearrangement is sterically inhibited, undergoes an initial retro-aldol cleavage on treatment with base (NaOH in propanol) to give anion (LI), having the thermodynamically more stable *cis*-*C*/*D* ring fusion.



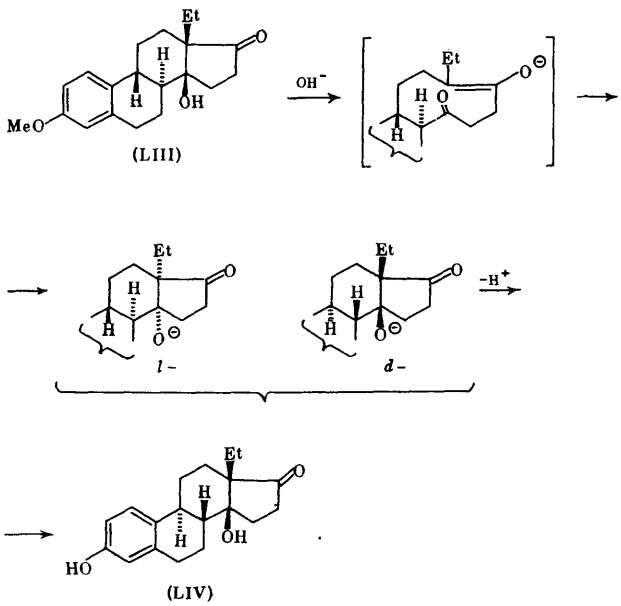
(L)

(LI)

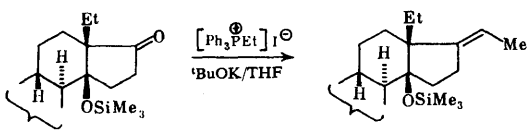
(LII)

The anion (LI) is known to undergo benzilic rearrangement[25] and, on subsequent acidification, affords the 13-*iso*-11;17-lactone (LII). The structure of the latter has been reliably established by X-ray crystallographic analysis.[26]

We have also discovered a novel rearrangement involving the *C/D* ring junction of a 14-hydroxy-17-ketosteroid. Thus, attempted Wittig olefination of the *trans-anti-cis*-hydroxyketone (LIII), obtained by reductive cyclisation,[27] resulted in isomerisation to the abnormal *trans-syn-cis*-isomer (LIV) rather than the expected side-chain formation at C_{17}. The rearrangement involves retro-aldol cleavage of the *C/D* ring junction, as shown below:[28]



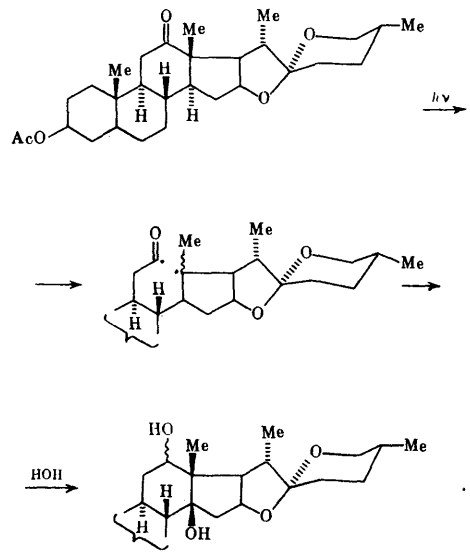
Wittig reaction does take place, however, if the 14-hydroxyl group is protected as the trimethylsilyl derivative:[27]



Strong nucleophiles (not associated with Wittig reagents) also induce the above *C/D* ring inversion[28] to give the same product (LIV) in high yield (>80%).[27] This methodology has proved attractive in the total synthesis of cardioaglycones having the natural *cis-C/D* ring fusion.

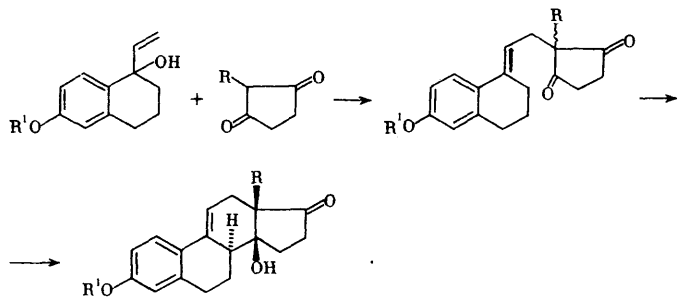
III. The two-centred inversion of the *C/D* ring junction and approaches towards the total synthesis of cardiotonic steroids

By virtue of their positive ionotropic effect on cardiac insufficiency, cardioglycosides have been broadly used medicinally. Their aglycones are steroidal, being characterised by a 14β-hydroxy group (or, in rare instances, by a 14β,15β-oxido group), as well as an unsaturated lactone residue appended at the 17β-position (a butenolide residue in cardenolides, and an α-pyrone residue in butadienolides).[29] The syntheses of such cardioaglycones have been carried out in several laboratories (for examples see Schonfeld et al.[30]). In the construction of the butenolide residue, C_{21}, steroids have been primarily used as starting material,[31] although references have also been given to syntheses based on 17-ketoandrostanes.[31,32] In all of these syntheses, the 14β-hydroxy group has been introduced via the corresponding Δ^{14}-steroid. Welzel and Stein devised a partial synthesis of digoxigenin via photochemical rearrangement of hecogenin, which is readily available from natural (plant) sources.[33] Irradiation initially affords an aldehyde, which then undergoes a Prins cyclisation:



Although it is customary to use cardioglycosides in experimental therapy, the aglycones themselves are also biologically active,[29,30] and the transformations of such aglycones have been studied from both the theoretical and practical viewpoint. Thus, it has been shown that 14β-hydroxy derivatives of estratriene possess inhibitory activity of Na^+,K^+-ATPase and may also have potential cardiotonic activity.[34]

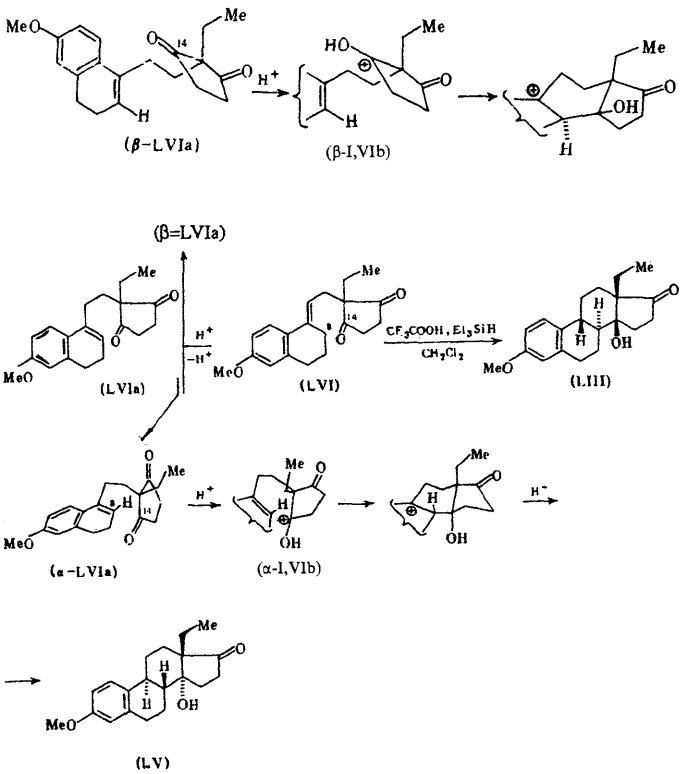
The incorporation of the 14β-hydroxy group in the estrane skeleton can be readily achieved by ring closure of the readily available 8,14-seco-$\Delta^{1,3,5(10),9(11)}$-estratetraene-14,17-dione (Torgov reaction):[35]



We have found that reductive ring closure of the secodiketone (LVI) (by a modified Torgov reaction)[27] leads stereoselectivity to the saturated *trans-anti-cis*-estrane (LIII).[36] The formation of the *trans-syn-cis-* (LIV) [37] and *trans-anti-trans*-isomer (LV) [38] was

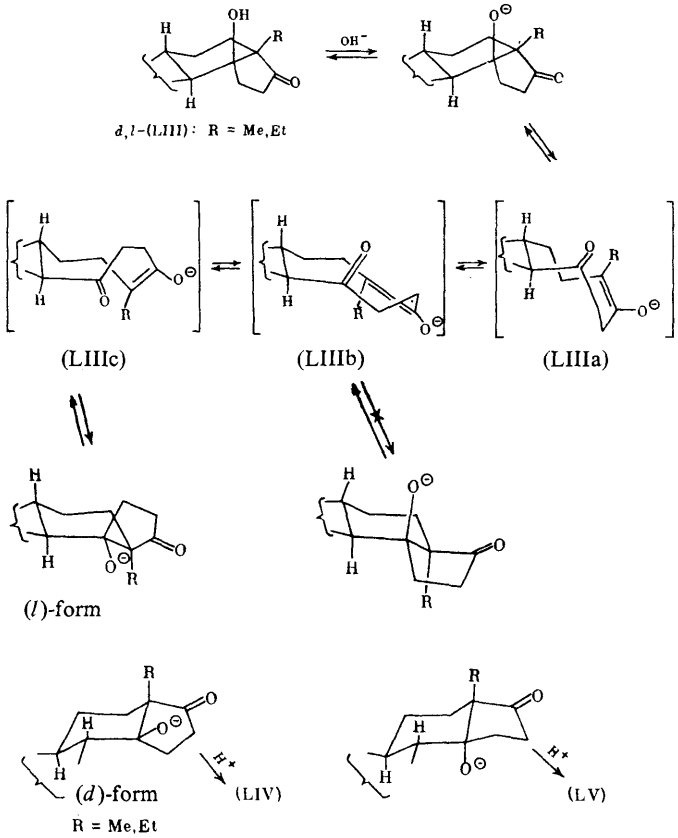
energetically unfavourable (see Scheme 1). Further details of this transformation are available.[39–41]

Scheme 1



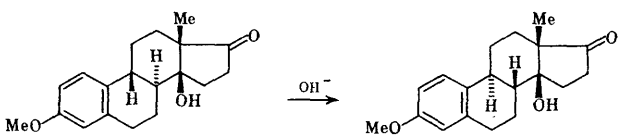
It has also been found that the product of reductive ring closure (LIII) [36] isomerises in the presence of a strong nucleophile (for example, under the conditions of the Wittig olefination) to give the thermodynamically more favourable (by 0.8 kcal/mole) natural isomer (LIV).[33] This isomerisation proceeds via an intermediate 13,14-secosteroid,§ formed as a result of retro-aldol cleavage of the $C_{13}-C_{14}$ bond (Scheme 2).[28] Further details are also available.[39,42]

Scheme 2



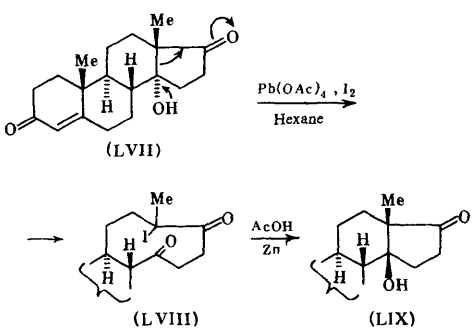
Thus, the (*l*)-diastereomer is obtainable from the *d*-diastereomer, and the (*d*)-isomer from the (*l*)-isomer.[28]

The C_{18}-unsubstituted analogue—(*d,l*)-3-methoxy-14β-hydroxyestra-1,3,5(10)-trien-17-one—under the same conditions also affords the natural isomer¶ as a result of retro-aldol cleavage and re-aldolisation:[44,45]

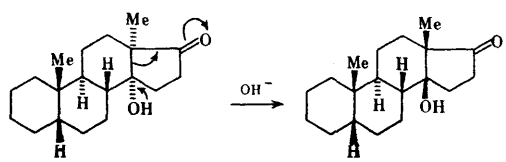


It should be pointed out (with reference to the mechanism depicted in Scheme 2) that although the formation of the 14α-hydroxy isomer (LV) is possible, in principle, its strain energy (31.9 kcal/mole) is significantly greater than that (29.1 kcal/mole) of the 14β-hydroxy isomer (LIV) and that (29.9 kcal/mole) of isomer (LIII).[39] Hence the formation of (LV), although possible on theoretical grounds,[42] is unlikely.

§The anionic form of the 13,14-seco-13(17)-en-17-one should be primarily in the conformation (LIIIc) since molecular models have shown that conformers (LIIIa), and especially (LIIIb), are severely hindered sterically. In actual fact, the 13,14-secosteroid (LVIII), obtained from (LVII), reacts with Zn dust in acidic media to give the natural isomer (LIX) as the sole product:[43]



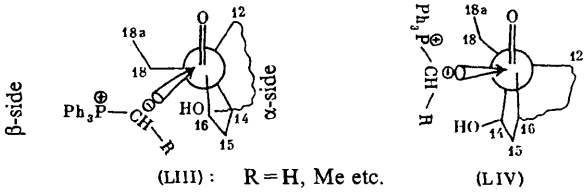
¶We also believe that the 18-retro-14α-hydroxysteroid[46] would isomerise to the natural form under the same conditions:[28]



The synthesis of the 14β-hydroxyestratriene (LIV), having the same configuration as natural cardioaglycones, can thus be achieved in two high-yielding stages—by reductive cyclisation of Torgov's readily available secodiketone, followed by isomerisation of the resulting (LIII). In the development of this method as a route to analogous estratriene and 19-norandrostane aglycones (the latter being obtainable by reduction of the former) with low toxicity, an important consideration was the choice of side-chain functionality at C_{17}. Here, we focussed our attention on stereochemical aspects of incorporating the C_{17} side chain by applying Wittig olefination with 17-oxosteroids (in competition with retro-aldol cleavage) and Grignard addition to the same substrates.

As mentioned above, *trans-anti-cis*-14-hydroxysteroids (LIII) undergo retro-aldol cleavage under the conditions of the Wittig olefination to give, ultimately, the natural isomers (LIV), which may then participate in the Wittig reaction. This interesting result can be explained as follows. As is evident from the Newman projection, based on X-ray crystallographic data,[36,37] the *cis*-orientation of the π-orbitals of the C—O bond (relative to the angular group) in the unnatural isomers (LIII) would necessarily direct *syn*-planar attack of the Wittig reagent,[47] approach of which would be sterically hindered (Scheme 3).[49,50] Replacement of the methyl group at C_{13}, or in the Wittig reagent, by ethyl or by a larger hydrophobic group adds significantly to this steric hindrance, and the Wittig reaction becomes even less likely.

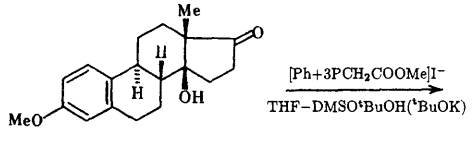
Scheme 3

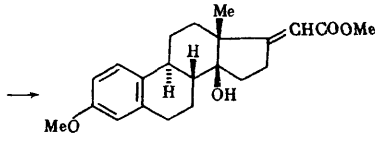


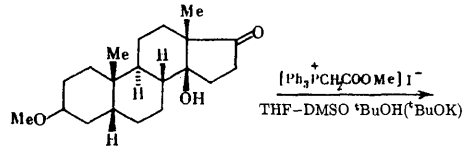
(LIII): R = H, Me etc. (LIV)

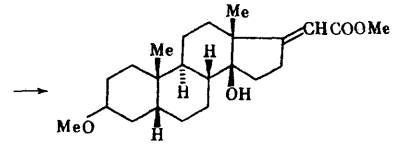
In the natural isomers (LIV), approach of the Wittig reagent from the β-side (*syn*-attack) proceeds considerably more easily to give the intermediate phosphonio-betaine complex (although, even here, large substituents in the vicinity of the reaction centre may still inhibit side chain formation).

Wittig olefination of natural 17-ketosteroids is exemplified below:[51–53]



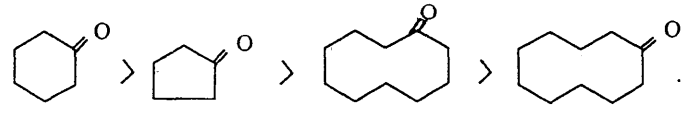






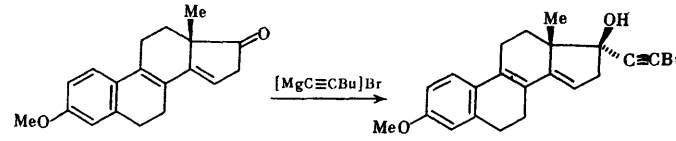
In these reactions, it is important that a hydrophilic group is present in the Wittig reagent, which facilitates olefination via intermolecular hydrogen-bonding with the 14-hydroxy group. The formation of 17-alkylidenesteroids is also favoured because in such instances there would be no repulsion (*syn*) between the substituent at C_{13} and the newly formed side chain at C_{17}.

Suppression of the Wittig reaction with the unnatural isomers (LIII) is apparently due to preferential deprotonation of the axial 14-hydroxy group by the nucleophilic reagent. This induces retro-aldol cleavage to give the corresponding 13,14-secosteroid, which then undergoes conformational isomerisation and re-aldolisation with the formation of the energetically more favourable natural isomers (LIV). The equatorial 14β-hydroxy group in the latter is inert to the incoming nucleophile as a consequence of either shielding by the neighbouring C_{13} axial substituent or the energetically unfavourable reversal of the isomerisation to give (LIII). Furthermore, the formation of the intermediate Wittig betaine complex depends on the size and nature of the cyclic ketone. Thus, it has been established[1] that the reactivity of the keto group decreases in the following order:

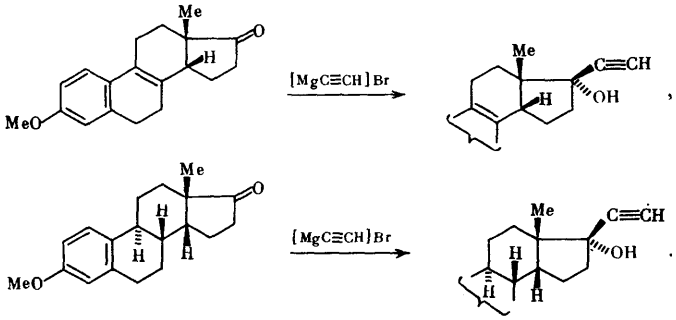


This explains why the keto group of the intermediate anions (LIIIa, b, c) (Scheme 2), which arise during the isomerisation of (LIII) to (LIV), is inert to Wittig reagents.

It is worth noting that, in *cis-C/D*-steroids, the angle ($\theta^{cis} \approx 110-120°$) between the plane of the *D*-ring and the remainder of the steroid skeleton is such that attack of nucleophiles from the α-side (Scheme 3) would be unfavourable.[54] However, in the corresponding *trans-C/D*-steroids and/or those containing endocyclic double bonds, the angle between the planes ($\theta^{trans} = 170-180°$) [55] is such that attack from the α-side is favourable on steric grounds so that the keto group at C_{17} is available for Wittig olefination or nucleophilic addition of Grignard reagents (to give 17β-alkyl derivatives):[50]



It should be further noted that Grignard addition does take place with 17-keto-*cis*-*C*/*D*-steroids having *trans-syn-cis* skeletal fusion or where there is a 8(9)-double bond, i.e. where a 13β-axial alkyl group and an equatorial 14β-hydroxy group or 14β-hydrogen are present:[56]



At the same time, 14β-hydroxyestratrienes of unnatural configuration and/or $\Delta^{9(11)}$-derivatives, where there is a 13β-equatorial and 14β-axial group, are sterically crowded in the vicinity of C_{17} so that the $sp^2 \rightarrow sp^3$ transformation at this atom (on formation of the intermediate Wittig betaine or on addition of Grignard reagents) is inhibited.

***

Steroids having a β-hydroxyketo residue undergo retro-aldol cleavage in basic media. Conformational isomerisation of the products, followed by re-aldolisation, may then take place. This is notably exemplified by the *C*/*D* ring inversion of 14-hydroxy-17-ketosteroids, of which the natural *trans-anti-cis*-isomers readily undergo retro-aldol cleavage in basic media (or under the conditions of the Wittig reaction) to give the corresponding 13,14-secosteroids. Conformational isomerisation of the latter, followed by re-aldolisation, leads to the energetically more favourable isomers having the *trans-syn-cis*-fusion characteristic of natural cardio-active steroids. This isomerisation may be applied in the synthesis of 14β-hydroxyestratrienes and (after reduction of the *A*-ring) analogues of cardioaglycones. 17-Ketosteroids with the natural configuration may be functionalised at C_{17}, e.g. by Wittig olefination or Grignard addition.

References

1. J March, R Paniko *Kurs Teoreticheskikh Osnov Organicheskoi Khimii* (A Course on the Theoretical Basis of Organic Chemistry) (Translated from the English language version and Edited by P A Yanovskoi), Mir, Moscow, 1975, p. 358
2. P S Wharton *J. Org. Chem.*, 1972, **37** 34
3. M Tanabe, D A Crowe *Tetrahedron Lett.*, 1965, **30** 2776
4. G A Artamkina, I P Beletskaya *Usp. Khim.*, 1987, **56**(10) 1717 [English translation in *Russ. Chem. Rev.*, 1987(10)]
5. P De Mayo *Molecular Rearrangements, Vol. 1*, Interscience, New York, 1961
6. P De Mayo *Molecular Rearrangements, Vol. 2*, Interscience, New York, 1964
7. N L Wendler *Molecular Rearrangements, Vol. 2*, Interscience, 1964, p. 1067
8. R P A Sneedon, R B Turner *J. Am. Chem. Soc.*, 1955, **77** 130; A S Meyer *Experientia*, 1955, **11**(3) 99
9. P J Sykes, R W Kelly *J. Chem. Soc. C*, 1968, (23) 2913
10. A A Akhrem, T V Ilyukhina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 1795
11. A A Akhrem, T V Ilyukhina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 2018
12. Z Hauptman, U Grefe, K Remane *Organicheskaya Khimiya* (Organic Chemistry) (Translated from the German language version and Edited by V M Potapov), Khimiya, Moscow, 1979, p. 354
13. A A Akhrem, T V Ilyukhina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 909
14. M H Benn, R Shaw *J. Chem. Soc. D*, 1970, 327
15. M L Lewbart, V R Mattox *J. Org. Chem.*, 1964, **29** 513,521
16. S Bernstein, M Heller, S Stolar *J. Org. Chem.*, 1961, **26** 5036
17. A A Akhrem, A V Kamernitskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 2792; A A Akhrem, A V Kamernitskii, V A Dubrovskii *Izv. Akad. Nauk SSSR Ser. Khim.*, 1963, 2237; C Monneret, C Tchernatinsky, H Q Khuong *Ann. Pharm. Fr.*, 1970, **28** 443
18. I Kouno, H Irie, N Kawano *J. Chem. Soc., Perkin Trans. 1*, 1984, 2511
19. H L Herzog, M J Gentles, A Mitchell, et al. *J. Am. Chem. Soc.*, 1959, **81** 6478
20. J Bascoul, B Cocton, P A Crastes *Tetrahedron Lett.*, 1969, 2401
21. L B Chin, R M Dodson *J. Org. Chem.*, 1959, **24** 879
22. G Horvath, G Ambrus *Biomed. Mass. Spectrom.*, 1977, **4** 376
23. K Annen, H Hofmeister, H Laurent, et al. *Tetrahedron Lett.*, 1984, **25**(14) 1453
24. H M Walborsky, S M Reddy *J. Org. Chem.*, 1988, **53**(20) 4851
25. P Kurath *J. Org. Chem.*, 1967, **32**(11) 3626
26. J S McKechine, I C Paul *J. Am. Chem. Soc.*, 1968, **90**(8) 2144
27. M K Dzhafarov, M V Dodonov, S N Ananchenko, et al. *Bioorg. Khim.*, 1988, **14**(5) 675
28. M K Dzhafarov *Dis. ... Kand. Khim. Nauk* (Dissertations of Candidates in the Chemical Sciences), Moscow State University Press, Moscow, 1988
29. F Sondheimer *Chem. Br.*, 1965, **1** 454
30. W Schonfeld, J Weiland, C Lindig, et al. *Arch. Pharm. (Weinheim. Ger.)*, 1985, **329** 414
31. A Kurek, M Gumulka, J Wicha *Chem. Commun.*, 1981, (1) 25
32. T Y R Tsai, A Minta, K Wiesner *Heterocycles*, 1979, **3**(12) 1397; K Wiesner, T Y K Tsai, R S Kumar *Helv. Chim. Acta*, 1984, **67** 1128
33. P Welzel, H Stein *Tetrahedron Lett.*, 1981, **32**(35) 3385
34. A V Platonova, A O Lailiev, S N Ananchenko, I V Torgov *Bioorg. Khim.*, 1982, **8**(4) 542
35. I V Torgov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, (2) 299
36. M K Dzhafarov, M V Dodonov, A V Platonova, et al. *Bioorg. Khim.*, 1986, **12**(7) 970, 981
37. M K Dzhafarov, M V Dodonov, A V Platonova, et al. *Bioorg. Khim.*, 1986, **12**(7) 981
38. M K Dzhafarov, S V Lindeman *Bioorg. Khim.*, 1987, **13**(5) 679
39. M K Dzhafarov, T V Timofeeva, Yu T Struchkov *Zh. Org. Khim.*, 1989, **25**(2) 342
40. A V Zakharychev, I Hora, S N Ananchenko, I V Torgov *Tetrahedron Lett.*, 1966, (30) 3585
41. N Makk, G Töth, E Tomorkeny *Steroids*, 1975, **25**(5) 611
42. M K Dzhafarov, T V Timofeeva, S V Lindeman, S P Ionov *V Vsesoyuz. Soveshchanie po Organicheskoi Kristallokhimii. Tez. Dokl.* (5th All-Union Conference on Organic Crystal Chemistry. Abstracts of Reports), Chernogolovka, 1987, p. 5

43. *13,14-Secosteroids,* CIBA Ltd. Neth. Appl. 6, 511, 534 (C1. C07c), 7 March 1966; Swiss Appl. 4 Sept. 1964, p. 23; *Chem. Abs.,* 1966, **65** 775b
44. M K Dzhafarov, S V Lindeman *VIII Vsesoyuz. Simpozium po Mezhmolekulyarnym Vzaimodeistviyam i Konformatsiyam Molekul. Tez. Dokl.* (8th All-Union Symposium on Intermolecular Interactions and Molecular Conformations. Abstracts of Reports), Novosibirsk, 1990, Part 1, p. 116
45. M K Dzhafarov, S V Lindeman, Yu T Struchkov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1991 (in press)
46. A R Daniewski, Z Valenta, P S White *Bull. Pol. Acad. Sci., Chem.,* 1984, **32**(1–2) 29
47. M Nogradi *Stereoselektivnyi Sintez* (Stereoselective Synthesis), Mir, Moscow, 1989, p. 406
48. M Schlosser *Top. Stereochem., Vol. 5* (Edited by E L Eliel, N L Allinger), Interscience, New York, 1970, p. 1
49. M K Dzhafarov, S P Ionov *Vsesoyuz. Soveshchanie po Problemam Prikladnoi Kristallokhimii* (All-Union Conference on Problems in Applied Crystal Chemistry), Voronezh, 1989 (in press)
50. M K Dzhafarov, T V Timofeeva, Yu T Struchkov *VI Vsesoyuz. Soveshchanie po Organicheskoi Kristallokhimii. Tez. Dokl.* (6th All-Union Conference on Organic Crystal Chemistry. Abstracts of Reports), Kiev, 1991
51. H-J Siemann, G Langbein, M Richter *Z. Chem.,* 1979, **19**(12) 451
52. M Wunderwald, B Schoenecker, G Schubert, K Ponsold, Ger. (East) DD 209, 463 (C1. C073J3/00), 1984, p. 11; *Chem. Abs.,* 1985, **102** 6947
53. B Schoenecker *J. Pharm. Sci.,* 1973, **2**(1) 9
54. W Y Wang, W Reusch *Tetrahedron Lett.,* 1988, (4) 1007
55. J F Griffin, W L Duax, C M Weeks *Atlas of Steroid Structure,* Plenum Press, New York, 1984, Vol. 2, p. 754
56. P Crabbe, A Cruz, J Iriarte *Can. J. Chem.,* 1968, **46** 349

Translated from *Uspekhi Khimii* **61** 689–710 (1992) U.D.C. 543.544:532.66:541.1

Physicochemical application of capillary chromatography

A V Vasil'ev, E N Aleksandrov
Nesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences, Moscow
Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow

ABSTRACT. The application of capillary gas chromatography in the determination of the free energy, enthalpy, and entropy of sorption, the saturated vapour pressure and activity coefficients, the assessment of the lipophilicity of volatile compounds, and the study of the properties of polymers and liquid crystals is described. The use of reaction capillary chromatography in kinetic studies of conformational conversions, thermal degradation, and photochemical reactions is examined. Studies on the use of capillary columns for determination of the second virial coefficients and viscosity of gases and the diffusion coefficients in gases, liquids, supercritical fluids, and polymers are analysed.

The bibliography includes 114 references.

Contents

I. Introduction 343
II Determination of equilibrium sorption parameters and related values 373
III. Application of capillary gas chromatography in chemical kinetics 378
IV. Study of the transport properties of different media 379

I. Introduction

High-performance capillary chromatography is a powerful method for the analysis of multicomponent mixtures in chemistry, biology, and medicine and in the monitoring of environmental pollution. Furthermore, the practical value of this type of chromatography is not purely restricted to analytical problems, as it is also a convenient method for the determination of physicochemical parameters, for which packed columns are traditionally used.[1–4] However, with regard to their physicochemical applications, capillary columns have a whole series of advantgages over packed columns, and in recent years they have been increasingly used for the determination of the thermodynamic properties of sorption, the study of the transport properties of gases and liquids, research on polymers and liquid crystals, and also in chemical kinetics.

Open tubular or capillary columns (CCs) were first proposed by Golay.[5,6] They are relatively narrow and long, coiled cylindrical tubes in which the stationary phase is distributed over the inner surface of the walls. Golay pointed out that the main characteristic of CCs is not the small magnitude of their internal diameter (50–800 μm) but their hollowness, which provides them with high permeability.[7] Because of the low pneumatic resistance of capillary columns it is possible to increase their length to 100 m or more and thus increase their efficiency approximately by a factor of 10^2 compared to packed columns. As a result, the accuracy in measuring retention parameters in capillary chromatography is 5–10 times greater than in chromatography with packed columns.[8] The high efficiency of CCs makes it possible to study several compounds in mixtures at the same time and to reduce the need for sample purity. When using capillary column for research, it is sufficient to have microgram quantities of the materials: micrograms of stationary phases and nano- or even pico-grams of volatile sorbates. Because of the lower sorptive capacity of CCs in comparison with packed columns and also their lower adsorption and catalytic activities, it is possible to study low-volatility, thermally labile, and chemically unstable compounds.[9–10] The extremly simple geometry of capillary columns and the possibility of preparing a readily controlled layer of the stationary phases make them ideal for measurement of diffusion coefficients in gases, liquids, and polymers. The aim of this review is to summarise the experience of using capillary columns in physicochemical studies.

II. Determination of equilibrium sorption parameters and related values

Of fundamental importance in gas chromatography is the distribution coefficient of compounds in the system mobile phase–stationary phase, which may be calculated from the chromatographic retention and volumetric phase ratio. From the distribution coefficient and its dependence on temperature and pressure it is possible to determine thermodynamic parameters of sorption, such as the free energy, enthalpy and entropy of sorption, the activity coefficient of the sorbate at infinite dilution in the stationary phase, the saturated vapour pressure and volatility of the sorbate, and finally the mixed second virial coefficient of the sorbate–carrier gas intermolecular interaction.[3]

Sources of systematic errors not orginating from the equipment in the determination of these parameters can result from nonlinearity of the sorption isotherm, solubility of the carrier gas in the liquid phase, nonequilibrium solution of the compound and its adsorption at the phase boundaries of gas–liquid and liquid–phase wall of capillary column.

1. Determination of differential molar free energies of solution

Golovnya and Samusenko[11–13] studied the change in Gibbs potential when different classes of organic compounds were dissolved in poly(ethylene glycol) PEG 40M deposited on the walls of glass CCs that had been deactivated with KF and Na_3PO_4 salts. By calculating the differences in free energies of sorption of compounds with and without the functional groups NO_2, OH, NH_2, Br, SH and CH_3 it was possible to eliminate the undetermined factors related to

the phase ratio in the columns:

$$\delta(\Delta G)_{X,H} = \Delta G_{RX} - \Delta G_{RH} = -RT\ln\left(\frac{t_{RX}-t_M}{t_{RH}-t_M}\right) = -RT\ln(t'_{RX}/t'_{RH}), \quad (1)$$

where t_{RX} and t_{RH} are the retention times of compound RX with functional group X and its hydrocarbon analogue RH (n-octane or benzene), t_M is the hold-up time, t'_{RX} and τ'_{RH} are the adjusted retention times of compounds RX and RH. It was established that the presence of salts and their chemical nature affect the retention of compounds with functional groups that can undergo a specific intermolecular interaction. Unfortunately, it is not clear whether this interaction occurs with ions dissolved in PEG 40M or whether it takes place on the surface of the salt crystals by an adsorption mechanism. The same method was used on glass CCs with the stationary phases OV-101, OV-17, PEG 40M and added KF to determine the increments of methyl groups to the sorption potentials of methylbenzenes,[13,14] methylpyrazines,[15] methylpyridines, methylpiperidines, and branched secondary aliphatic amines.[14,16] From the relationships that were established, the authors developed schemes to predict the retention indices of methylpyrazines[15] and methylpyridines[17] for their identification on columns of varying polarity.

Grigor'eva et al.,[18,19] by using glass CCs with a thick layer of immobilised siloxane SE-54, studied the change in free energy of sorption of mono- and bi-functional carbonyl-containing compounds in relation to the number of their methylene units. An anomalously small retention of the primary homologues was detected for series of methyl and butyl n-alkyl ketones and fatty acid methyl esters. A similar pattern occurs for a series of dimethyl series of α,ω-dicarboxylic acids. The anomalies in the retention of the primary homologues in the above series were not observed when the more polar stationary phases OV-210, PEG 40M, SP-2300 and Silar 10 C were used.

2. Determination of the enthalpy and entropy of sorption

The heat of solution of a sorbate can be determined by studying its retention at different temperatures. On incorporating the Karger relationship:[20]

$$\Delta G = -RT\ln K = -RT\ln(k\beta), \quad (2)$$

the Gibbs–Helmholtz equation can be given in the form:

$$-R\left[\frac{\partial(\ln k\beta)}{\partial(1/T)}\right]_p = \Delta H, \quad (3)$$

where the heat of solution is determined as the gradient of the tangent to the curve of the logarithm of the capacity factor (k) against temperature on $-R\ln k$ and $1/T$ coordinates. It is worth noting that it is not necessary to know the distribution coefficient K in order to determine ΔH, since the phase ratio (β) is virtually independent of temperature.

A number of authors[21,22] determined the heat of solution of light aliphatic and alicyclic hydrocarbons (C_5–C_8) in squalane by using copper and steel capillary columns. When precise measurements of the absolute molar heats of solution were carried out,[22] the linear dependence of the enthalpy of solution on temperature and the nonideality of the gas phase were taken into account (see Section 3). By careful maintenance of a constant temperature (±0.01 °C) and pressure at the column inlet (±0.001 atm), the error in determination of ΔH was not more than 3%. Although the hydrocarbons studied are not very susceptible to adsorption, the latter may in principle affect the accuracy in determination of heats of solution since metal CCs have high adsorptive activity. Moreover, their extensive irregular surface[23] is difficult to cover completely with the stationary phase.

Mohnke and Heybey[24] determined the specific retention volumes of permanent gases and methane in glass CCS with zeolite 5A at different temperatures, and from them calculated the enthalpies of adsorption ΔH_{ads}. In addition they determined the differences between the enthalpies and entropies of adsorption of methane and deuteromethane on a capillary columns with a layer of activated charcoal. Suslov et al.[25] determined the retention indices of hydroxy and amino derivatives of adamantane on glass capillary columns with OV-101 and XE-60 at different temperatures. By using the formulae proposed in two earlier studies,[26,27] Suslov et al.[25] calculated the free energies, enthalpies, and entropies of sorption of the adamantane derivatives from the derived values of the indices and experimental specific retention volumes of n-alkanes.

Berezkin and Korolev[9,10] estimated the error in the gas chromatographic determination of the heats of solution of compounds with varying polarity in thin layers of immobilised siloxane SE-30 resulting from their adsorption on the walls of quartz CCs. By using the "internal standard" method,[28] the authors[9,10] determined the true distribution constants for a number of compounds in the system gas–liquid phase at four temperatures, and from these values they calculated the true heats of solution of these compounds in SE-30. Furthermore, from the chromatographically determined distribution constants of the compounds in the system mobile phase–stationary phase they determined the apparent heats of solution of the same compounds while neglecting adsorption. Comparison of the true and apparent values showed that neglect of adsorption led to a 13–20% overestimation of the experimental heats of solution of polar compounds, while for n-tridecane this difference was 4%. This relatively large contribution of adsorption for polar compounds may be due partly to the low thickness of the phase layer (74 nm) and partly to the effect of the benzoyl peroxide used as an initiator for immobilisation of SE-30.[9,10] The use of this initiator is known to result in a considerable increase in adsorption activity of capillary columns with alkylpolysiloxanes.[29–30]

3. Effect of the nonideality of the gas phase on the equilibrium sorption parameters and a determination of the second virial coefficients of gases

As has already been mentioned, it is necessary to take into account the nonideality of carrier gases in precise physicochemical measurements. This manifests itself particularly clearly in high-performance capillary gas chromatography. Thus, replacement of the "completely ideal" carrier gas H_2 by N_2 produces such a marked change in selectivity for separation of the components of a sample of gasoline on a CC with a poly(dimethylsiloxane) phase that inversion of the peak yield occurs.[31]

At medium pressure and when the carrier gas does not dissolve in the stationary phase, the distribution coefficient depends on the mixed second virial coefficient of sorbate and carrier gas B_{sG}:[32,33]

$$\ln K = \ln K^0 + \frac{2B_{SG} - V_S^\infty}{RT} p_o J_3^4, \quad (4)$$

where K^0 is the distribution constant at zero pressure of carrier gas, V_S^∞ is the molar volume of sorbate in the stationary phase, J_3^4 is the pressure drop factor $\{J_3^4 = {}^3/_4[(p_i/p_o)^4 - 1]/[(p_i/p_o)^3 - 1]\}$, and p_i and p_o are the pressures at the inlet and outlet of the column respectively. In order to calculate the mixed second virial coefficient of sorbate–carrier gas, the second virial coefficient of the carrier gas

must be known.[31] The second virial coefficients frequently serve as reference values in calculations and design in many fields of science and technology.

Huang et al.[34] put forward an original method for the experimental determination of second virial coefficients of gases (B_{GG}) using CCs without a stationary phase. The viscosity of gases and the coefficient (α) of the linear dependence of viscosity on pressure are determined at the same time as B_{GG} with this method. By integrating Poiseuille's equation, in which the pressure and viscosity are presented in the form of exponential series, and neglecting the terms with a higher order of insignificance, Huang et al.[34] derived equation (5), which relates B_{GG}, α, and the viscosity of a gas at zero pressure (μ_0) with the experimental parameters:

$$\frac{64p_o u_o}{p_i^2 - p_o^2} = \frac{d^2(1 + B_{GG}p_o/RT)}{L \quad \mu_0}[1 - (\alpha + B_{GG}/RT)p_o J_2^3], \qquad (5)$$

where p_o and u_o are the pressure and velocity of gas at the column outlet, p_i is the pressure at the inlet, L and d are the length and internal diameter of the column, J_2^3 is the pressure drop factor $\{J_2^3 = {}^2/_3[(p_i/p_o)^3 - 1]/[(p_i/p_o)^2 - 1]\}$. The experimental equipment comprises a system of two identical capillary columns that are connected via a valve. The pressures at the inlet and outlet of the system p_i and p_o are kept at a constant level, and the gas velocity is controlled by the valve, with readings taken from manometers between the columns before and after the valve. The authors proposed a simple graphical method for determining B_{GG}, μ_0, and α from the experimental values of the pressures and flow rate of gas. The calculated error in the determination of B_{GG} and α for compounds with a boiling point close to room temperature is not more than 1%. By varying the composition of the gas mixture, it is readily possible with this system to determine the concentration dependence of B_{GG}, μ_0, α, from which the intermolecular interaction potential in the gas phase can be calculated.[34]

4. Determination of the saturated vapour pressure of compounds with low volatility

In contrast to other methods, the gas chromatographic method of determining saturated vapour pressure does not require the compound under study to be highly pure, but on the other hand it can be used to record simultaneously the vapour pressures of several components that are present in very small quantities in mixtures. Virtually all the studies on the gas chromatographic method for determining vapour pressure on capillary columns are devoted to highly toxic materials that contaminate the environment. The method is based on the assumption that the adjusted retention time of sorbates ($t'_R = t_R - t_M$) is inversely proportional to their saturated vapour pressure. This assumption is only strictly valid for ideal solutions in which the environment of a molecule is similar to the condensed state of pure sorbate. Thus, this approximation is closer the greater the similarity between the molecules of volatile substances and the stationary phase.

It follows from the Clausius–Clapeyron equation for the vapour of substances that

$$d(\ln p_i^0) = \left(\frac{\Delta H_i}{\Delta H_{st}}\right) d(\ln p_{st}^0), \qquad (6)$$

where p_i^0 and p_{st}^0 are the saturated vapour pressures of the substance under study and a standard, ΔH_i and ΔH_{st} are their heats of evaporation. In the approximation used, the relative retention of a pair of sorbates is inversely proportional to their relative volatility:

$$k_i/k_{st} = p_{st}^0 / p_i^0, \qquad (7)$$

and

$$\ln p_i^0 = \ln p_{st}^0 - \ln(k_i/k_{st}). \qquad (8)$$

Incorporating Eqn. (6), we can write

$$\ln(k_i/k_{st}) = (1 - \Delta H_i/\Delta H_{st}) \ln p_{st}^0 - C, \qquad (9)$$

where C is a constant.

A compound which is chemically similar to the substance being studied and having a known heat of evaporation, boiling point, or saturated vapour pressure is used as the standard.[35] It is assumed in this case that $(\Delta H_i/\Delta H_{st})$ is independent of temperature over a wide range. The values of the constants $(\Delta H_i/\Delta H_{st})$ and C are determined graphically, by plotting the dependence of $\ln(k_i/k_{st})$ on $\ln p_{st}^0$ at different temperature. The required vapour pressure is calculated from the equation

$$p_i^0 = p_{st}^{0(\Delta H_i/\Delta H_{st})} \exp C, \qquad (10)$$

which follows from Eqns. (8) and (9).

The saturated vapour pressures of polychlorinated biphenyls were determined in a similar manner using a short glass CC (1 m × 0.25 mm) with an Apolane-87 phase.[36] Isobutyl 2,4,5-trichlorophenoxyacetate was used as the standard. The values of p_i^0 extrapolated to 25 °C were $2 \times 10^{-4} - 4.5 \times 10^{-6}$ mmHg. The error in determining p_i^0 was not more than 30%. However, at 25 °C the sorbates are solids, and therefore the derived vapour pressures will probably be somewhat overestimated, since all the calculations related to a gas-liquid equilibrium at the temperature of chromatographic separation (60–130 °C). The author's argument about the need to use the most nonpolar stationary phase is also questionable, since the sorbates are compounds with medium polarity. Subsequently, in order to determine the vapour pressure of organochlorine and polyaromatic compounds, Bidleman[37] used a quartz CC (1 m × 0.22 mm) with immobilised poly(dimethylsiloxane) BP-1 in addition to a column with an Apolane-87 phase. He used n-alkanes (C_{18} and C_{20}) and dibutyl phthalate as standards. However, the use of dibutyl phthalate gave values of the vapour pressure of nonpolar sorbates that were too low, so it was recommended to use $C_{14}-C_{16}$ n-alkanes when $p_i^0 = 10^{-1}-10^{-2}$ mmHg and $C_{22}-C_{24}$ n-alkanes when $p_i^0 < 10^{-6}$ mmHg as standards.

In order to assess the accuracy of the gas chromatographic determination of p_i^0, the data obtained were correlated with known values of the saturated vapour pressure. Although the temperature of separation of the components on capillary columns is considerably lower than their boiling points, it may be assumed that the experimental values of vapour pressure (p_{GC}) do in fact correspond to the vapour pressures above supercooled liquids (p_l). The equilibrium vapour pressure above a solid (p_{sol}) at 25 °C may be calculated from the entropy of fusion ΔS_f and melting point T_m of the compound respectively:[38]

$$\ln(p_l/p_s) = \frac{\Delta S_f(T_m - 298)}{298R}. \qquad (11)$$

Since the values of the entropy of sorption of a large number of compounds average out to 56.5 kJ mol^{-1} deg^{-1}, in the calculations frequent use is made of the empirical equation of MacKay:[39]

$$\ln(p_l/p_s) = 6.8(T_m - 298)/298.$$

Bideleman[37] found that the experimental vapour pressure values (p_{GC}) correlate well, but in the majority of cases they do not match the saturated vapour pressure values (p_l) determined by other methods. The correlation coefficients of the linear relationship

$$\log p_{GC} = m \log p_l + b \qquad (12)$$

for columns with Apolane-87 and BP-1 were 0.97–0.98, with the smallest deviation of p_{GC} occurring for the column with Apolane-87.[37] However, the column with BP-1 proved more convenient for a determination of the vapour pressure of chlorinated derivatives of phenol and hydroquinone.[40] The relationship between p_{GC} and p_l which was derived for chlorophenol was used in a chromatographic determination of the saturated vapour pressure of chloroguaiacols, chloroveratroles, and 4-nonylphenol.[40]

Kim et al.[41] studied the effect of different experimental factors on the accuracy of the gas chromatographic determination of the saturated vapour pressures of 20 organophosphorus pesticides with different structures. Parathion, methylparathion, diazinone, and dibutyl phthalate were used as standards. The length of the capillary columns (from 1 to 27 m) and the nature of the nonpolar stationary phases (SE-30, SE-54, RSL-100) did not have much effect on the magnitudes of the experimentally determined vapour pressures. To achieve a relative standard deviation of less than 10% it was necessary to determine the retention coefficients at five or more temperatures at 5 °C intervals or at three temperatures at 15 °C intervals. Comparison of the vapour pressures derived by the gas chromatographic method with the vapour pressures determined by the gas saturation method showed that the greatest accuracy in the gas chromatographic determination of vapour pressure is achieved when a standard that is closest in nature to the components under study is used. The lowest accuracy was recorded in the determination of saturated vapour pressures of polar compounds and components that were solids at room temperature.[41]

By using a 75 centimetre-long CC with grafted poly[dimethyl-(5%)-diphenylsiloxane] DB-5 (0.25 μm), Eitzer and Hites[42] determined the saturated vapour pressures of a number of polychlorinated dibenzo-*p*-dioxins and dibenzofurans. *p,p'*-DDT, which is eluted in a similar manner to the components being studied, was chosen as the standard. The vapour pressure of DDT was repeatedly determined by independent methods. Like the components under study, DDT is detected using a high-sensitivity electron capture detector, which makes it possible to decrease the quantity of sample to a minimum and hence exclude the possibility of overloading short CCs.[38] The authors[42] established a good correlation between the derived vapour pressure values and the retention indices of the respective dioxins and dibenzofurans determined on a CC of the same type (DB-5).[43,44] From the correlative equation obtained it is possible to predict the saturated vapour pressures of many compounds of these classes from their gas chromatographic retention indices. A comparison of the vapour pressure values determined on a column with DB-5 with the values determined by other methods showed that the gas chromatographic method gives underestimated pressure values for dibenzo-*p*-dioxins and dibenzofurans with a low chlorine content and values that a overestimated for their highly chlorinated analogues.[42]

Hinckley et al.[38] also determined the saturated vapour pressure of a number of organochlorine and organophophorus compounds and phthalate esters, using *p,p'*-DDT as a standard. The vapour pressures were 10^{-2}–10^{-4} Pa (25 °C). The authors concluded[38] that the main reasons for the lack of agreement between the vapour pressure values determined by chromatography and by other methods lie in the experimental errors in the determination and also in differences between the activity coefficients and of the compounds being studied in the stationary phase. In general, ideality of the solutions in the stationary phase is not essential for the gas chromatographic method. It is only necessary that the degree of nonideality for the compound being studied and the standard is the same. Thus, equations (7)–(9) for nonideal solutions must contain the additional terms γ_{st}/γ_i and $\ln(\gamma_{st}/\gamma_i)$ respectively, and the accuracy of this method depends on the similarity between the activity coefficients of the compound under study and the standard in the stationary phase. The authors concluded that the gas chromatographic method is of limited suitability for determining the saturated vapour pressure of polar compounds because of the difficulty in selecting a suitable polar standard due to the marked differences between the activity coefficients of polar compounds.[38]

5. Determination of activity coefficients

Lunskii and Paizanskaya[45] recently put forward a method for the determination of activity coefficients at infinite dilution from the retention indices and saturated vapour pressures of sorbates. The retention indices of hydrocarbons from the gasoline fractions of unfractionated condensates were determined on glass CCs with squalane and dinonyl phthalate. For compounds having similar activity coefficients, the dependence of the retention indices on the logarithm of the partial saturated vapour pressures comprises a series of parallel lines with the same slope, governed by the relative retention of the n-alkanes used to determine the retention indices. Points that correspond to compounds with a similar molecular structure lie on each straight line of this series. The activity coefficients are determined from the values of the intercepts on the y-axis. It is also necessary to know the saturated vapour pressure of the n-alkanes used and their activity coefficients in the stationary phases for the calculation. It was established from the data obtained that isoalkane and naphthenic hydrocarbons form athermal solutions in squalane while in dinonyl phthalate their activity coefficients decrease with increase in temperature. For aromatic hydrocarbons the reverse effect occurs when the phases are changed. Solutions of all these hydrocarbons in squalane exhibit negative deviations from Raoult's law, while in dinonyl phthalate both negative and positive deviations occur.[45]

6. Determination of the lipophilicity of volatile compounds

Lipophilicity is an important property of biologically active compounds, and it is frequently determined as the logarithm of the distribution constant ($\lg K$) of these compounds in the system octane–water. The direct determination of distribution coefficients of a very large number of chemical compounds investigated at regular intervals for biological activity is difficlt using a static method or reverse-phase liquid chromatography.

In order to make use of the extensive quantity of gas chromatographic data, Kuchar et al.[46,47] developed a method for the indirect determination of lipophilicity of homologous series of structurally similar compounds from their retention indices on nonpolar and polar capillary columns. The distribution constant in the system octanol–water can be represented as the product of the distribution constants in the systems octanol–gas and gas–water: $K_{o/w} = K_{g/w}K_{o/g}$. Unfortunately, gas chromatographic determination of distribution constants in these sytems is impossible because of the high volatility of water and octanol, so normal stationary phases (SFs) are used instead,

assuming a similarity between water and a polar SF (PSF) and between octanol and a nonpolar SF (NSF):

$$K_{o/w} \cong K_{g/PSF} K_{NSF/g},$$

$$\log K_{o/w} \cong \log(K_{NSF}/K_{PSF}) + A,$$

or

$$\log K_{o/w} = \log(V'_{R,NSF}/V'_{R,PSF}) + B,$$

where A and B are constants.

By further assuming a linear relationship between the adjusted retention volumes (V'_R) of the compounds and their retention indices ($I = \alpha \log V'_R + \beta$), it was possible to derive the relationship

$$\log K_{o/w} = CI_{NSF} - DI_{PSF} + E, \quad (13)$$

where C, D, and E are constants. By using, on the one hand, a database of Kováts indices determined on quartz CCs with SE-30 phases [poly(dimethylsiloxane)] and OV-351 (a copolymer of poly(ethylene glycol) and nitroterephthalic acid) phases[48–50] and, on the other hand, the values of lipophilicity calculated by additive methods, the authors determined the coefficients in Eqn. (13) for a large number of homolytic series of aliphatic, olefinic and aromatic esters and their chloro and nitro derivatives.[46,47] It transpired that for groups of homolytic series of structurally similar compounds the coefficients in Eqn. (13) were similar, and their lipophilicity could be calculated approximately from the common correlative equations. The high statistical significance of these equations (r = 0.921 to 0.999) is an indication of the suitability of the chosen column system for an indirect determination of lipophilicity. At the same time, the similarity between the systems SE-30–OV-351 and octanol–water is very arbitrary, and the retention volume is in fact related nonlinearity to the Kováts indices, especially for the primary members of the homolytic series.[51] Moreover, it was established that the Kováts indices on polar stationary phases cannot serve as parameters for the relative solubility of compounds since the n-alkanes used to determine them are retained to a significant extent through adsorption on the surface of the polar phase.[52–54] All these factors limit the applicability of this method to an approximate determination of lipophilicity.

The most accurate method of assessing the lipophilicity is a direct determination of the distribution constant in a static experiment. In order to determine the distribution coefficients of highly lipophilic compounds, Haky et al.[55] analysed the composition of the equilibrium water and octanol phases on a quartz CC with immobilised poly[phenyl-(5%)-methylsiloxane] DB-5. The internal standards used were anthracene and fluorene, which have well-established distribution coefficients. The recorded values of lipophilicity matched the literature data within the limits of experimental reproducibility (±0.2 units of $\log K_{o/w}$). Thus, by combining the distribution method with a quantitative analysis of the phases on a high-performance capillary column, it was possible to determine with reproducibility and accuracy the lipophilicity of compounds up to values of $\log K_{o/w} = 5.7$.[55]

7. Study of the properties of polymers

The solubility of compounds in industrial polymers is of interest in terms of its technological, hygiene and sanitation, and toxicological aspects. Capillary columns have been used to study the solubility of organic copounds in polyisobutylene, poly(vinyl acetate), poly(dimethylsiloxane),[56,57] polystyrene,[58] and poly-ethylene.[59] It was established in three studies[56,57,59] that the specific retention volumes of organic compounds in high-molecular-weight polymers deposited in capillary columns is higher than in packed columns. The specific retention volumes of 13 organic compounds, including THF, alkanes, alkenes, and arenes in a relatively thick layer (~1.4 μm) of low-density polyethylene (LDPE), dynamically deposited on a CC made of stainless steel, were measured over a wide temperature range (50–175 °C).[59] Because of the significantly nonequilibrium nature of the sorption, the retention volumes were extrapolated to zero flow of carrier gas. From the experimental finding and a considerable quantity of literature data, it was possible to derive correlative equations that related the specific retention volumes on HDPE (V_g) at different temperature with the critical parameters of the sorbates:

$$\ln(V_g p_c/100) = a + b(T_c/T)^2, \quad (14)$$

where p_c, and T_c are the critical pressure and temperature of the sorbates; a and b are constants. The correlation coefficients for equations of the type (14) are 0.991 and 0.987 for molten and rubbery LDPE. By using these equations, it is possible at given temperatures to determine the solublity of any nonpolar or medium-polar compounds in polyethylene when their critical pressure and temperature are known.

According to the results of Pawlisch et al.[58] the graphs of the dependence of exit time of the chromatographic peak maximum on the velocity of the carrier gas frequently have considerable curvature, and extrapolation to zero flow can lead to errors in the determination of true retention volumes. The same authors determined the retention volumes of benzene, toluene, and ethylbenzene on a glass CC with thick layers (7–12 μm) of polystyrene from the magnitudes of the primary peak features by means of numerical treatment of the computer signal. Subsequently the activity coefficients at infinite dilution and the Flory–Huggins interaction parameters $\chi_{1,2}$ for these compounds were calculated from the specific retention volumes.

Barrales-Rienda et al.[60] recently determined the specific retention volumes of C_9–C_{13} n-alkanes and C_6–C_{10} aliphatic alcohols in poly[*N*-(n-octadecyl)maleimide] at different temperature. The polymer was deposited on a steel CC (resulting thickness of layer 1.67 μm) using a static method. From the data obtained the authors calculated the actvity coefficients at infinite dilution, the Flory–Huggins parameters $\chi_{1,2}$, and the solubility parameters δ_1 and δ_2. Furthermore, the temperature dependences of the activity coefficients and specific retention volumes were used to determine the partial molar heats of mixing and solution, the sum of which corresponded to the heats of evaporation of the pure sorbates, as calculated from the Clausius–Clapeyron equation. In a similar manner Roth et al.,[61] using glass CCs, determined the excess molar enthalpies of solution of C_8–C_{12} n-alkanes in polysiloxanes. It was found that the values of the excess enthalpies of solution in poly(dimethylsiloxane) SE-30 were positive, while in poly[methyl-n-alkyl(C_8–C_{18})siloxanes] they were negative, which was an indication of the stronger intermolecular interaction between n-alkanes and polysiloxanes having long aliphatic side chains.

8. Study of the properties of liquid crystals

Liquid-crystalline compounds are used in gas chromatography as stationary phases that have unique selectivity towards stereoisomers. In a sense liquid-crystalline phases combine the high capacity of stationary phases with the structural selectivity of adsorbents.

Kirst et al.[62] studied the temperature dependences of the structural selectivity, capacity, and efficiency of copper CCs (40 m × 0.35 mm) with *p,p'*-methoxyethoxyazoxybenzene (MEAB), *p,p'*-azoxyphenetole (AOP), and their eutectic mixture. The

temperatures of maximum structural selectivity, determined from the ratio of the adjusted retention times of *p*- and *m*-xylenes, do not coincide with the temperatures of maximum capacity. The efficiency of the columns increases with temperature. MEAB displays the most favourable combination of these parameters on which the separation of *p*- and *m*-xylenes is dependent. The structural selectivity of the liquid-crystlline phases in capillary columns, as in packed columns, decreases with the thickness of their layers.[62]

Andronikashvili et al.[63] studied the possibility of measuring the temperatures of phase transitions of liquid crystals in steel and copper CCs (50 m × 0.25 mm). The above-mentioned MEAB and *p*-ethoxybenzylidenetoluidine (EBT) were used as the liquid-crystalline phases, It was established that the solidification temperatures of the nematic mesophases are virtually independent of the quantity of phases in the columns and the wall material. The mesomorphic–isotropic transition temperature ($T_{M\text{-}I}$) of MEAB varies by 15 °C with a change in quantity of this phase. The wall material of the columns affects the values of $T_{M\text{-}I}$ of the phases studied in different ways. Thus, on changing from steel columns to copper columns the mesomorphic–isotropic transition temperature for MEAB decreases by 8 °C while for EBT it increases by 27 °C.

The same authors determined the contribution of adsorption to the retention of organic compounds on a liquid-crystalline phase. The "internal standard" method, which assumed in particular that the surface of the walls was completely covered by the liquid-crystalline phase and that the gas–SF boundary remained unchanged on varying the proportion of the latter, was used.[28] Benzene was used as a nonadsorbing standard. It was found that the adsorption of toluene, ethylbenzene, *m*-, *p*-, and *o*-xylenes amounts to 3% of their retention values on MEAB at 95 °C. The contribution of the adsorption of n-alkanes (C_6-C_8) is an order of magnitude less.[63]

N,N' Bis(*p*-butoxybenzylidene)-α,α'-bis(*p*-toluidine) (BBBT) was treated as the stationary phase for the separation of isomeric tricyclic and tetracyclic polyaromatic hydrocarbons on stainless steel CCs.[64] The temperature dependence of the capacity of the column in the nematic mesophase region of BBBT was studied.

Russo et al.[65] recently investigated glas CCs with liquid-crystalline phases on layers of graphitised carbon and kaolin deposited on the internal walls. The phases used were *p,p'*-azoxydiphenetole (ADP) and the above-mentioned BBBT. A study was made of the stereoselectivity and efficiency of the columns in relation to the nature of the support, quantity of the phases, and temperature. It was found that on lowering the temperature, with BBBT changing from a nematic state to a smectic state, the coefficient of selectivity for separation of phenanthrene and anthracene decreased slightly, but because of the accompanying increase in viscosity of BBBT the efficiency of the columns decreased sharply. The use of kaolin has a marked stabilising effect on the efficiency of columns with BBBT and reduces the lower temperature limit by 40 °C for using columns with ADP. Thus, the use of adsorbents as supports is promising in terms of increasing the range of working temperatures and increasing the service life of capillary columns with liquid-crystalline stationary phases.

III. Application of capillary gas chromatography in chemical kinetics

1. Reaction capillary chromatography

Reaction gas chromatography has found extensive application in chemical kinetics.[1–4] Chemical reaction in the columns takes place in parallel with chromatographic separation of its products, which assists their detection and identification using sensitive and selective detectors.[66] Capillary columns are closer to the ideal model of a chromatographic reactor than packed columns, and they can be used to separate the chromatographic zones of the reaction products and the initial reactants more completely, thus assisting a study of the section of the chromatogram lying between them which characterises the reaction occurring in the column.[67]

Möller et al.[68] examined the possibility of using reaction capillary gas chromatography for a determination of thermodynamic and kinetic reaction parameters. The decomposition of dicyclopentadiene in a 60 metre-long copper CC with a Flugizon phase was studied at 189–207 °C.[69] The extent of reaction was assessed from the decrease in area of the peak due to dicyclopentadiene eluted from the column:

$$m_0/m = \exp(k_{exp} t'_R), \quad (15)$$

where m_0 and m are the quantities of dicyclopentadiene before entry and after exit from the column, k_{exp} is the experimental rate constant of reaction, t'_R is the adjusted retention time of dicyclopentadiene. Unfortunately, decomposition occurs simultaneously in both the stationary liquid phase and the carrier gas, which complicates a determination of the rate constants in each of these phases. The value of k_{exp} that is determined experimentally comprises a total rate constant in each of the phases:

$$k_{exp} = k_{SF} + (t_{CG}/t_{SF})k_{CG}, \quad (16)$$

where k_{CG} and k_{SF} are the rate constants of reaction in the carrier gas and stationary phase, t_{CG} and t_{SF} are the residence times of the reactant in the carrier gas and SF, which correspond to the hold-up time and adjusted retention time t_M and t'_R. In order to determine k_{CG} and k_{SF}, it was necessary to vary the phase ratio in the column, which was achieved by blowing off Flugizon at a high temperaure. Flugizon is a mixture of alkylnaphthalenes, so that after blowing off it is most probable that not only the phase ratio changes but also the actual composition of the stationary phase is altered. The authors calculated the rate constants for decomposition of dicyclopentadiene in Flugizon (k_{SF}) at different temperatures, but to calculate the activation energy they used hypothetical rate consant values ($\bar{k}$), which were determined by assuming that the rate constants of reaction in the carrier gas and SF were equal:

$$m / m_0 = \exp(\bar{k} t_R), \quad (17)$$

where t_R is the unadjusted retention time of dicyclopentadiene. The rate constants of reaction in the carrier gas and SF differ, and this approach results in errors. Furthermore, the kinetic data may be distorted because of the high catalytic activity of the copper surface of the capillary column.

2. Study of conformational conversions

Lai et al.[67] used quartz CCs (60 m × 0.2 mm and 25 m × 0.3 mm) with poly(dimethylsiloxanes) OV-1 and CP-Si15 to study the kinetics of conformational conversions in 9,10-bis(2,3-dimethylphenyl)phenanthrene. At 225 °C the *syn* and *anti* isomers of 9,10-bis(2,3-dimethylphenyl)phenanthrene are completely separated, while between them on the chromatogram there is a relatively long empty section of the zero line corresponding to the absence of conformational conversion between the isomers. On increasing the temperature the section between the peaks rises. The peak areas correspond to the number of molecules not participating in conformational conversions while the area of the elevated section between the peaks represents the number of molecules undergoing

conformational conversion in the column. With a decrease in velocity of the carrier gas the residence time of a sample in the hot column increases, and the number of molecules participating in conformational conversions increases. The rate constants for the forward and reverse *syn* → *anti* conversion were calculated from the decrease in peak area of the respective conformer with an increase in its residence time in the column. The values of the rate constants determined at different temperatures were used to calculate the activation energies of the forward and reverse conversions, which were 145 and 115 kJ mol^{-1} respectively. Since, in the opinion of Lai et al.,[67] the conformational conversions probably occur only in the stationary phases, it would be more appropriate to use in the calculations the adjusted retention times, corresponding to the residence of the conformers in the SF (the reaction zone), rather than the total residence time of the isomers in the columns.

The same authors recently studied the kinetics of isomerisation of acetal, butanal, and isobutanal oximes, as well as sterically hindered methylphenylanthracenes and phenanthrenes on CCs with a dimethylsiloxane phase and FFAP.[70] In order to simplify the calculations it was assumed that the rate constants of isomerisation in the carrier gas and SF were equal. The Arrhenius method was used to determine the activation energies, which constituted 100–140 kJ mol^{-1} for the rotational isomerisation of methylphenylanthracenes and phenanthrenes and about 70 kJ mol^{-1} for *syn* ⇄ *anti* conversions of oximes. Lai et al.[70] concluded that it is only possible to determine the conversion barrier in those cases where the initial concentration of a conformer in a binary mixture is not less than 5%.

3. Study of photochemical reactions

A glass capillary column is an ideal reactor for studying photochemical reactions on the surface and in thin layers. The absence of packing and the transparency of the walls permit the free access of radiation to photolabile compounds.[66] In CCs it is possible to deposit different nonvolatile supports and layers and readily batch small quantities of volatile compounds and thus study various photochemical reactions between them.

Laster et al.[66] tested the suitability of glass CCs (10 m × 0.3 to 0.5 mm) for a study of photochemical processes at the gas–solid support phase boundary in a gas adsorption form of chromatography. The photochemical demethylation of dimethylaniline adsorbed on the surface of alizarin was studied as a model. The latter was deposited on the "fluffy" internal surface of a capillary column obtained by etching the walls with 2-chloro-1,1,2-trifluoroethyl methyl ether.

Alizarin, like other anthraquinone derivatives, has strong electron-withdrawing properties in its excited triplet state. Samples of dimethylaniline vapour were introduced either in batches or continuously using a T-shaped diffusion saturator. On irradiation of the CC of the chromatograph in a thermostat with visible light from a halogen lamp, the peak due to dimethylaniline disappeared and in its place a peak due to the product of the photochemical reaction subsquently appeared, identified by chromatography–mass spectrometry as methylaniline. It was established that the frontal method with continuous introduction of sample vapour achieved a higher sensitivity and reproducibility than the development method with batched introduction of sample. In the frontal method a variant of vacancy chromatography occurs. After irradiation with light, two peaks appear at the outlet of the column—a negative vacancy peak due to decomposed dimethylaniline and a positive peak due to the reaction product. The logarithm of the dependence of the degree of reaction on the intensity and duration of column irradiation and the linear dependence on the concentration of the initial reactant indicated that the reaction was first-order with respect to dimethylaniline.[66]

IV. Study of the transport properties of different media

In order to measure diffusion coefficients in gases, liquids, and supercritical fluids, capillary columns without stationary phases are used, while for measurement of diffusion coefficients in polymers the latter are deposited as a uniform layer on the inner walls of capillary columns. The advantages derived from the methods of measuring diffusion coefficients using chromatographic equipment are the simplicity of instrumentation, high output, relatively high accuracy, and the possibility of studying diffusivity under conditions of limiting dilution.

The theory of dispersion of the zones of a nonsorbing compound in hollow cylindrical tubes was developed by Taylor[71] and Aris.[72] The height equivalent to a theoretical plate (HETP), which represents the dispersion of a zone, is defined as the sum of two components, the first of which is due to longitudinal diffusion of a compound in the mobile phase (MP) while the second results from resistance to mass transfer due to the parabolic nature of the flow profile of the MP in a cylindrical tube:

$$H = \frac{2D_{m,o}}{u_o} + \frac{d^2 u_o}{96 D_{m,o}}, \qquad (18)$$

where H is the height equivalent to a theoretical plate, $D_{m,o}$ is the diffusion coefficient in the MP at the column outlet, u_o is the velocity of the MP at the outlet, d is the internal diameter of the column. For a Gaussian elution curve the HETP is defined as

$$H = \frac{L}{N} = \frac{L}{5{,}45} \frac{(W_{0,5})^2}{t_R}, \qquad (19)$$

where L is the length of the column, N is the number of theoretical plates, t_R and $W_{0.5}$ are the exit time of the peak maximum and its width at the half-height. Having determined the value of the HETP, $D_{m,o}$ is calculated from Eqn. (18):

$$D_{m,o} = \frac{u_o}{4}(H \pm \sqrt{H^2 - d^2/12}). \qquad (20)$$

The sign in front of the square root in Eqn. (20) is usually negative, except when a gas with low flow rates is used as the MP.

1. Determination of diffusion coefficients in gases

Tubes with a diameter of 4–5 mm are mainly used to determine diffusion coefficients in gases (D_g).[73–75] When working with capillary columns both a continuous elution method[76] and a stopped flow method[77] have been used.

At the optimum flow rate of gas (u_{opt}) the values of HETP are at a minimum, and the parameter u_{opt} is simply related to the diffusion coefficient of the compound in the gas and the internal diameter of the column:

$$u_{opt} = (8\sqrt{3D_g}) / d. \qquad (21)$$

Using Eqn. (21), Knox and McLaren[78] determined d_g for ethylene in nitrogen from the value of the optimum flow rate in a capillary tube made of nylon (16.64 × 0.88 mm). The continuous elution method

has high output but at the same time it is necessary to have a precise knowledge of the internal diameter of the column and to take into account extracolumn dispersion of the zone, which in the case of using CCs may be fairly considerable.[78,79] In a subsequent study[77] the same authors put forward an alternative chromatographic method for determining D_g which avoids these difficulties. In this method, when the zone of diffusant approaches the centre of the column the flow of carrier gas is stopped and broadening of the zone occurs solely through longitudinal diffusion, which is proportional to the duration of flow stoppage (θ) and the diffusion coefficient of the component in the gas:

$$\sigma_l^2 = 2D_g\theta, \tag{22}$$

where σ_l^2 is the variance of the zone in units of length. After an interval of time θ the flow of gas is restored. The variance of the zone in time units (σ_t^2) recorded by the detector at the column outlet is made up by the extracolumn variance (σ_{ec}^2), the variance of the zone in a column by movement of gas (σ_c^2), and the variance of the zone throughout the period of flow stoppage (σ_θ^2):

$$\sigma_t^2 = \sigma_{ec}^2 + \sigma_c^2 + \sigma_\theta^2. \tag{23}$$

The variance of the peak is measured for different durations of flow stoppage (θ varies from 1 to 20 min). The σ_{ec}^2 and σ_c^2 variances do not depend on the value of θ. Thus, a graph of the variance of the peak against the duration of flow stoppage is a straight line from whose slope the diffusion coefficient is determined ($\tan\alpha = 2D_g/u_O^2$). D_g for ethylene in nitrogen was determined to an accuracy of 2% with this method using nylon tubes (8.34 m × 0.88 mm and 16.40 m × 0.88 mm).[77] A limitation of this method is the need for a small pressure drop in the tube. Thus, with a pressure difference of more than 20 mmHg the velocity of gas cannot be normalised up to the time of peak exit, which results in an overestimated value of the experimental diffusion coefficient.[77]

With a low velocity of carrier gas in a tube of small diameter the contribution of longitudinal diffusion to dispersion is much larger than that of resistance to mass transfer in the gas, and the second term in Eqn. (18) can be neglected:

$$H = 2D_{g,o}/u_o. \tag{24}$$

Taking into account the ratios of the zone variances at the outlet in units of length (σ_l^2) and time (σ_t^2) as well as the average linear rate and velocity of carrier gas at the outlet (u_o), we obtain:

$$D_{g,o} = L^2\sigma_t^2 / 2t^3J^3, \tag{25}$$

where t is the exit time of the peak maximum, J is the Martin pressure drop factor.[80] Thus, in order to determine the diffusion coefficients by a continuous elution method in capillary columns at small flow rates there is no need to have an accurate knowledge of the internal diameter of the column. Lochmüller et al.[79] derived an equation that was similar to Eqn. (25) but which did not include the J factor.

According to the law of additive variance of a chromatographic peak, the apparent dispersion is the sum of dispersions inside the column and outside it:

$$\sigma_t^2 = \sigma_{ec}^2 + \sigma_c^2. \tag{26}$$

In turn the extracolumn contribution is the sum of the variances caused by dispersion of the zone at the inlet and in the detector as well as the broadening of the signal in the detector during its amplification and recording.

When two tubes of different length are used, the extracolumn contribution can be excluded by subtracting the variance of the peak obtained on the shorter reference column from the variance of the peak obtained on the main column.[76] Lochmüller et al.[79] determined D_g for argon in helium from a graph of the linear dependence of the apparent variance of the peak on the length of the tubes employed (from 27 to 62 m):

$$\sigma_t^2 = \sigma_{ec}^2 + \frac{2D_{g,o}}{u_0^3}L. \tag{27}$$

When a microkatharometer was used as the detector the value of σ_{ec}^2 was 35 s^2. This method (subtraction of the systematic dispersion of the zone in columns with different length) is also convenient in that as a result only dispersion of the dilute "wings" of the zone are taken into account and hence the potential effect of a high concentration of diffusant in the centre of the zone is eliminated.[79]

In a recent study[81] an attempt was made to compare the 3 methods for the chromatographic determination of diffusion coefficients in a gas: 1) from Eqn. (20) without taking into account the pressure drop; 2) from Eqn. (20) including corrections for the pressure drop in the column (the J correction factor of Martin[80] and f_g correction factor of Giddings[82]

$$D_{g,o} = \frac{L}{4tJ}\left[\frac{H}{f_g} + \sqrt{\left(\frac{H}{f_g}\right)^2 - \frac{d^2}{12}}\right]$$

and 3) by the computer fitting of the van Deemter curve for a nonsorbing compound. In the latter method use was made of a HETP equation which contained, in addition to the usual terms for longitudinal diffusion and resistance to mass transfer in the gas, an additional term that was linearly dependent on the gas velocity. The latter term, according to Bemgard et al.,[81] can result from interphase resistance through friction of the gas against the walls of the CC and nonideal laminarity of its flow. However, according to the calculations of the authors,[81] the contributions from these phenomena do not make up more than 1% of the experimental values of $D_{g,o}$.

The dispersion of C_4, C_6, and C_{12} n-alkanes and toluene was studied in a quartz capillary column (100 m × 0.32 mm) without a stationary phase in relation to the flow rate of gas (H_2, 2–60 cm s^{-1}). It was established that the diffusion coefficient values determined by the first two methods depend on the gas velocity and the coefficients calculated when the pressure drop was taken into account increase with the flow rate, while they decrease when the pressure drop is ignored. Extraplation of both dependences to zero flow rate gives the same diffusion coefficient value, which agrees with the value determined by the third method, thus indicating that it is true.

A comparison of the diffusion coefficients determined in this manner with the values predicted by theory from the most accurate Fuller–Schettler–Giddings equation[83] showed that the theory gives overestimated values of D_g, which are higher the greater is the length of the n-alkane molecule. Bemgard et al.[81] did not find any correlation between the difference in predicted and experimental values of D_g and the boiling point of the products studied. In this case the geometry of the molecule evidently has a more significant effect on the magnitude of D_g, since the above-mentioned equation is based on a solid sphere model and the difference must be greater the more well-defined are the anisotropic properties of the diffusant molecules.

The gas chromatographic determination of the diffusion coefficients of compounds with low volatility presents certain difficulties, mainly because of their adsorption on the inner walls of the tubes. In order to suppress the adsorption sites on the surface of the walls during determination of D_g for polar compounds, trace amounts of these compounds were added to the carrier gas.[84]

In order to determine the diffusion coefficients of heavy n-alkanes, Vasil'ev et al.[85,86] used an even more radical method of deactivating the surface—silanisation of a glass CC with hexamethyldisilazane. There is also some difficulty in introducing the vapour of components with low volatility as a narrow zone into the column. Batched introduction systems that achieve an initial zone width in the capillary columns of the order of 10 or even 1 ms have recently been developed.[87,88] However, when low velocities of carrier gas are used, the width of the chromatographic zone in time units is so great that good results are obtained with the use of a conventional splitter inlet, which is widely used in capillary chromatography.

According to the results of Vasil'ev et al.,[85] extracolumn dispersion when an inlet with divided flow and coventional chromatographic equipment are used is about 0.5 s^2. With splitter introduction of the sample and the use of a flame ionisation detector the contribution of extracolumn dispersion was reduced to 0.1% of the peak dispersion and this eliminated the need for its compensation on reference columns.[85,86] When the flow rate of gas was 6—18 mm s^{-1} the pressure drop was negligible and the contribution from resistance to mass transfer was 0.1—0.4%, so these were ignored. Samples of pure alkanes were introduced into the splitter at the minimum level for accurate determination of the peak width to be achieved with maximum sensitivity. In order to include the sight inhibition of zone movement as a result of residual adsorption of heavy alkanes, the factor $(1 + k)^{-2}$, where k is the capacity factor ($0 \leqslant k \leqslant 0.13$), was introduced into Eqn. (25). Using this method, D_g values for C_5—C_{24} n-alkanes in helium and n-$C_{18}H_{38}$ and n-$C_{24}H_{50}$ in hydrogen, nitrogen, and argon were determined in silanised glass tubes (1.10 m × 0.25 m and 2.05 m × 0.28 mm).[85,86] It was found that the dependence of the diffusion coefficients of n-alkanes in helium at 200 °C corrected to normal atmospheric pressure on the number of carbon atoms in the molecule ($5 \leqslant n \leqslant 24$) within the limits of experimental accuracy obeyed the equation:

$$D_g^* = 0.081 + 3.553/(n + 1.083). \quad (28)$$

A similar dependence for a more restricted series of n-alkanes ($6 \leqslant n \leqslant 11$) was approximately represented by a linear equation.[89] Although the approximation was carried out on D_g values calculated from the Fuller equation,[83] the deviations of the points from a straight line were hyperbolic in nature, similar to Eqn. (28). The values of D_g calculated from Eqn. (28) for $n = 5$ and 6 were similar to the experimental values for n-pentane and n-hexane determined previously.[84] Indirect evidence for the accuracy of the D_g values determined for alkanes with low volatility may be provided by the good correspondence between the theoretical efficiency calculated from them and the experimental efficiency of the best capillary columns.[86]

2. Determination of diffusion coefficients in liquids

Capillary tubes made of stainless steel have generally been used to determine diffusion coefficients in liquids (D_l) using the disperson method of Taylor.[90—92] By combining convective dispersion with molecular diffusion in an axial direction, it was possible after a short period of time to obtain considerable dispersion of the zone. The chromatographic equipment used in this method is of simple design and allows for considerable variations in the nature of the diffusant, diffusion medium, and temperature.[93] The reproducibility of the values of D_l obtained by the Taylor method usually constitutes 1—3%.

Alizadeh et al.[94] developed a detailed theoretical basis for use of the Taylor method in determining diffusion coefficients in liquids. Analytical expressions were derived for calculation of corrections to the final volumes of a sample being introduced, recording registers of the detector and connecting tubes, and also corrections to take account of the concentration dependence of D_l. It was shown that small changes in the diameter of the column and the eccentricity of its cross-section had virtually no effect on the values of the experimental diffusion coefficients. Subsequently, Wakeham,[95] taking into account the requirements elaborated by Alizadeh et al.,[94] designed a capillary liquid chromatograph in which the error in determination of D_l did not exceed 0.5%.

Evans et al.,[90] by using a steel CC (9.14 m × 0.775 mm), studied the temperature dependence of the diffusion coefficients of spherically symmetric molecules in alcohols. The slope of lines from plots of $\ln D_l$ against $1/T$ were used to determine the activation energies of diffusion; these were 12.6 kJ mol^{-1} in methanol and 23.4 kJ mol^{-1} in octanol. In a later study,[91] in which a CC (61 m × 0.762 mm) was used, an exponential relationship between D_l for spherically symmetric molecules, the viscosity, and temperature was established. Tominaga et al.[92,96] used a column (50.0 m × 0.8 mm) to study temperature dependence of D_l for aromatic compounds in water and established that the dependence of $\ln D_l$ on the reciprocal of the absolute temperature ($1/T$) was curvilinear over a wide temperature range (8—160 °C). The calculated activation energies of diffusion were slightly dependent on the size of the diffusant molecules and decreased almost hyperbolically with an increase in temperature.[96] According to the data obtained, the diffusion coefficients of benzene in water and for self-diffusion of pure water are similar and decrease to an equally marked extent with temperature.

3. Determination of diffusion coefficients in supercritical fluids

The diffusion coefficients of compounds in supercritical fluids are approximately equal to the average values of their diffusion coefficients in gases and liquids.[97] A knowledge of diffusion coefficients under near- and super-critical conditions is necessary for supercritical fluid chromatography[98] and in the design of fluid extractors used in the food and pharmaceutical industries.[99]

Flexible quartz CCs without a stationary phase are mainly used to determine diffusion coefficients D_f in fluids. According to the assessment of Springston and Novotny,[97] D_f can be determined to an accuracy of 5% by the Taylor dispersion method. The same authors analysed the possible sources of fixed errors.[97] Thus, it was found that the secondary flow of a fluid MP in coiled columns was insignificant,[98] while the velocity of the MP was sufficiently high for the first component in Eqn. (18) to be neglected.[97] Thus, D_f could be determined from the slope of the mass exchange path of the van Deemter curve for capillary columns without a stationary phase. In the majority of cases the differentials of pressure and density of the fluid phase in the columns were small, and these were neglected.[98,100—104] Extracolumn contributions to dispersion also usually had no effect on the experimental values of D_f. In some

cases a variant of the reference column method has been used to take into account the initial dispersion of the zone during introduction.[76] The zone is recorded twice by a UV detector, before and after its passage through the main column. The first detector is placed between a short reference precolumn (1.3–1.8 m) and the main diffusion column of length 46–100 m.[102,104] The compounds are commonly introduced into the columns as solutions in organic solvents, but the dependence of the experimental values of D_f on the nature of the solvent is either only slight[100] or does not occur at all.[97,101,104] Thus, when the fluid phases (propane, CO_2) are used as solvents, the experimental diffusion coefficients of phenanthrene are similar to those obtained when solutions of phenanthrene in xylene[105] and methanol in isooctane[101] are used as samples. Adsorption of compounds on the column walls may well result in errors, so asymmetric peaks are not used to calculate D_f. It has been noted, however, that adsorption only occurs with low densities of the fluid phases.[97,101]

Springston et al.[97] and Olesik et al.[105] studied the effect of the internal diameter of the column (94–200 μm) and the sample concentrations (15 μg ml^{-1}–2.0 mg ml^{-1}) on D_f in order to test the reproducibility of the results. The highest reproducibility was achieved with columns of diameter 0.2 mm and samples with a concentration that was close to the investigated upper limit of 2.0 mg ml^{-1}. By using a chromatograph that was specially designed for physicochemical measurement under supercritical conditions, whose accuracy in the maintenance of temperature and pressure was ±0.01 °C and ±0.2 atm respectively, the authors of two studies[98,105] reduced the relative standard deviations of the experimental values of D_f to 1–2%. With this precision it was possible to detect a difference between the diffusion coefficients of polyaromatic hydrocarbons and their predeuterated analogues.

The diffusion coefficients of normal and branched symmetric C_3–C_{10} ketones, C_{18} fatty acids with a varying degree of unsaturation, liquid crystals, and squalane in fluidised CO_2 were determined with the use of a CC (46.23 mm × 0.41 mm). The values of $\ln D_f$ decreased linearly with an increase in density of the mobile phase. The authors established that for isomers or compounds with similar molecular weights, a decrease in the degree of molecular branching and an increase in their rigidity resulted in a decrease in their diffusion coefficients in fluid CO_2.[104]

CCs were used to study the temperature dependence of diffusion coefficients in fluids for the systems: benzene–CO_2 and methyl linolenate–CO_2;[100,103] anthracene–propane and phenanthrene–propane.[98] In all cases with constant densities of the fluid phases (ρ) the values of $\ln D_f$ were inversely proportional to the absolute temperature. From the slope of lines plotted on the coordinates of $\ln D_f$ against $1/T$, calculations were made of the activation energies of diffusion, which were equal to 2.4 and 5.0 kJ mol^{-1} for anthracene and phenanthrene in fluidised propane (ρ = 0.3771 g ml^{-1});[98] 4.52 kJ mol^{-1} for methyl linolenate in CO_2 (ρ = 0.8 g mg^{-1});[103] and 4.7 kJ mol^{-1} for napthalene in CO_2 (ρ = 0.6 g ml^{-1}).[106]

4. Determination of diffusion coefficients in polymers

The dispersion method of Taylor is not suitable for determining diffusion coefficients in polymers (D_p), since polymers cannot be used as mobile phases because of their high viscosity. However, by depositing polymers as a uniform layer on the inner walls of capillary columns as stationary phases, it is possible to assess their diffusion properties from the resistance to mass transfer in the layers. The resistance to mass transfer (C_l) in a uniform layer of liquid phase of thickness d_f is simply related to the diffusion coefficient:

$$C_l = 2d_f^2 / 3D_p. \quad (29)$$

Cramers et al.[107] used this approach to determine D_p for n-alkanes (C_9–C_{20}) in relatively thick films (1.06–2.35 μm) of polysiloxanes CP-Sil 5 and OV-1 immobilised on the walls of quartz CCs. Three methods for determining the resistance to mass transfer in the SF were tested. The first method was based on a determination of the difference between the experimental HETP and the calculated sum of the contributions from longitudinal and dynamic diffusion in the carrier gas as predicted by the Golay–Giddings equation.[85,108] However, a twofold increase in the thickness of polymer layers resulted in an almost twofold increase in D_p values calculated from Eqn. (29).

Better results were obtained with the second method for determining C_l, which was based on the method of "corresponding" velocities[109] corrected for the compressibility of the carrier gas.[110] The efficiency of the columns was determined by using different carrier gases (helium and nitrogen) with velocities proportional to the diffusion coefficients in each of them:

$$\bar{u}_1/\bar{u}_2 = D_{g,1}J_1/D_{g,2}J_2, \quad (30)$$

where $\bar{u}_1$ and $\bar{u}_2$ are the mean linear velocities of the gases, $D_{g,1}$ and $D_{g,2}$ are the diffusion coefficients, J_1 and J_2 are the Martin[80] pressure drop factors for the first and second carrier gases. The resistance to mass transfer in the stationary phase was defined as the ratio of the differences between the HETPs for each of the gases to the dfference in velocities of the latter:

$$C_l = [(H_1/f_1) - (H_2/f_2)]/(\bar{u}_1 - \bar{u}_2), \quad (31)$$

Here H_1 and H_2 are the HETPs, f_1 and f_2 are the Giddings[82] pressure drop factors for the first and second gases. It is clear that this method does not require a knowldge of the absolute values of $D_{g,1}$ and $D_{g,2}$; only their ratio is important, which for may diffusants is the same.[73,111] Cramers et al.[107] calculated the values of $D_{g,1}$ and $D_{g,2}$ from the Fuller equation,[83] which is recognised as the most accurate.[112] Nevertheless, the values of C_l were dependent on the absolute velocities of the gases. In order to eliminate this dependence, a correction to the ratio of the diffusion coefficients in helium and nitrogen was required. The optimum value determined for this (3.16)[107] agreed with the ratio of the experimental values of D_g for octadecane in these gases (3.15).[86]

The third method involved the computer fitting of van Deemter curves. In the opinion of Cramers et al.,[107] this method does not satisfactorily separate the contributions from resistance to mass transfer in the carrier gas and in the stationary phase. This is also supported by the results of Sandra et al.,[113,114] which estimated D_p for n-alkanes and aromatic compounds in thick films of polysiloxanes PS-255 (5 μm) and RSL-300 (3 μm) immobilised on the walls of quartz CCs. Thus, the experimental values of D_p in polyphenylsiloxane RSL-300 for the heavier homologues are higher than for the lighter alkanes whose molecules are, moreover, less bulky.

Pawlisch et al.[58] noted that when resistance to mass transfer in polymer layers predominates in the total dispersion of the zone, the shape of the peak is very sensitive to the diffusivity of the sorbates in them. A twofold decrease in D_p results in marked asymmetry of the form of tailng.

The same authors determined the diffusion coefficients of aromatic compounds in polystyrene (MW 266000) deposited as a uniform thick layer (7–12 μm) in silanised glass CCS, while the

contribution from longitudinal diffusion and resistance to mass transfer in the carrier gas was neglected. Numerical treatment of the computer signals was used to determine the primary and secondary features of the elution curves, and from them the diffusion coefficients in the polymer were calculated. It was established that an increase in temperature from 110 to 140 °C resulted in an increase in D_p values by a factor of 10^2. The graphs of $\ln D_p$ against $1/T$ were linear. The activation energies of diffusion calculated from the graphs for benzene, toluene, and ethylbenzene were 8.4, 10.0, and 10.6 kJ mol^{-1} respectively. Thus, in view of the possibility of obtaining readily controlled, highly uniform polymer layers, the use of glass capillary columns for studying the diffusion properties of polymers may have considerable future potential.

References

1. A V Kiselev, A V Johansen, K I Sakodynskii, et al. *Fiziko-khimicheskoe Primenenie Gazovoi Khromatografii* (Physicochemical Application of Gas Chromatography), Khimiya, Moscow, 1973, p. 256
2. J R Conder, C L Young *Physicochemical Measurements by Gas Chromatography*, Wiley Interscience, Chichester, 1979, p. 632
3. J R Laub, R L Pecsok *Physicochemical Application of Gas Chromatography*, Wiley, New York 1978, p. 300
4. R Kobayashi, T Kragas *J. Chromatogr. Sci.*, 1985, **23**(1) 11
5. M J E Golay *Gas Chromatography (1957 Lansing Symp.)* (Editored by V J Coates, H J Noebels, I S Fagerson, Academic Press, New York, 1958, p. 1
6. M Golay *2nd International Symposium on "Gas Chromatography': Abstracts of Reports, Amsterdam, 1958* (Translated into Russian), Izd. Inostr. Lit., Moscow, 1961, p. 39
7. M Golay *"Gas Chromatography": Proceedings of the 3rd International Symposium (Edinburgh, 1960)* (Translated into Russian), Mir, Moscow, 1964, p. 187
8. V G Berezkin, L Soyak *Zh. Fiz. Khim.*, 1982, **56**(6) 1467 [English translation in *Russ. J. Phys. Chem.*, 1982(6)]
9. V G Berezkin, A A Korolev *Chromatographia*, 1986, **21**(1) 16
10. V G Berezkin, A A Korolev *Zh. Fiz. Khim.*, 1987, **61**(5) 1402 [English translation in *Russ. J. Phys. Chem.*, 1987(5)]
11. R V Golovnya, A L Samusenko *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981(9) 2060
12. R V Golovnya, A L Samusenko *Khromatographicheskie Metody i ikh Primenenie v Neftekhimicheskoi i Neftepererabtyvayushchei Promyshlennosti: Material I Mezhdunarodnoi Konferentsii Stran SEV (Bratislava 1982)* [Chromatographic Methods and their Application in the Petroleum and Oil Refining Industries: Material from the Ist Conference of Comecon Countries (Bratislava 1982)], Bratislava, 1982, p. 71
13. R V Golovnya, A L Samusenko *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, (9) 1993
14. A L Samusenko, R V Golovnya Chromatographia, 1988, **25**(6) 531
15. R V Golovnya, A L Samusenko, L B Dmitriev *Zh. Anal. Khim.*, 1987, **43**(4) 699
16. R V Golovnya, A L Samusenko *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, (3) 517
17. R V Golovnya, A L Samusenko *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, (10) 2234
18. D N Grigor'eva, R V Golovnya, A V VAasil'ev *Zh. Anal. Khim.*, 1989, **44**(7) 1274
19. D N Grigor'eva, A V Vasil'ev, R V Golovnya *Zh. Anal. Khim.*, 1991, **46**(2) 283
20. B L Karger *Anal. Chem.*, 1967, **39**(8) 24A
21. U I Kulikov, Yu R Egiazarov, A M Korol' *Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk*, 1976, (4) 49
22. V Pacàkova, J Svegjola, E Šmolkova *Collect. Czech. Chem. Commun.*, 1977, **42**(10) 2850
23. B A Rudenko *Kapillaryarnaya Khromatografiya* (Capillary Chromatography), Nauka, Moscow, 1978, p. 221
24. M Mohnke, J Heybey *J. Chromatogr.*, 1989, **471** 37
25. I A Suslov, B A Rudenko, A P Arzamastsev *Zh. Anal. Khim.*, 1988, **43**(2) 328
26. R V Golovnya, Yu N Arsenyev *Chromatographia*, 1971, **4**(6) 250
27. A S Lischiner, S A Voitkevich, B A Rudenko, S S Yufit *Chromatographia*, 1973, **6**(7) 314
28. V G Berezkin *J. Chromatogr.*, 1974, **91** 559
29. S R Lipsky, W J McMurray *J. Chromatogr.*, 1982, **239** 61
30. G Schomburg, H Husmann, S Ruthe, M Herraiz *Chromatographia*, 1982, **15**(9) 559
31. R J Lamb *Anal. Chem.*, 1984, **56**(12) 2115
32. D H Everett *Trans. Faraday Soc.*, 1965, **61**(512) 1637
33. A J B Cruickshank, M L Windsor, C L Young *Proc. R. Soc. London, A*, 1966, **295**(1442) 259
34. J-Ch Huang, R Madey *J. Chromatogr. Sci.*, 1982, **20**(5) 218
35. D J Hamilton *J. Chromatogr.*, 1980, **195**(1) 75
36. J W Westcott, T F Bidleman *J.Chromatogr.*, 1981, **210**(2) 331
37. T F Bidleman *Anal. Chem.*, 1984, **56**(13) 2490
38. D A Hinchley, T F Bidleman, W T Foreman, J R Tuschall *J. Chem. Eng. Data*, 1990, **35**(3) 232
39. D MacKay, A Bobra, D W Chan, W Y Shiu *Environ. Sci. Technol.*, 1982, **16**(10) 645
40. T F Bidleman, L Renberg *Chemosphere*, 1985, **14**(10) 1475
41. Y H Kim, J E Woodrow, J N Seiber *J. Chromatogr.*, 1984, **314** 37
42. B D Eitzer, R A Hites *Environ. Sci. Technol.*, 1988, **22**(11) 1362
43. J R Donnelly, W D Munslow, R K Mitchum, G W Sovocool *J. Chromatogr.*, 1987, **392** 51
44. M D Hale, F D Hileman, T Mazer, et al. *Anal. Chem.*, 1985, **57**(3) 640
45. M Kh Lunskii, I L Paizanskaya *Zh. Fiz. Khim.*, 1987, **61**(12) 3238 [English translation in *Russ. J. Phys. Chem.*, 1987(12)]
46. M Kuchar, H Tomková, V Rejholec, I O O Korhonen *J. Chromatogr.*, 1986, **356**(1) 95
47. M Kuchar, H Tomková, V Rejholec, I O O Korhonen *J. Chromatogr.*, 1987, **398** 43
48. I O O Korhonen, M A Lind *J. Chromatogr.*, 1985, **322** 83; **322** 97; **323** 331; **324** 113; **325** 433
49. J K Haken, I O O Korhonen *J. Chromatogr.*, 1985, **319** 131
50. I O O Korhonen *J. Chromatogr.*, 1986, **356** 285; **357** 107; **360** 63; **363** 277
51. R V Golovnya, D N Grigor'eva *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, (6) 1246
52. G Gusev, S Rash, V G Berezkin, A Orav *Eesti NSV Tead. Akad. Toim. Keem.*, 1986, **35**(3) 205
53. B R Kersten, C F Poole *J. Chromatogr.*, 1987, **399** 1
54. V G Berezkin, A A Korolev *J. High Resolut. Chromatogr.*, 1989, **12**(9) 617
55. J E Haky, B Leja *Anal. Lett.*, 1986, **19**(1/2) 123

56. R N Lichtenthaler, D D Liu, J M Prausnitz *Macromolecules*, 1974, **7**(5) 565
57. Yu S Lipatov, A E Nesterov *Macromolecules*, 1975, **8**(6) 889
58. C A Pawlisch, A Macris, R L Laurence *Macromolecules*, 1987, **20**(7) 1564
59. H-S Tseng, D R Lloyd, T C Ward *J. Appl. Polym. Sci.*, 1985, **30**(5) 1815
60. J M Barrales-Rienda, J Vidal Gancedo *Macromolcules*, 1988, **21**(1) 220
61. M Roth, J Novak, P David, M Novotny *Anal. Chem.*, 1987, **59**(11) 1490
62. S I Kirsh, A A Fedyanin, N T Karabanov *Zavod. Lab.*, 1983, **49**(12) 5
63. L G Andronikashvili, N T Arustamova, N T Sultanov, K G Markaryan *Zhidkie Kristally v Kapillyarnoi Khromatografii* (Liquid Crystals in Capillary Chromatography), Metsinereba, Tbilisi, 1982, p. 98
64. W L Zielinksi, Jr., R A Scaubar, M M Miller *J. Chromatogr.*, 1981, **209**(1) 87
65. M V Russo, G Goretti, A Liberti, A Ubaldi *8th International Symposium on Capillary Chromatography, Riva Del Garda, 1987* (Edited by P Sandra), Huethig, Heidelberg, 1987, Vol. 1, p. 223
66. W G Laster, J B Pawliszyn, J B Phillips *J. Chromatogr. Sci.*, 1982, **20**(6) 278
67. Y-H Lai, P J Marriott, B-C Tan *Aust. J. Chem.*, 1985, **38**(2) 307
68. E Möller, D Haberland *Wiss. Z. E. M. Amdt-Univ., Greifswald, Math.-Naturwiss. R*, 1984, **33**(3) 22
69. E Möller, H Pscheidl, D Haberland *Z. Chem.*, 1985, **25**(5) 195
70. P J Marriott, Y-H Lai *J. Chromatogr.*, 1988, **447**(1) 29
71. G Taylor *Proc. R. Soc. London, A*, 1953, **219** 186; 1954, **223** 446; **225** 473
72. R Aris *Proc. R. Soc. London, A*, 1956, **235** 67; 1959; **252** 538
73. V R Maynard, E Grushka *Adv. Chromatogr.*, 1975, **12** 99
74. C E Cloete, T W Smuts, K De Clerk *J. Chromatogr.*, 1976, **120**(2) 175
75. J Amouroux, B Sanchez, A Saint-Yrieix *Bull. Soc. Chim. Fr., I*, 1978, (11 – 12) 462
76. J C Giddings, S L Seager *J.Chem. Phys.*, 1960, **33**(5) 1579
77. J H Knox, L McLaren *Anal. Chem.*, 1964, **36**(8) 1477
78. J H Knox, L McLaren *Anal. Chem.*, 1963, **35**(4) 449
79. C H Lochmüller, B M Gordon *J. Chromatogr. Sci.*, 1978, **16**(2) 74
80. A T James, A J P Martin *Biochem. J.*, 1952, **50** 679
81. A K Bemgard, A L Colmsjö *J. Chromatogr.*, 1990, **522** 277
82. G H Stewart, S L Seager, J C Giddings *Anal. Chem.*, 1959, **31**(10) 1738
83. E N Fuller, P D Schettler, J C Giddings *Ind. Eng. Chem.*, 1966, **58**(5) 18
84. G L Hargrove, D T Sawyer *Anal. Chem.*, 1967, **39**(2) 244
85. V G Garbuzov, A V Vasil'ev, R V Golovnya *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, (3) 611
86. A V Vasil'ev, R V Golovnya *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, (12) 2760
87. G Gaspar, R Annino, C Vidal-Madjar, G Guiochon *Anal. Chem.*, 1978, **50**(11) 1512
88. R Tijssen, N van den Hoed, M E Van Kreveld *Anal. Chem.*, 1987, **59**(7) 1007
89. L S Ettre *Chromatographia*, 1983, **17**(10) 553
90. D F Evans, T Tominaga, C Chan *J. Solution Chem.*, 1979, **8**(6) 461
91. S-H Chen, D F Evans, H T Davis *AIChE J.*, 1983, **29**(4) 640
92. T Tominaga, S Yamamoto, J Takanata *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**(4) 941
93. S-H Chen, H T Davis, D F Evans *J. Chem. Phys.*, 1981, **75**(3) 1422
94. A Alizadeh, C A Nieto de Castro, W A Wakeham *Intern. J. Thermophys.*, 1980, **1**(3) 243
95. W A Wakeham *Faraday Symposium of the Chemical Society: "Chromatography, Equilibria and Kinetics", No. 15*, Royal Society of Chemistry, London, 1980, p. 145
96. T Tominaga, S Matsumoto, T Ishii *J. Phys. Chem.*, 1986, **90**(1) 139
97. S R Springston, M Novotny *Anal. Chem.*, 1984, **56**(11) 1762
98. M Roth, J L Steger, M V Novotny *J. Chem. Phys.*, 1987, **91**(6) 1645
99. L G Randall *Sep. Sci. Technol.*, 1982, **17**(1) 1
100. H H Lauer, D McMangill, R D Board *Anal. Chem.*, 1983, **55**(8) 1370
101. P R Sassiat, P Mourier, M H Caude, R H Rosset *Anal. Chem.*, 1987, **59**(8) 1164
102. A Kopner, A Hamm, J Ellert, et al. *Chem. Eng. Sci.*, 1987, **42**(9) 2213
103. F Funazukuri, S Hachisu, N Wakao *Anal. Chem.*, 1989, **61**(2) 118
104. N Dahmen. A Kordikowski, G M Schneider *J. Chromatogr.*, 1990, **505**(1) 169
105. S V Olesik, J L Sleger, N Kiba, et al. *J. Chromatogr.*, 1987, **392** 165
106. R Feist, G M Schneider *Sep. Sci. Technol.*, 1982, **17**(1) 261
107. C A Cramers, C E van Tilburg, C P M Schutjes, et al. *J. Chromatogr.*, 1983, **279** 83
108. C A Cramers, F A Wijnheymer, J A Rijks, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1979, **2**(6) 329
109. R H Perrett, J H Purnell *Anal. Chem.*, 1962, **34**(10) 1336
110. J C Giddings, P D Schettler *Anal. Chem.*, 1964, **36**(8) 1483
111. R H Perrett *Anal. Chem.*, 1965, **37**(11) 1346
112. I Nagata, T Hasegawa *J. Chem. Eng. Jpn.*, 1970, **3**(2) 143
113. P Sandra, I Temmerman, M Verstappe *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1983, **6**(9) 501
114. F David, M Proot, P Sandra *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1985, **8**(9) 551

Translated from *Uspekhi Khimii* **61** 711–733 (1992) U.D.C. 541.183.2

Present state of research on the sorption of inorganic compounds by oxide hydroxides from aqueous solutions

S I Pechenyuk
Institute of the Chemistry and Technology of Rare Elements and Mineral Resources, Kola Science Centre of the Russian Academy of Sciences

ABSTRACT. The general trends and methods of studying sorption from solutions on oxide hydroxide surfaces are discussed, including coprecipitation and sorption on previous activated sorbents. The models of the sorption mechanism and of the interrelation between different types of sorption are examined.

The bibliography contains 166 references.

Contents

I. Introduction 385
II. Trends in the study of sorption processes on oxide hydroxides 386
III. Models of the sorption mechanism on oxide hydroxides 389
IV. Interrelation between the properties of the sorbate, of the sorbent, and of the ionic medium and the sorption mechanism 393
V. Conclusions 394

I. Introduction

Inorganic sorbents are used in all branches of industry and in the protection of the environment. They are used when aqueous solutions must not be contaminated with when the appropriate sorbents are cheap and simple to prepare and to regenerate, and stable towards radiation.[1] Oxide hydroxides (which are also known as oxyhydrates, hydroxides, and hydrated oxides†) come closest to these requirements, offering a high sorption activity in conjunction with a relatively simple synthesis (mainly the oxide hydroxides of iron, titanium, zirconium, aluminium, and tin[1]). Iron, aluminium, and titanium are widely distributed in nature, and their use is preferred on ecological grounds. The marked variation in the properties of oxide hydroxides prepared by different methods[2–8] has stimulated extensive studies of sorption on these materials. Workers who have synthesised oxide hydroxides by different methods have obtained results which are difficult or even impossible to reconcile. A search for regularities in this stream of data should help to assess the prospects of the various trends in research, to systematise and correlate existing data, and to identify bright spots in which fundamental studies of these topics could be developed. The aim of the present review is to outline some regularities in this field of study. The discussions will be confined to work published between 1976 and 1989.

A logical analysis of existing data requires first of all a clear definition of the concepts of sorption and coprecipitation. As has been pointed out,[2,9] sorption is a process in which a substance (the sorbate) is captured by previously synthesised sorbents, whereas in coprecipitation the capture takes place during the deposition of the sorbent from a solution containing the sorbate. It follows from these definitions that coprecipitation (as compared to sorption) is a process with time limitations set by the rate of formation of the precipitate of the macrocomponent (sorbent); subsequent processes in which the microcomponent (sorbate) is captured from the solution come under the definition of sorption, which has no time limits. During the contact between the sorbent and the sorbate the deposited sorbent can undergo transformations leading to the achievement of the most stable structure for the given conditions: this occurs in all the systems but is particularly important in systems with coprecipitation. A redistribution of the sorbate between the solid and the liquid phase could take place as a consequence. The initial picture can also be blurred by changes in the state of the sorbate in solution. Furthermore the time limitation, i.e. the instant when the true coprecipitation comes to an end, is poorly defined, and therefore it is often dismissed from the discussion consciously or unconsciously.

The result of the extraction by sorption depends on the time of sorption, and therefore a knowledge of the kinetics and mechanisms of all the changes taking place in the system is a necessary condition for a correct use of the sorbent, i.e. for the best results. Sorption processes are often used to remove microcomponents in solution in the presence of macrocomponents at a concentration 3–10 orders of magnitude higher. Therefore the ratios of the sorbent and the sorbate to the macrocomponents and the participation of the latter in the sorption process should be carefully monitored.

We shall review the principal directions of the experimental studies of the sorption of inorganic compounds from aqueous solutions on oxide hydroxides, which constitute (together with studies of the sorption on carbons from the gas phase and on organic sorbents from solutions) the largest group of studies in the modern science of reactions at a phase boundary (interface science). The writer does not claim to have reviewed the topic exhaustively: he has merely collected the most interesting (or typical) results of current research.

† Hydroxides, hydrated oxides, and oxide hydroxides are different chemical compounds,[2] but in the publications reviewed here the terms are applied indiscriminately to what are essentially oxide hydroxides: the products of the reaction of oxides with H_2O, both stoichiometric and nonstoichiometric.

II. Trends in the study of sorption processes on oxide hydroxides

Studies in which the adsorbate is coprecipitated with the sorbent occupy a major place in the current work on oxide hydroxides, but most of the authors fail to distinguish between the concepts of sorption and coprecipitation and discuss their results in terms of either concept, taken at random.[10–28] The experimental foundations of most of this work consist in determining the equilibrium sorption (or coprecipitation) of the microcomponents as a function of the nature of the macrocomponent (sorbent) and of the pH of the system for a fixed composition of the ionic medium. As we have already pointed out, these quantities should be treated as quasiequilibrium quantities.

Thus, the coprecipitation of the cations of the *s*, *p*, and *d* metals and of some anions with the oxide hydroxides of Fe, Ti, Zr, La, Y, Cd, Th, Be, Mg, Sc, and Nd has been studied at pH 4–14.[10–15]

The basic conclusion most often reached in that work is that the coprecipitation of the cations increases with the acidic properties of the collector, whereas (conversely) the coprecipitation of the anions decreases. The strength of the capture of the anion decreases as its aciditiy increases. We should stress that in the whole of this work the acid–base properties of the collectors are characterised only qualitatively, and the state of complex formation of the sorbates is ignored. The need to allow for the rate of establishment of equilibrium and for the forms in which the sorbate can exist in solution has been pointed out,[10] but even in later work this rate was not determined. Some reports[11,12,22,23] draw attention to the behaviour of the sorbate in solution, but the effect of the ionic strength and of the pH on the behaviour of the sorbent is ignored, in spite of the mention of gels of freshly precipitated oxide hydroxides which undergo uncontrolled spontaneous changes over long periods under the conditions of the experiment, especially in response to changes in the pH of the suspension (pH_s).[3–8]

The results of these studies of coprecipitation in combination with sorption[10–31] consist of tabulations of pH values at which various microcomponents can be removed from a solution of given macrocomposition by coprecipitation with a stated macrocomponent.

Another approach to the study of sorption processes, which is dominant among Russian scientists, is based on the theoretical model of classical ion exchange. The methodology of the study of sorption in inorganic sorbents is the same as in studies of organic ion-exchange resins, as is clearly shown in Belinskaya's review.[32] Many typical examples can be quoted:[33–51] in most cases granulated sorbents are preferred, in spite of the known fact that the drying and heat treatment needed during the granulation can seriously degrade the sorption properties.[1] Classical methods are used, like the limited volume[34,35] and the column dynamics method.[33,37–48] Studies of the sorption kinetics of both simple and complex ions in these systems show that the rate-limiting step is usually internal diffusion within the grain).[31–35] This approach is also being used to study problems of sorption selectivity, such as the sorption of SO_4^{2-} and NO_3^- on hydrated zirconium dioxide,[33] but it leads to partial, empirical results, whereas this type of problem is already basically solved (see below).

Unfortunately, the Soviet workers whose approach we are discussing seemed unaware (judging by their lists of references) of the immense amount of information on sorption problems obtained by foreign scientists, and made no attempt to interpret their own results in terms of alternative, more fully developed approaches.

Since complex formation is a phenomenon with universal ramifications we should pay special attention to studies of the sorption of complex ions of given compositions (classical complexes). The platinum metal complexes have been studied most widely. We can distinguish two groups of studies, each devoted to the same sorbates, carried out over approximately the same period, and containing much kinetic information: references 37–54 and 55–75. The compounds studied in this work included the complexes of composition MX_4^{2-} [where M = Pd(II), Pt(II) and X = Cl^-, Br^-, CN^-, CNS^-, NO_2^-], $M'Cl_6^{n-}$ [where M′ = Pt(IV), Ir(IV), Ir(III), Os(IV), Ru(IV), Ru(III), Rh(III)], and $Ir_3O(SO_4)_6Y_3$ (where Y = H_2O, SO_4^{2-}, and HSO_4^-). Abovskaya, et al. have studied the aquo complex of Pd(II)[48] and sulphate solutions of Rh(III) containing several complex forms.[49] The sorbents used in that work[37–54] included oxide hydroxides (hydrated oxides, or oxides, in the authors' terminology) of titanium (IV), zirconium(IV), tin(IV), and aluminium(III), whereas other workers[55–75] used crystalline oxide hydroxides (oxyhydrates in the authors' terminology) of the REE and many samples of amorphous oxide hydroxide of iron(III) (ferrogels), differing in the nature of the initial iron(III) salt and in the precipitation conditions (pH, oxidiser, temperature, time, etc.).

Both groups of papers discuss the kinetics of the process, including the temperature dependence of the rate, the influence of the nature and of the concentration of the ionic medium, and the effect of the composition of the products. Some papers[55,73–75] also discuss the interaction of the sorbents with the supporting electrolytes. That work leads to the following conclusions.

The sorption of anionic complexes on the granulated oxide hydroxides of Ti, Zr, Sn, and Al is fast (equilibration time τ_{eq} = 10–60 min at 20 °C) and is characterised by diffusion-limited kinetics, i.e. the activation energy E_a of the process (kJ mol^{-1}) is 30–40 for MCl_6^{n-}, 19–25 for $PdCl_4^{2-}$,[37–48] and 22 for $PtCl_6^{2-}$ on γ-Al_2O_3.[54] On the other hand the sorption of aquo complex is very slow (τ_{eq} = 4–20 h), E_a = 18.5 kJ mol^{-1} for rhodium(III).[49] Increasing the concentrations of the components and of the supporting electrolyte slows the sorption of the complexes on the oxide hydroxides of Ti, Zr, and Sn;[37–50] furthermore increasing the ionic stength suppresses the sorption, i.e. it lowers the degree of utilisation of the sorption capacity of the sorbents, which is not large for these oxide hydroxides, reaching a maximum (30 mg metal g^{-1} of sorbent) for ZrO_2. The SO_4^{2-} ions interfere most strongly with the sorption fo MCl_6^{n-} and $PdCl_4^{2-}$ on TiO_2 and ZrO_2. Ageing the solutions of the complexes (sorbates) increases the sorption from aqueous solutions but lowers the sorption from solutions in hydrochloric acid.[37–48]

The composition of the sorbed forms immediately after the establishment of the sorption quasiequilibrium is the following: $PdCl_4^{2-}$ [51,52] and $PtCl_6^{2-}$ [54] are sorbed on γ-Al_2O_3; $PtCl_3H_2O^-$ on ZrO_2; $PtCl_6^{2-}$, $OsCl_6^{2-}$, and $OsCl_5H_2O^-$, $RhCl_6^{3-}$, $IrCl_6^{3-}$, $IrCl_6^{2-}$, and $IrCl_5H_2O^-$, and $PdCl_4^{2-}$, are sorbed on ZrO_2, TiO_2, and SnO_2.[37–48] This means that the forms predominantly present in solution are sorbed without change in composition. Upon ageing the complexes in the sorbent phase undergo a slow aquation, giving $OsCl_5H_2O^-$ and $OsCl_4(H_2O)_2^0$, $RhCl_4(H_2O)_2^-$ and $RhCl_2(H_2O)_4^+$, $IrCl_3(H_2O)_3$, and $PdCl_3H_2O^-$.[37–50]

These complexes are also sorbed undecomposed and almost instantaneously at room temperature on ferrogels from solutions not containing a supporting electrolyte,[55,57,63] and the capacity of the ferrogel can reach 2×10^{-3} mol g^{-1} of $Fe(OH)_3$, i.e. more than 400 mg of Pt, Ir, and Os on 1 g of $Fe(OH)_3$.[55] However, in the presence of a supporting electrolyte (more than 0.05 mol dm^{-3}) the

chemistry of the sorption process is radically altered.[55,57] On the surface of the ferrogels (in the presence of a supporting electrolyte) and of the REE oxide hydroxides (whether or not on ionic background is present) we observed a process which has been described in detail[55,58] and called heterogeneous hydrolysis. The rate of this process is strongly dependent on the nature of the complex, the sorbent, and the ionic background, and also on the temperature (E_a = 60–130 kJ mol^{-1}); it usually corresponds to a first-order equation in the concentration of the complex-forming metal or of the sorbate [in the latter case, except $PdCl_4^{2-}$, $OsCl_6^{2-}$, and $Pt(CNS)_4^{2-}$]. The observed rate constants K_H vary with these factors from 10^{-5} ($PtCl_4^{2-}$ [64]) to 0.2–0.5 s^{-1} ($RuH_2OCl_5^{2-}$ at 80 °C[55,65]). Heterogeneous hydrolysis takes place gradually against a background of hindered transformations of the complex sorbate in the solution, spontaneously in the pH-static regime, and not associated with oxidation–reduction or photochemical changes in the complex.[55] The products of the heterogeneous hydrolysis are the amorphous hydroxides of the central atom (CA),[55,59] strongly bound to the surface of the sorbent: the rate of detachment of the ligands from the CA is equal to the rate of transfer of the latter from the bulk of the solution to the surface of the sorbent. The rate of this process is directly proportional to the basicity of the sorbent [characterised[55] by the pH at the point of zero charge (pH_{PZC} or pH^0)] and depending in a complicated way on the concentrations of NaCl and Na_2SO_4 in the system. This dependence can be represented by the linear equation

$$K_H = a \pm bC_{el},$$

where C_{el} is the concentration of NaCl or Na_2SO_4 and the sign of the second term is determined by the nature of the sorbent and of the electrolyte.[58,62,63] It has been shown[73–75] that this is the result of the interaction of the sorbent with the supporting electrolyte, which alters the basicity of the sorbent.

Ageing the solutions of complex sorbates accelerates the heterogeneous hydrolysis; increasing the ionic strength of an electrolyte ($NaClO_4$) inert towards the sorbate and the sorbent suppresses the reaction;[66] the rate is unaffected by the charge on the complex anion.[67] A correlation has been found between the stability (or the lability) of the complex sorbate and the rate of the heterogeneous hydrolysis: the rate increases with increasing lability and with decreasing stability of the complex, and *vice versa*. The possibility of heterogeneous hydrolysis itself is determined by the stability of the complex. Thus, complexes with β = 10^{36}–10^{40} [$Pt(Cn)_4^{2-}$, $Fe(Cn)_6^{3-}$, $Fe(CN)_6^{4-}$] do not undergo heterogeneous hydrolysis.[55] The process has a pseudoequilibrium character, with sorption isotherms of the high affinity type;[76] the pseudoequilibrium capacity can reach (0.5–3.0) × 10^{-3} mol of complex g^{-1} of sorbent for the ferrogels and Ln_2O_3.[72] The reactions of these complexes with MCO_3 (M = Ca, Sr, Ba) are of the heterogeneous hydrolysis type.[68] A complex dependence exists between the rate of heterogeneous hydrolysis and the concentrations of sorbate and sorbent.[55]

We should also mention a group of papers describing sorption on previously activated oxide hydroxide sorbents [goethite, magnetite, haematite, jarosite, and amorphous hydroxides of iron(III)] at high temperatures (100–190 °C) from sulphuric-acid solutions of iridium and ruthenium in the form of sulphato or aquo hydroxo complexes of indeterminate composition.[77–81] It was shown that in these cases the sorption is irreversible, as in heterogeneous hydrolysis, and slow, that the capcity of the sorbents is low, and that the complex sorbates are fully or partially decomposed during the sorption.[81]

Lastly, we cannot fail to mention the work of Nechaev,[82–85] distinguished by an original approach to the mechanism of sorption on oxide hydroxides [for example, the sorption of $AuCl_4^-$ on the crystalline oxides of iron (III)]. Nechaev tried to relate the sorption equilibrium constants to the ionisation potentials of the oxide surfaces at pH^0.[83] He determined the composition of the sorbed forms and established that the sorption is accompanied by partial aquation of the $AuCl_4^-$.[82,84] The sorption of $AuCl_4^-$ and of its aquo derivatives was found to be described by Langmuir isotherms; the surface charge is of secondary importance in the sorption process, whereas the electronic structure of the surface plays a dominant role and determines the sorption activity of the oxides [at least, in respect of Au(III)].[85] However, the traditional (deeply "equilibrium") approach to the study of sorption and the fact that all the conclusions apply only to a single, easily hydrolysed and reduced complex ($AuCl_4^-$) detract from the value of the results.

In the foreign literature the studies of direct sorption on previously prepared sorbents greatly outnumber the studies of coprecipitation.[86,87] The vast majority of publications is based on the concept of an electrically charged oxide hydroxide surface. When in contact with H_2O or with an aqueous solution of electrolyte (sorbate) this surface can be identified with an electrode surface in contact with a solution,[88] and the appropriate definition of a potential-determining ion can be applied to it. For the oxide hydroxides these ions are H_3O^+ and OH^-;[89,90] their distribution between the bulk of the solution and the sorbent surface creates a surface charge q and a potential $\Psi(x)$ at the interface. The concepts of specific and of nonspecific sorption are also used. When the sorption energy E_s is Coulombic,

$$E = q\Psi(x),$$

i.e. when the interaction is purely electrostatic, the sorption is treated as nonspecific; in the opposite case the sorption is specific, i.e. it is accompanied by the formation of new chemical bonds. Because of the difficulty of determining $\Psi(x)$ and E_s experimentally (whereas the surface charge is easily measured[89–91]) the type of sorption is determined by using the point of zero charge PZC and the pH_{PZC} (pH^0)‡. The symbol pH^0 defines the pH of the so-called zero solution, for which the electrode has an equilibrium potential $\Psi(x)$ = 0[88] and the surface charge of the sorbent is q = 0. In the absence of specific sorption of the electrolyte ions pH^0 is independent of the concentration of electrolyte.

Simple cations and anions are mostly used as sorbates in the work of foreign scientists. Studies of sorption equilibria also seem to be predominant. Measurements of pH^0 and studies of the dependence of q on the nature and concentration of the electrolyte are a major part of most of these investigations. A specific link between the magnitude and other characteristics of the sorption and of the surface charge of the oxide hydroxide is sought, defined by the relationship between the pH^0 values of the sorbent, the pH of the suspension (pH_s) in the sorption system, and the concentration and nature of the supporting electrolyte. Since the previous review of the pH^0 and pH_{IEP} values was published[93] in 1965 it seems useful to complement the existing[93] data with information extracted from work published during the last two decades (Table 1).

‡ pH_{PZC} should be distinguished from pH_{IEP} (the pH of the isoelectric point), defined[92] as the pH of a solution in which the potential of the solid (ζ) is zero, i.e. the charge at the boundary of the diffuse layer of solution is zero.

Table 1. ph of the point of zero charge (pH^0) of some oxide hydroxides.

Oxide hydroxides	Method of preparation	Electrolyte	Concentration of electrolyte mol dm^{-3}	pH^0	Refs.
α-Fe_2O_3	Boiling a solution of $Fe(NO_3)_3$ for 18 dyas	KCl		9.2	[112]
	Natural	KCl		5.4–6.0	[91]
	After Atkinson [112]	KCl		6.3	[114]
	Reagent	KCl		8.4	[101]
				8.4	[107, 109]
	After Atkinson [112]	KCl		8.5	[92]
		K_2SO_4, $Ca(NO_3)_2$	0.1	9.6 6.5	[92] [92]
	Heating γ-Fe_2O_3 at 550 °C for 2 h in air				
	washed with H_2O	KCl		3.2	[97]
	washed with KOH (pH 9)	KCL		6.7	[97]
	Precipitation from a solution of $Fe(NO_3)_3$ by adding	KNO_3		8.6 (20 °C)	[124]
	NaOH and ageing at 150 °C in an autoclave			7.6 (20 °C)	[124]
α-FeOOH	Precipitation from a solution of $Fe(NO_3)_3$ by KOH at pH 12 and ageing in the in the mother liquor at 60 °C for 24 days	KCl		7.6	[112]
	After Atkinson [112]	$NaNO_3$		7.6	[125]
		KNO_3		7.5	[108]
		$NaNO_3$	0.1	10.2	[126]
β-FeOOH	Crystallisation of ferrogel in a chloride medium	KCl		7.6	[113]
				8.5	[127, 128]
γ-Fe_2O_3	Dehydration of α-FeOOH at 350 °C and cooling in air for 1 h				
	washed with H_2O	KCl		3.3	[97]
	washed with KOH (pH 9)	KCl		5.5	[97]
Fe_3O_4	Natural	KCl		6.4	[119]
	ditto	KCl		6.5	[91]
	ditto after HCl treatment	KCl		3.8	[91]
Ferrogel	Precipitation from a solution of $Fe(NO_3)_3$ by sodium hydroxide at pH 8, freshly prepared	$NaNO_3$	0.1	7.9–8.0	[102]
	Precipitation from a solution of $FeCl_3$ at OH/Fe = 4	$NaNO_3$	0.1	8.1	[114]
	Precipitation from a solution of $Fe(NO_3)_3$ at OH/Fe = 4	$NaNO_3$	0.1	8.4	[114]
	Precipitation from a solution of $Fe(NO_3)_3$ at pH 7	$NaNO_3$	0.1	8.1	[109, 110]
	Precipitation from a solution of $FeCl_3$ by a saturated solution of NH_4OH	$NaNO_3$	0.1	8.5	[125]
	Precipitation from a solution of $Fe(NO_3)_3$ by sodium hydroxide at pH 7 and ageing in the mother liquor for 3 h	$NaNO_3$	0.1	7.9	[109]
Ferrogel, freshly prepared	Precipitation from a solution of $FeCl_3$ by sodium hydroxide at pH 7.5	NaCl	1.0	7.7	[55,75]
		NaCl	0.01	6.3	[55,75]
		Na_2SO_4	0.5	8.3	[55,75]
Ferrogel	Precipitation from a solution of $Fe_2(SO_4)_3$ by sodium hydroxide at pH 7.5	NaCl	1.0	6.2	[55,75]
		$NaClO_4$	0.01	5.8	[55,75]
	Precipitation from a solution of $Fe_2(SO_4)_3$ by sodium hydroxide at pH 7.5	NaCl	1.0	8.7	[55,75]
		$NaClO_4$	0.01	5.8	[55,75]
	Precipitation from a solution of $FeCl_3$ by sodium hydroxide at pH 9	NaCl	1.0	8.7	[55,75]
	Same gel, aged in a solution of 1 M NaCl for 1 h at 80 °C	NaCl	1.0	8.3	[55,75]
Ferrogel	Same gel, aged in a solution of 0.5 M Na_2SO_4 for 1 h at 80 °C	NaCl	1.0	5.1	[55,75]
Y_2O_3	Reagent, ItO-03, B form	$NaClO_4$		7.45	[73]
		NaCl		7.60	[73]
		Na_2SO_4	0.01	7.85	[73]
		Na_2SO_4	0.1	8.55	[73]
		Na_2SO_4	0.5	8.75	[73]
Sm_2O_3	Reagent, SmO-E, C form	NaCl		7.45	[73]
		Na_2SO_4	0.1	7.90	[73]
			0.5	8.80	[73]
Yb_2O_3	Reagent, ItbO-03, B form	NaCl		7.15	[73]
		Na_2SO_4	0.1	7.25	[73]
		Na_2SO_4	0.5	8.25	[73]
TiO_2	Hydrolysis of $TiCl_4$, ageing in mother liquor for 3 weeks, rutile	KNO_3		5.6 (20 °C) 5.1 (50 °C)	[124] [124]
	Precipitation from a solution of $Ti(SO_4)_2$ by 2 M NaOH, washed and dried at 50 °C, anatase	$NaNO_3$		6.0	[129]
	Rutile			5.8 ( )	[126]
ZrO_2	Prepared by a method similar to that described for TiO_2 [129]	$NaNO_3$		9–10	[129]
$ZrO_2.4H_2O$	Precipitation from a solution of $ZrOCl_2$ by sodium hydroxide at pH 3.8–4.1, dried, the precipitation conditions do not affect pH^0	NaCl		6.5	[130]
	Reagent	LiCl, NaCl		4.3	[131]
	Reagent	KCl, CsCl		5.1	[132]
CeO_2	Prepared like TiO_2 [129]	$NaNO_3$		7	[129]
ThO_2	Ditto			10–11	[129]
α-Cr_2O_3	Precipitated from a solution of $Cr(NO_3)_3$ by the slow hydrolysis of $CO(NH_2)_2$ at 95 °C	KNO_3		6.35	[108]
γ-Al_2O_3	Reagent	KNO_3		4.6 (15 °C) 5.25 (20 °C) 5.3 (25 °C)	[133] [133] [133]
$Al(OH)_3$	Synthetic gibbsite	NaCl	0.5	9.5	[126]
RuO_2	Heated at 400 °C	KNO_3		5.4	[96]
90% RuO_2 + +10% IrO_2	Heated at 500–700 °C for 6 h	KNO_3		5.45	[139]

Notes. 1. The concentration of the supporting electrolyte is shown in cases of specific sorption or when the pH^0 value is quoted for specified concentrations of electrolyte. 2. pH_{IEP} is 7.9 for α-Fe_2O_3 (washed with KOH) and 6.8 for γ-Fe_2O_3 (washed with KOH).

The factual material thus obtained can be summarised as follows. In the absence (and only in the absence) of specific sorption pH^0 occurs at the intersection of all the $q = f(pH_s)$ curves for different concentrations of electrolyte,[88–92,94] and this quantity alone fully characterises the oxide (or oxide hydroxide).[94] In many cases (the oxides and oxide hydroxides of Cu, Fe, Al, Ru[95,96]) the oxide hydroxides have lower pH^0 values than the corresponding "dry" oxides, but opposite examples can also be seen in Table 1 (for Zr, Ti, and Al). The K^+, NO_3^-, and ClO_4^- ions are usually sorbed nonspecifically,[97–99] whereas the ions Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Li^+,

Zn^{2+}, Ga^{3+}, Eu^{3+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, SO_4^{2-}, PO_4^{3-}, SeO_3^{2-}, $P_3O_{10}^{5-}$, and F^- are specifically sorbed.[89,90,92,99,100–111]. Cl^- can be sorbed both specifically and nonspecifically.[91,112–114]

The specific sorption of cations produces a shift in pH^0 of the oxide hydroxide sorbent towards lower values, and the sorption of anions has the opposite effect. Specifically sorbed ions can displace nonspecifically sorbed ions, but not *vice versa*.[98,99] The sorption of M^{2+} and M^{3+} cations produces a change in pH_s, and is strongly dependent on this parameter if the latter is fixed and controlled. The dependence on pH_s of the equilibrium and (or) pseudo-equilibrium sorption of the cations, and the abiity of the cations to form hydroxo complexes, have a dome-like or near-exponential shape (stretched S) leading to a plateau.[29,101–106,115–117,119,120]

The first shape of this dependence is characteristic of cations which easily form stable and readily soluble hydroxo complexes, for example Zn^{2+}, Cr^{3+}, and Al^{3+}; the second is found for cations which do not possess this property, for example Co^{2+}.[115–117] The sorption of cations on oxide hydroxides is accompanied by the removal of one or two protons from one sorpton centre. At low adsorptions the sorption of M^{2+} is described by the Langmuir isotherm,[116,117] and at high adsorptions by the Freundlich[106] and Frumkin isotherms:[115] this is attributed to the energy nonuniformity of the sorption centres on the surface of oxide hydroxides.

IR spectroscopy identifies three types of surface hydroxyl groups, containing oxygen attached to the surface in mono-, bi-, and tridentate configurations.[105] At low coverages the first (and most active) type is used, and when these are occupied the energetically less favourable positions come into play. The same effect is seen in the kinetics of the process:[106] on increasing the sorbent/sorbate ratio the rate of sorption of cations (Cd^{2+}) increases because of the increased proportion of the more active centres, and *vice versa*. As reported[105,106] the rate of sorption of M^{2+} cations is quite high, and the sorption quasiequilibrium is established in 10–30 min at room temperature.

The isotherms for the sorption of anions (for example, PO_4^{3-}) on highly active oxide hydroxide sorbent samples (for example, ferrogels[109–111]) belong to the high affinity type of isotherm (H type[76]). At pH = const the sorption of the anions increases with the ionic strength of the solution. Three regions can be observed in the sorption isotherms. Ageing the ferrogels lowers their capacity towards PO_4^{3-} ions and their rate of sorption.[109–111] The sorption of PO_4^{3-} ions decreases the pH^0 value of the ferrogel.[109] Comparing data from different laboratories[55,109,111,121] shows that the properties of ferrogel surfaces are unstable and sensitive to influences from the sorbate and from the ionic medium. The sorbability of the anions increases with their acidity[122] and with decreasing pH_s.[123]

A few (but very important) studies of the effect of temperature and composition of the oxide hydroxide on its surface properties have been reported.[94,96,99,124,126,133–137] In the case of magnetite[135] and of haematite and rutile[124] it has been shown that pH^0 decreases with increase in temperature and increases when the temperature is lowered: for example, pH^0 for α-Fe_2O_3 in KNO_3 solutions is 9.5 at 5 °C, 8.6 at 20 °C, and 7.6 at 60 °C.[124] An increase in temperature also increases the slope of the $\partial q/\mathrm{q}pH$ curves slightly, and makes the branches of the $q = f(pH_s)$ curves lying in the acidic and the alkaline region respectively more asymmetric. The sorption equilibrium constants increase with temperature,[135] and the $\Delta G^0_{\mathrm{ads}\,H^+}$ values correspondingly increase somewhat; the effect of the ionic strength on the surface charge also increases only slightly with temperature.[124] On the other hand for γ-al_2O_3 pH^0 increases from 4.45 to 8.95 (even in solutions of KNO_3) when the temperature is increased from 10 to 50 °C.

Thus the response of pH^0 for an oxide hydroxide to a change in temperature depends first and foremost on its chemical nature. It is found that in the mixed oxide hydroxides RuO_2 + IrO_2 [134] and TiO_2 + Al_2O_3 [137] pH^0 is the mean of the pH^0 values of the components.[134,137] Heat treatment of the oxides also produces different effects on pH^0, depending on their chemical nature and method of preparation.[96,134] It has been established that homo- and heterodispersed sols of α-Fe_2O_3 have identical pH^0 values.[94] This is consistent with the report[134] that pH^0 is unrelated to the specific surface S_{sp} of the oxide hydroxide. Lastly we shall mention a study[138] of the kinetics of charge transfer (electrons and protons) through the interface in suspensions of α-Fe_2O_3 and α-FeOOH by the pulse radiolysis method. It was shown that the rate of charge transfer is strongly dependent on pH_s: the rate constants vary between 10^{-1} and 10^4 s^{-1} in the pH_s range 3–11.

III. Models of the sorption mechanism on oxide hydroxides

The model of the sorption mechanism should describe the distribution of the sorbate (and preferably also of the components of the supporting electrolyte) near the reactive surface (or interface) as well as the thermodynamics and the kinetics of the process. The criteria for evaluating the quality of the model were clearly formulated by Barrow and Bowden:[139] it could be useful to re-state them in their entirety. An ideal model should be effective, comprehensive, realistic, and predictive. An **effective** model should offer a detailed description of the observations: otherwise, its fundamental hypothesis is incorrect. Effectiveness is a necessary but not a sufficient quality of the model. A **comprehensive** model can be used unmodified in a wide range of conditions. A **realistic** model is consistent with generally accepted theories of the behaviour of the components of the system. A predictive model leads to a new understanding of the phenomena and offers wider prospects of exploiting them in different circumstances.

Studies of sorption processes are divided mainly into two streams, which we can call simply the western and the eastern stream. The western stream consists mainly of the Dutch–American school, to which we owe a systematic and "well equipped" theory of the sorption of ions in an electrical double layer.[89–92,94–96,100–115,119,120,124,126] This group of studies is distinguished by a very precise formulation of the problem, a strictly methodical approach, and high-grade processing of the experimental data. It is noteworthy that the research problems are considered from the standpont of preconceived ideas. While this is one of the main strengths of the approach it also introduces a certain weakness by lowering the probability of unexpectedly discovering interesting new results.

The eastern stream consists of the work of Indian and Soviet scientists (mainly the latter). It is characterised by the absence of firm preconceptions experimental results are interpreted by any suitable theory or theoretical fragment capable of explaining the experimental facts. Of course this classification of the two streams is not absolute, and a mutual "diffusion" of the two approaches and conceptions can be detected.[55,73,75,97,99,116,117,129,132]

Before proceeding to a detailed discussion of the models we should make the following comments. Whatever the actual compounds used as the sorbents (hydroxides, oxides, or even

carbonates) the effects observed in studies of sorption from aqueous solutions in real experimental systems relate to sorption on oxide hydroxides. This is suggested both by numerous studies of structure formation in oxide hydroxides[3–8,140–142] and by studies of the interaction of H_2O with oxides,[131,143–146] and has been repeatedly confirmed by the work of western scientists.

Let us begin our examination of the sorption models with the most fully developed theories. The foundations of the coordination chemical theory of sorption on oxide surfaces were laid in the 1980's.[95,147,148] The basic hypothesis of this theory is that H_2O molecules are dissociatively sorbed on the oxide surface during its contact with an aqueous solution or with a moist atmosphere: as a result the surface is covered with a layer of hydroxyl groups having a density of 2–10 OH nm^{-2},[148] which undergo fast protolytic reactions with the solution. This establishes an equilibrium distribution of the charges in advance of the other sorption processes. On a neutral surface (at the point of zero charge) the numbers of positively and of negatively charged centres are equal. At the contact with a solution of $pH < pH^0$ the surface (now in the oxide hydroxide form) becomes positively charged, whereas at pH > the surface charge is negative. As was stated above pH^0 is determined experimentally: attempts to calculate it on theoretical grounds have proved unsuccessful.[95] The sorption process is primarily electrostatic.

On a given oxide hydroxide cations are sorbed at $pH_s > pH^0$ and anions at $pH_s < pH^0$.[120,123] However, cation sorption takes place (in part) in the region of positive surface charge,[129,149] and therefore simple electrostatic models are inappropriate. A deeper understanding of the sorption can be gained from considerations of the complex formation between the cations and the OH^- groups of the boundary layer and of the replacement of these groups by anions:[148] the site binding model.[105,120] The possibility of these processes and their special features are related to the stucture of the electrical double layer (EDL) at the interface. The characteristics of the EDL are the equilibrium constants of the surface ionisation and of the surface complex formation K, the surface charge q, the capacity, and the potential $\Psi(x)$.

Barrow and Bowden[139] have constructed three models of the sorption in the EDL, composed of one, three, and four planes of ions respectively (Fig. 1). All three models give expressions for the sorption equilibrium constants.

According to the one-plane model all the adsorbed ions are accommodated in a single plane and have the same potential: the neutral $-S-OH$ surface, which joins the centres of the $-SO_3^-$, $-S-OH$, and $-S-OH_2^+$ groups. The expressions for the equilibrium constants contain the term $\exp(nF\Psi/RT)$, where n is the valency of the sorbed ion, F and F are well known constants, and T is the temperature. The surface complex is written as $-SA$.

According to the three-plane model H^+ and OH^- are located in a separate internal plane s, the electrolyte ions and the sorbate ions are in the next layer, and the expression for the equilibrium constant contains the term $\exp[-F(\Psi_\beta-\Psi_0/RT)$; the surface complex is written as $-SOH_2^+-A^-$ or $-SOH_2^+-HA$.

According to the four-plane model[150] H^+ and OH^- are again located on the innermost potential plane while the next plane contains the sorbed ions and the next the ions of electrolyte (see Fig. 1). The sorption centre is described as $-S\begin{matrix}OH\\OH_2\end{matrix}$, and the sorption complex as $-S\begin{matrix}OH\\A_1\end{matrix}$ or $-S\begin{matrix}A_1\\OH_2\end{matrix}$; the expression for the equilibrium constant contains the term $\exp(-nF\Psi_\alpha/RT)$. The sorbate can replace both the $-OH$ and the $-OH_2$ group, i.e. it can react with the surface irrespectively of its charge. From this pont of view all the surface centres are vacant, so that the sorbate reacts with centres caryring an average charge. In the case of a polyvalent sorbate this model allows interaction with all forms of ions in solution (though some are known to be preferred), i.e. it offers a choice between the particles in solution but not between the surface centres. However, even in the sorption of the PO_4^{3-}, F^-, SO_4^{2-}, and SiO_3^{2-} anions on goethite[139] none of these models is ideal. Many arbitrary assumptions are needed to produce a satisfactory agreement between calculation and experiment. Special attention must be paid to the concentration of the sorbate, the pH of the medium, and the contact time of the phases.

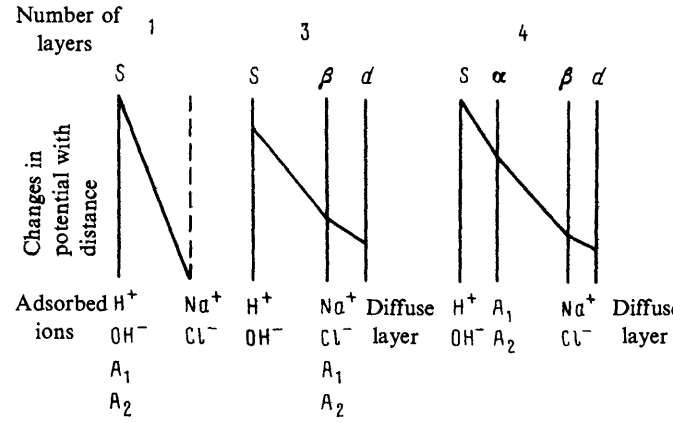


Figure 1. Three models of the interaction between the solution and the adsorption surface of the ions.[139] The bulk of the adsorbent is on the left, that of the solution is on the right; the diagrams show the proposed localisation planes of the individual classes of ions and the changes in electrical potential with distance.

These models ignore the steric factor (the size of the sorbate ions) and they treat the surface of the sorbent as uniform and nonporous, and therefore they cannot be applied to gels.[151] However, as shown by Perram,[146] a layer of oxide hydroxide gels can readily be formed on oxide surfaces in contact with water, and this observation led to the development of the EDL theory.

There have been attempts[105,106,120] to treat the surface of the oxide hydroxide sorbent as energtically nonuniform (heterogeneous) to account for the difference in sorption at low and at high coverages. The simplest two-position model[106] stipulates the formation of $-S-M(OH)_n(-Cd(OH)_2)$ from uniform $-S-OH$ centres at low coverages (i.e. low adsorption densities) through reversible reactions of the first order in the sorbate, and the use of other centres (of various types) in the region of high coverges. A more general solution of this problem is proposed by van Riemsdijk, et al.:[120] the heterogeneous surface is represented as an assembly of uniform subsurfaces, and the sorption on each of these is

described by a standard (Langmuir or Freundlich) isotherm. The heterogeneous surface is described by the symbol $-S\begin{vmatrix} O^- \\ OH^0 \\ OH_2^+ \end{vmatrix}$, and and centres with different energies are treated as subsurfaces. Models similar to the four-plane model[139] are used, and it is assumed that the form of the energy distribution function of the adsorption centres is retained when the ions are adsorbed.

Hiemstra, et al.[152] proposed a many-centre model of the adsorption on the oxide hydroxide–solution interface (multisite complexation, MUSIC) in which different OH groups are coordinated by one, two, or three metal ions; the model was thought to account for the microheterogeneity of oxide surfaces. It was tested on gibbsite, goethite, haematite, rutile, and silicon dioxide:[126] different crystallographic faces were found to make different contributions to the formation of the surface charge and to the PZC. Faces which (in general) remain uncharged over a wide range of pH were identified, and it was shown that in a crystalline oxide pH^0 is determined by the behaviour and by the presence of faces containing the greatest number of OH groups coordinated by only one metal atom from the lattice. Successful attempts to calculate the pH^0 were made.[152,126] It was shown that the binding centres model is a special case of the multisite complexation model.

Westall and Hohl[153] pointed out that the sorption energy is very difficult to divide into an electrostatic and a chemical component, though this procedure could lead to a rational choice between many possible models relying on similar law of mass action (LMA) and material balance equations but different descriptions of the EDL. Attempts to formulate a strictly quantitative description of the sorption of electrolytes on oxide hydroxide surface have also met other problems. Thus, the maximum sorption always exceeds the possible monolayer sorption,[154] and furthermore all the surface models are based on the conception of the EDL of a single particle is a large volume of electrolyte solution, though the presence in solution of a large number of dispersed particles (as is always found in real systems) shoud have a profound effect on the parameters of the EDL. The mathematical description of the EDL is very complicated even for a single particle, and for a more complex system it is quite impossible at present.[151]

Recent reports (for example, by Spitz, et al.[155]) have stressed that no quantitative descriptions of the surface–sorbate interaction based on the concept of acid–base interactions have so far been put forward. One contributor to a recent monograph,[76] Lyklema, described the sorption of ions on solid surface by rejecting all mathematical procedures and relying wholly on qualitative relationships. He defended his approach by the following argument: it is impossible at present to determine the sorption of an electrolyte, since different methods give different results; furthermore the sorption in the EDL of ions of a single type can also not be determined, and therefore it is reasonable to describe the process in terms of uncharged particles; lastly, the problem of potential-determining ions is far from clear. Evidently, a comprehensive mathematical description of sorption from solutions of electrolytes on oxide hydroxides is not likely to be available in the near future. Nevertheless it does not follow that all current attempts to produce such a description are meaningless.

Let us consider, as a typical example of the work of the eastern stream, a group of Indian and Japanese publications.[143,156–158] Venkataramani and Gupta[143] studied the sorption of H_2O on the oxides of titanium(IV), bismuth(III), and thorium(IV), and on magnetite: they measured the sorption isotherms and made pH-metric titrations of the oxide samples in a medium of $NaNO_3$. The reversibility of the sorption of H_2O was demonstrated, the effect of the preparative conditions (method of precipitation, and ageing) was studied, and the content of $-OH$ and $-ONa$ surface groups in the samples was determined. However, the results[143] cannot be used to predict the adsorption behaviour of the oxides because there is no link between the results and information on pH^0 and on the structure of the EDL, and also because no attempt has been made to determine pH^0.

Other publications in this group[156,157] discuss data on the sorption of M^{2+} and M^{3+} cations on magnetite and an amorphous iron(III) oxide from the standpoint of a typical ion exchange model. Inoue, et al.[158] treat the oxide hydroxides of tin(IV) and niobium(V) as ion exchangers with weakly acidic functional groups, interpreting the functional groups and the liquid layers near the solid surface as an exchange phase in which the electrostatic bond and the LMA have the same significance as in solutions. They correctly point out that the simplified approach in which the sorption is treated as a typical ion exchange phenomenon cannot be applied to oxide hydroxides, i.e. it does not correctly explain the effect of the experimental conditions on the sorption capacity and on the distribution coefficient. Nevertheless they make a sharp distinction between ions bound by Coulombic forces (free ions in the bulk phase) and ions attached to the functional groups by a coordinate bond ("undissociated" ions in the ion exchanger phase). They use the pH_{TEP} concept, but in fact they are operating with pH^0 since they use a nonspecifically sorbed electrolyte (NaCl) to determine this parameter. The failure to distinguish between these quantities detracts from the universality of the method, though not from its effectiveness.

We should stress the fact that complex cases are known in which none of the existing sorption models can offer a suitable explanation. For example, the sorption of UO_2 ions on the surface of the oxides of Ti(IV), Th(IV), Zr(IV), Ce(IV), and others[129,149] in the region of positive surface charge produces a shift of pH^0 towards the right. The authors put forward the concept of attack of the OH surface group by the sorbate ions without previous deprotonation: this process is energetically most favourable for dimeric and trimeric sorbate cations and their neutral molecules, and is called electrical sorption by the authors. Under these conditions the sorbate in the sorbent phase forms bridges between pairs of neighbouring surface on groups. Another example is heterogeneous hydrolysis,[55] discussed below.

The ion exchange model of this process is very widely used in the Soviet publications. It is based on the oxyacid theory of amphotericity,[159,160] according to which amphoteric oxides (hydroxides, oxide hydroxides, oxide hydrates) show cation or anion exchange properties according to the pH_s. The cation exchange properties (selectivity, capacity) of an oxide hydroxide decrease and its anion exchange properties increase. The rate of ions exchange is limited by diffusion in the boundary layer or in the sorbent grain (outer and inner diffusion), and the sorbability of the ions depends on their charge and size. The attraction towards exploiting the analogy with organic ion exchangers, which is obvious for this approach, can be seen in a group of mainly Soviet publications.[31–54] Thus, in Belinskaya's review[32] the inorganic sorbents are treated as polymeric ion exchangers with functional goroups which dissociate at the $-M-O^-$, $-M-OH$, and $-M-O-H$ bonds, though some experimental facts are admittedly incompatible with this scheme.

The discrepancy is avoided by assuming compensation of the charge on the polymeric ion exchanger skeleton (usually assumed to be negative) by mobile cations. The mathematical description of ion exchange is a well known process which can be applied to inorganic sorbents without special difficulties. In many resports[26–54] the discussion is limited to a qualitative explanation of the results in terms of the ion exchange model.

A group of papers[10–25] develops the interpretation of the sorption process (coprecipitation) as an acid–base interaction between the sorbate and the sorbent. This model is based only on static (pseudoequilibrium) experiments on the sorption of metal cations. The mechanism assumes the adsorption of hydrolysed forms of the cations with a minimum charge, i.e. $M(OH)_n^0$. It is suggested that the sorbate is attached to the sorbent by forming tin bridges between $M(OH)_n$ and the oxide hydroxide sorbent (collector).

The coprecipitation of cations begins at pH values of the system which define the onset of hydrolysis and of the formation of simple or polynuclear products in solutions of the elements being coprecipitated. The formation of coordinationally saturated complexes of the sorbate suppresses the sorption (coprecipitation) by this mechanism. Coprecipitation takes place at a pH of the medium lower than the pH for the deposition of the sorbate, suggesting a shift in the hydrolysis equilibrium of the sorbate.[16] The acid–base interaction model is qualitative and does not provide a basis for the mathematical description of the sorption equilibrium or for any prediction. The process is examined exclusively from the point of view of the behaviour of the sorbate: the behaviour of the sorbent, including the presence of charge and of an EDL on its surface, is totally ignored. As the authors themselves point out,[10–25] the observed phenomena could equally be described in terms of ion exchange, but this means using a different model to discuss the results.

An interesting analysis of this group of papers was published by Artyukhin,[30] whose conclusions are still valid. The great diversity of the points of view on the sorption mechanism and the failure to allow for the linked hydrolytic equilibria in the formulation of the sorption equilibria are stressed. It is pointed out there there is no direct proof of the sorption of both neutral and charged forms of the sorbate, and that data on the equilibrium (or quasiequilibrium) limited to pH-metric measurements are an insufficient basis for the construction of a model of the mechanism of the process. In the processing of the experimental results[29,30] an attempt was made to demonstrate the sorption of metal cations in the uncharged hydroxo form over the whole range of pH; the preferential sorption of uncharged forms implies the absence of an electrostatic barrier (which is a reasonable assumption when discussing the sorption of cations on a positively charged surface). It is concluded that all the sorptions lead to the formation of an uncharged compound in the sorbent phase. We consider this to be a special case, applicable to the aquo cations of metals, as shown by many published results.[37–54] It is assumed that any form of the sorbate, including forms present in solution in negligibly small amounts, can be responsible for the distribtion of the sorbate. Clearly, this is a problem of major importance for constructing a mechanism of the sorption on oxide hydroxides. To complete the picture we should mention (without going into details) the use of the isomorphous coprecipitation[28] and of the coordination model.[24,27]

Let us now consider the heterogeneous hydrolysis mechanism, proposed by the present writer. This is a kinetic model of a nonequilibrium process, unlike any other model used in adsorption studies. As was shown in section II, heterogeneous hydrolysis takes place with formation of uncharged hydroxo complexes as the reaction product, as in the sorption of M^{n+} cations.[10–30] The high rate of formation of these products for metals such as zinc, cobalt, nickel, and copper in noncomplexing ionic media allowed the construction of a model[16–25,29,30] of sorption involving the uncharged form $M(OH)_n^0$ as the sorbed species. However, a study of the process with sorbate in the form of stable complex ions (as in heterogeneous hydrolysis) shows that in reality the mechanism is more complex.

We should stress that not one of the sorption models previously suggested (electrostatic, ion-exchange, coordination, complex formation with the functional groups of the sorbent, acid–base, isomorphous coprecipitation) can effectively describe heterogeneous hydrolysis. The rate of the heterogeneous hydrolysis and its temperature dependence suggest first and foremost that the rate-determining step of the process is a relatively slow chemical reaction. The established participation of the electrolyte and of H_2O in the heterogeneous hydrolysis,[64,66,73,74] its uncontrollable pH-static regime,[55,60–62] the localisation of the process on the sorbent surface,[72] and its progress against a background of hindered reactions of the sorbate and of the sorbent[55] show that heterogeneous hydrolysis is a multistage chemical reaction which includes, however, an adsorption step. The uncharged form of the sorbate in heterogeneous hydrolysis is the last, and does not react. We have proposed[55] a three-stage model of the mechanism, including the fast reversible adsorption of the dominant form of the sorbate complex, the slow reversible aquation of the complex on the sorbent surface, and the fast partially reversible dissociation of the aquo complex formed on the surface of the oxide hydroxide sorbent with compensation of the additional surface charge, which defines the condition of the spontaneous pH-static regime. The observed rate constant of the heterogeneous hydrolysis can be expressed as the rate constant of a heterogeneous reaction:[161,162]

$$K_{\text{H}} = K_x k_{a_x}^{-1} k_{\partial_x}^{-1} C_x C_{\text{M}}^{-1} \left(1 + \sum_i k_{a_i} k_{\partial_i}^{-1} C_i \right)^{-1},$$

where K_d is the rate constant of the aquation of the i-th form of the complex reacting on the sorbent surface; k_{a_x}, k_{∂_x}, k_{a_i}, κ_{∂_i} are the rate constants of the adsorption and of the desorption of the reacting and of any other i form of the sorbate complex present in solution; C is the concentration of the forms; C_{M} is the total concentration of the complex-forming metal.

The rate of aquation, characterised by K_x, is several orders of magnitude greater than the rate of aquation of the sorbate complex in solution,[55] which also produces sparingly soluble uncharged hydroxo forms. Heterogeneous hydrolysis shows a similarity to the processes described in various papers,[37–54] since it includes stages of adsorption and of chemical reaction of the sorbed substances, but it differs from them in the high rate of the second stage and in the fact that the sorbate is not held on the sorbent surface in the form of the initial component. The model is effective, realistic, and comprehensive for the platinum metal group, and it has a predictive value in conjunction with quantitative data on the stability and the lability of the complex sorbates and on the basic properties of the sorbent.[55]

Data[55,58,72,75] on the pseudoequilibrium properties of the heterogeneous hydrolysis and on the interactions of the sorbents with the supporting electrolytes show that the strongly basic OH groups of the sorbent take part in the heterogeneous hydrolysis reactions, and that the presence and concentration of these groups are determined by the pH^0 value of the sorbent.

The weakness of the model lies in the impossibility of mathematically relating the rate of the process to the concentration of the basic centres of the sorbent furthermore the rate of the process cannot be calculated theoretically, since the calculation would require a knowledge of the stability constants and of the rates of aquation of the sorbate complexes, of the acid–base equilibria of the OH groups on the sorbent surface, of the rates of protolysis of the aquo forms of the sorbate in the sorbent phase, of the rate of the phase transformations of the sorbent, and of all the activity coefficients. Most of these quantities are unknown, and furthermore the form of the mathematical equations linking them to the rate is also unknown. The model also offers no information on the character of the bond between the sorbate and the sorbent during the intermediate and the final stages of the process, when the assumption of a combination of van der Waals and electrostatic bonds is not incompatible with observations.

IV. Interrelation between the properties of the sorbate, of the sorbent, and of the ionic medium and the sorption mechanism

In his analysis of the status of research on sorption by inorganic compounds and of coprecipitation Melikhov[9] observed that very little published information is available on the relationship between the sorption and the states of the surface region of the sorbent and of the sorbate in this region and (we add) in the solvent, and that insufficient attention is being paid to this problem. Workers in the eastern stream are specially prone to ignore the interrelation of three aspects of the sorption process: the structure formation in the sorbents (in our case, the oxide hydroxides), their surface properties (which depend directly on the previous aspect), and the sorption itself. On the other hand, as was shown by Khvostova and Pichugina[163] (for the platinum metals, though their conclusions apply also to other metals), the real composition, i.e. the nature and the relative amounts of the complex forms in solution, determine the degree of removal of an element by extraction, electrode position, cementation, etc., and obviously also by sorption. The addition of any other reagent, including the solvent, produces a shift of the equilibrium aquation, hydrolysis, and of other reactions (substitution, polymerisation, complexation of the ions, etc.) in the solution, and thus affects the sorption process to the extent of inducing a change in the mechanism.[37–75] However, this obvious consideration is often ignored, and in many cases even the initial complex forms of the sorbed element are not established.[15,25,27,28]

Let us now examine the few disconnected data on this topic and establish possible interrelationships between the three aspects of the sorption process defined above.

The following propositions can be considered to be established beyond dispute. I. Crystalline oxides (and oxide hydroxides) have a much lower sorption activity than their corresponding amorphous phases; their capacity is lower,[55,72,78,82–84,99,106,156] their kinetics are more sluggish,[60,65,77–80] and their selectivity is lower, i.e. they have sorption isotherms of the Langmuir or Freundlich type instead of "high affinity" isotherms.[72,106,116,117,156] 2. The presence of ligands in the solution, and their nature, have a strong influence on the magnitude and on the kinetics of the sorption;[22,23,25,47–49,55,77,87,164] metal ions bound in complexes are much less sorbable than unbound ions. 3. Ions in the sorbed state undergo chemical reactions, especially hydrolysis, much more readily than free ions in solution.[55,101–106,115–118] 4. The supporting electrolyte interacts with the sorbent[73–75,90–92] (see also Table 1) and with the sorbate,[55] strongly influencing both the kinetic and the (pseudo)equilibrium characteristics of the sorption process.

We shall consider, as a specific example of the establishment of interrelations between the properties of the sorbate, of the sorbent, and of the ionic medium and the sorption mechanism, a group of papers on the sorption of complex anions of the platinum metals on the oxide hydroxides of titanium(IV) and zirconium(IV),[37–50] on ferrogels, and on the oxide hydroxides of the REE.[55–75] These studies are specially suitable for our analysis because they include kinetic data, which allow various effects of the properties of the components to be displayed though they remain constant during equilibrium measurements.

The analysis of these studies[37–50,55–75] shows first of all that at least two stages are needed for the sorption process; the adsorption stage itself and a preliminary chemical interaction of the sorbate with H_2O, the supporting electrolyte, and the sorbent surface. The composition of the sorption complex and the rate of transformation of the sorbate in the sorbent phase depend on the nature of the sorbate and of the sorbent, but the participation of the ionic medium is very substantial in both cases. In the first stage this effect is seen as a competing interraction between the sorbate and the background ions, which lowers the extent of sorption (say) of the complex anions when the concentration of NaCl or of Na_2SO_4 is increased.[37–50] In the second stage the effect is seen in the form of the interaction of the supporting ions with the sorbate and the sorbent, as shown most clearly by the dependence of the rate of heterogeneous hydrolysis on the concentration of the ligand in solution and by the change in the sorption properties of the REE oxide hydroxides and of the ferrogels[55–75] under the influence of the ionic medium.

Obviously, the slow changes in the chloro complexes sorbed on the surface of the titanium(IV) and zirconium(IV) oxides[37–47] bear some similarity to heterogeneous hydrolysis, but the rates of these reactions are so small that the authors[37–47,50] could not detect the complete detachment of the ligands. This process can be represented as the second stage of the heterogeneous hydrolysis infinitely stretched out in time, whereas the sorption of the complexes on the surface of the titanium(IV) and zirconium(IV) oxide hydroxide surfaces is interpreted as the fixed first stage of the proposed[55] three-stage mechanism of heterogeneous hydrolysis. The difference in mechanism between the first[37–50] and the second group of studies[55–75] is due to a difference in the characteristic properties of the sorbent surface: its size and its energy nonuniformity, but the property of the sorbent mainly responsible for the change from the ion exchange to the heterogeneous hydrolysis mechanism is probably its basicity.[55]

The basicity of the sorbents has been characterised[55] by the pH^0 values, which are well correlated with other quantities determined by the basicity (the Cartledge ionic potential and the pH of the saturated solutions of hydroxides, calculated from the solubility products,[165] Fig. 2). This allows us to compare oxide hydroxides of different structure groups, arbitrarily assuming them to have equal basicities. The correlation can also be made in terms of data obtained[166] by characterising the acid–base properties of oxides through the heats and the isotherms of the sorption of NH_3 and CO_2 from the gas phase. According to that work[166] the basicity of the oxides increases in the series

$$BeO, TiO_2, ZrO_2, Nb_2O_5, Ga_2O_3 < ThO_2,$$

$$MgO, ZnO, Al_2O_3 << CaO, Nd_2O_3, La_2O_3,$$

whereas by using the Table 1 we obtain

$Al_2O_3, TiO_2,$

$ZrO_2 < \alpha\text{-}Cr_2O_3 < Fe_3O_4 < CeO_2 < Yb_2O_3 < Sm_2O_3 < ThO_2.$

The two sequences are satisfactorily consistent.

It is also clear that pH^0 is strongly dependent on the method of preparation of the oxide hydroxide. According to the pH^0 values (see Table 1) the bulk (or surface) positive charge of the metal oxide hydroxides produced at the contact with aqueous solutions of electrolytes decreases in the sequence

Fe^{3+} hydrogels (with $pH_{bas} > 8-9$)$Ln_2O_3.nH_2O > Cr_2O_3 > Al_2O_3 >$

$>$ FeOOH(goethite, akaganeite, lepidocrocite) $> ZrO_2 > TiO_2$.

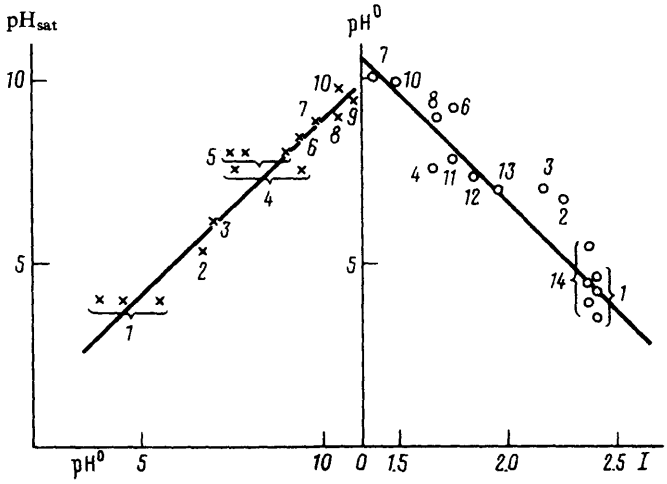


Figure 2. Correlation between pH^0, the ionic potential *i*, and the pH of a saturated solution of oxide hydroxides:[55] *1*, $TiO(OH)_2$; *2*, $ZrO(OH)_2$; *3*, $Cr(OH)_3$; *4*, $Cu(OH)_2$; *5*, $Y(OH)_3$; *6*, $Zn(OH)_2$; *7*, $Pb(OH)_2$; *8*, $La(OH)_3$; *9*, $Ni(OH)_2$; *10*, $Cd(OH)_2$; *11*, $Sn_2O_3.nH_2O$; *12*, $Y_2O_3.nH_2O$; *13*, $Yb_2O_3.nH_2O$; *14*, $Sn(OH)_4$.

The easy replacement of sorbed complex anions by simple anions (for example, SO_4^{2-}) [37–48] is characteristic of nonspecific, electrostatic bonds (see Section III). The strength of the electrostatic bond to a protonated oxide hydroxide surface is determined by the density of surface charge. At low surface charges the electrostatically bound sorbed groups experience negligibly small interactions from the weakly electrophilic sorbent surface (TiO_2, ZrO_2), and therefore the rate and the extent of transformation of the sorbed complex ions on the crystalline oxide hydroxides of Ti, Zr, Sn, and Fe are small, the sorption is reversible,[37–50] and these sorbents are not suitable for removing metals (typical complex formers) from media containing complexing salts.

As the density of surface charge and the basicity of the surface are increased the ratio of the rates of the adsorption stage and of the transformation of the sorbate in the sorbent phase is altered: though the rates of adsorption and desorption remain high, the rate of the second stage increases. Thus, in the hydration and protonation of the dry REE oxides the surface becomes saturated with basic hydroxyl groups which are not removed from the surface into the bulk of the solution when the acid content of the system is limited. Therefore the matrix of the Ln_2O_3 oxide has a decreased affinity for electrons and for hydroxyl groups, even when the surface has a positive charge. This nucleophilicity weakens the metal–anionic ligand bonds in the sorbed complex, and facilitates its transformations (aquation, in the case of heterogeneous hydrolysis). The ferrogels and the carbonates of the alkaline-earth metals show a similar behaviour.[55]

Thus the basicity of the oxide hydroxide sorbent determines the sorption mechanism and the changes in basicity define the boundary between "ion exchange" and heterogeneous hydrolysis. These considerations are convincingly confirmed by the observation that lowering the basicity of a ferrogel by removing the excess of OH groups during cryogranulation while retaining its large specific surface and amorphous structure alters the character of the sorption process and converts the heterogeneous hydrolysis into "ion exchange".[55]

By using the pH^0 as a characteristic of the basicity of the oxide hydroxide, the stability constants of the complex sorbate, and data on the interaction of the ionic medium with the sorbate and the sorbent we have formulated the group of principles which should guide the choice of conditions for the sorption extraction of complex-forming metals from complex-forming media.[55]

1. The complete sorptional removal of complex-forming metals form complex-forming media containing high concentrations of electrolytes without changing the composition of the solution is possible only under conditions of fast and exhaustive transformations of the sorbate in the sorbent phase.

2. The process which ensures this condition is heterogeneous hydrolysis.

3. Metals can be effectively precipitated from complex-forming media by heterogeneous hydrolysis if the stability constant of the complex does not exceed $10^{38}-10^{40}$; the process is completed in practically convenient times if the half-life of the ligand in the sorbate complex is less than 2–3 days at temperatures between 20 and 100 °C.

4. Sorbents suitable for heterogeneous hydrolysis in salt media include the crystalline (or gel) oxide hydroxides with $pH^0 \geqslant 6.5$ [i.e. the oxide hydroxides and the carbonates of Cu(II), Ni(II), Cd, Pb(II), Zn, etc.].

5. To remove metals which form labile but stable complexes in the presence of high concentrations of ligand we must use neutral or weakly alkaline gel sorbents; for systems with low concentrations of ligand and (or) inert complexes in salt media the most effective sorbents are crystalline oxide hydroxides of the Ln_2O_3 type.

V. Conclusions

The great majority of studies of sorption on oxide hydroxides deals with sorption equilibria (or pseudoequilibria): little attention has been paid to its kinetics, in spite of the reported observation[106] of very strong energy nonuniformity of the sorbent surface. Fairly simple cases of sorption of aquo cations and acid anions are usually considered; the mathematical description of the sorption is very complex, and is based on many more or less arbitrary assumptions. The treatment of the results often reduces to the traditional models of Langmuir sorption and ion exchange. Most of the publications are aimed primarily at the behaviour of either the sorbent or the

sorbate. Sorption experiments are carried out either in the absence of an ionic background or in solutions of electrolytes indifferent to the sorbate. Crystalline phases are predominant among the sorbents. Studies of the EDL do not resolve the contradiction in the effects of pH_s on the sorption process. There is no information on the effect of interactions of the electrolyte with oxide hydroxide gels on the sorption properties of the latter (except the ferrogels[55]), and very little has been published on the composition and distribution of the sorption products on the sorbent surfaces, on the changes in structure and properties of the sorbent during the sorption, and on the effect of the temperature, composition, and concentration of the ionic medium on the rate and the mechanism of the sorption process. Very diverse partial models of the sorption mechanism have been put forward. We are therefore unable to formulate the general principles to be followed in the selection of practical sorption conditions and to propose a comprehensive predictive model.

Unfortunately, work based on the so-called equilibrium measurements of sorption during coprecipitation contains little information and is non-predictive because the coprecipitation with metal oxide hydroxides [usually of Fe(III), Ti(IV), Zn(IV), Sn(IV), Al(III), etc.] usually produces gel-like deposits with a very high sorption capacity (the corresponding crystalline phases have a much lower activity[72,75,78,79]). Flynn[6] has stressed that gel phases are nonequilibrium systems containing an excess of free energy. Therefore equilibrium measurements during coprecipitation are, in reality, nonequilibrium measurements, and in the case of complex sorbates they depart from equilibrium in respect of both the sorbent and the sorbate. These data are points on a kinetic curve of very long duration. An important contribution to the understanding of the behaviour of these sytems was made by Egorov,[2] but unfortunately his book has not received the attention which it deserved. Only by combining data on the phase formation in gels, which are plentifully available,[3–8,141,142] with data on the interactions between gels and electrolytes, of which very few are available at present, will a convincing explanation be found for the results of a large group of investigations.[10–30,86,87,101,103]

Concerning the potential application of sorptional extraction in practice we note that the prejudice of many workers in favour of crystalline granulated oxide hydroxide sorbents (in preference to gel sorbents) is based on the widespread belief that the former are more convenient and can be use repeatedly (see, for example, Simanova and Boichinova[50]), whereas the latter cannot, and also on considerations of cost and ecological effects. Both arguments are largely misconceptions. As regards convenience, one thinks of the use of sorbents in columns in automated industrial processes, ignoring the stringent requirements of stable dynamic regimes and absence of impurities in the solution, which do not apply to the use of gel-like sorbents in a static regime. The gel sorbents can be used with simpler apparatus. As regards cost and ecological considerations we should consider the whole cycle of operations involved in the synthesis of granulated oxide hydroxides; precipitation from a salt solution, washing formation, drying, and heat treatment. Though the cost of this overall process is lower than the cost of synthesising organic sorbents (resins) it is quite considerable. The volume of water needed to wash the precipitated gel should also be compared with the volume of water which can be purified by the sorbent thus produced. The synthesis of the gel sorbents includes only the first (or the first and second) stage of this synthetic cycle. In view of the much higher sorption activity of the gels we recommend their use in many practical applications.

The capacity and the selectivity of a sorbent do not vary in the same sense; repeated use of the sorbent assumes a stable structure and stable properties. A careful analysis shows that these advantages of the sorbents always occur in pairs, i.e. two of them exclude the third. But are all three always required?

The following situations are met in practical cases of sorptional concentration.

1. The extraction (recovery) of a valuable microcomponent from a very large volume of solution (for example, gold from sea water). This requires stability of the sorption properties and a high capacity, whereas the selectivity (extent of removal) is less important since the process is repeated until the sorbent is saturated. In this case the granulated sorbent is definitely preferable.

2. The intensive purification of large volumes of very dilute solutions from trace impurities (for example, the purification of drinking water from heavy metals). Here selectivity is important, a high capacity is desirable, but the possibility of repeated use is less important. A gel sorbent could be preferred.

3. The extraction (recovery) of valuable microcomponents from small volumes of solutions, usually technological and containing high concentrations of electrolytes (for example, platinum metals from electrochemical production solutions) in order to minimise the loss of valuable materials in the technological cycle. In this case selectivity is important; the use of the total capacity and the repeated use of the sorbent are effectively excluded. A gel sorbent is preferred.

4. The concentration of trace components in analytical chemistry: in this case selectivity is the only requirement.

We should also note that in the second and the third case the kinetics of the sorption are very important, whereas in the first and the fourth case they are of secondary importance.

Thus the crystalline, granular, and gel sorbents all have a place in the practical exploitation of the method, but for different purposes.

This analysis of published data on sorption on oxide hydroxides has identified the main gaps in this area and has shown the need to fill these gaps, to systematise experimental facts more fully, and to unify the procedures and the terminology used in the research. The range of materials under study must be expanded further, and relationships between the properties of the sorbates and of the sorbents and between the sorption mechanism and the prospects of practical application of the sorption methods of concentrating components must be established.

References

1. D E Shanks, E Y Noble, A M Pierzschala, D I Bauer *Rept. Invest. Bur. Mines, US Dep. Inter.*, 1983, (8816)
2. Yu V Egorov *Statika Sorbtsii Mikrokomponentov Oksigidratatsii* (Statics of the Sorption of the Microcomponents of Oxyhydration), Atomizdat, Moscow, 1975, 189 pp.
3. E Matijevic, P Schleiner *J. Colloid Interface Sci.*, 1978, **63** 509
4. N C Datta *J. Sci. Ind. Res.*, 1981, **40** 571
5. W Schneider *Comments Inorg. Chem.*, 1984, **3** 205
6. C M Flynn *Chem. Rev.*, 1984, **84** 31
7. W Schneider *Chimia*, 1988, **42** 9
8. M A Blesa, E Matijevic *Adv. Colloid Interface Sci.*, 1989, **29** 173

9. I V Melikhov, D G Berdonosova, M A Prokof'eva, et al. *Logika Razvitiya i Naukometricheskii Analiz* (Logic of Development and Information-measuring Analysis), Izd. Moskov. Univ., 1976, 70 pp
10. V I Plotnikov, Thesis, Alma-Ata, 1972, 238 pp.
11. V I Plotnikov, I I Safonov *Radiokhimiya*, 1983, **25** 161
12. V I Plotnikov, V P Novikov *Zh. Anal. Khim.*, 1977, **32** 633
13. V L Kochetkov, V I Plotnikov *Desyatoe Vsesoyuznoe Soveshchanie po Khimii, Analizu, i Tekhnologii Blagorodnykh Metallov. Tezisy Dokladov* (Abstracts of Papers Presented to the Tenth All-Union Conference on the Chemistry, Analysis, and Technology of Noble Metals), Novosibirsk, 1976, Vol. 2, p. 215
14. V L Kochetkov, A G Sarmurzina, V I Plotnikov *Khimiya i Khimicheskaya Tekhnologiya* (Chemistry and Chemical Technology), Izd. Kaz. Univ., Alma-Ata, 1978, p. 222
15. V L Kochetkov, V I Plotnikov, T I Taurbaeva *Radiokhimiya*, 1985, **27** 257
16. A I Novikov *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1965, **11**(3) 64
17. A I Novikov *Soosazhdenie s Gidratirovannymi Oksidami* (Coprecipitation with Hydrated Oxides), Izd. Tadzh. Univ., Dushanbe, 1972, p. 5
18. A I Novikov, N A Knyazev *Soosazhdenie s Gidroxsidami* (Coprecipitation with Hydroxides), Izd. Tadzh. Univ., Dushanbe, 1977, p. 5
19. A I Novikov, L A Egorova, G Oak *Soosazhdenie s Gidroxsidami* (Coprecipation with Hydroxides), Izd. Tadzh. Univ., Dushanbe, 1977, p. 62
20. A I Novikov, A Rakhmonberd'iev *Soosazhdenie s Gidroxsidami* (Coprecipitation with Hydroxides), Izd. Tadzh. Univ., Dushanbe, 1977, p. 28
21. A I Novikov V I Ruzankin *Radiokhimiya*, 1973, **15** 641
22. B O Khamidov, Kh Akhmedov, A I Novikov *Zh. Anal. Khim.*, 1975, **30** 822
23. A I Novikov, B O Khamidov, Kh Akhmedov *Zh. Anal. Khim.*, 1974, **29** 2442
24. S Rustamov, A I Novikov, Sh Davlyatov *Soosazhdenie s Gidratirovannymi Oksidami* (Coprecipiation with Hydrated Oxides), Izd. Tadzh. Univ., Dushanbe, 1972, p. 186
25. S Rustamov *Dep. TadzhNIINTI* 03.12.85, No.49-Ta, Dushanbe, 1985, 22 pp
26. A I Novikov, S Rustamov *Zh. Neorg. Khim.*, 1971, **13**(1) 134 [English translation in *Russ. J. Inorg. Chem.*, 1971(1)]
27. G M Varshal, G I Malofeeva, L S Shulik *Zh. Anal. Khim.*, 1977, **32** 44
28. V Sh Barkan, T N Greiver *Zh. Neorg. Khim.*, 1977, **22**(8) 2197 [English translation in *Russ. J. Inorg. Chem.*, 1977(8)]
29. P I Artyukhin *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1981, **12**(5) 23
30. P I Artyukhin *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1982, **1** 53
31. A I Novikov, V F Samoilova *Radiokhimiya*, 1989, **31**(1) 72
32. F A Belinskaya *Ionnyi Obmen i Ionometriya* (Ion Exchange and Ionomery), Izd. Leningrad. Univ., No. 6, 1988, p. 17
33. V V Strelko, V N Belyakov, A I Bortun, S A Khainakov *Zh. Fiz. Khim.*, 1990, **64**(2) 408 [English translation in *Russ. J. Phys. Chem.*, 1990(2)]
34. T S Sokolova, V V Vol'khin, E A Shul'ga, G A Starkova *Izv. Vyssh. Uchebn. Zaved, Tsvetnaya Metallurgiya*, 1989, (3) 35
35. A N Sunin, T A Zharova *Dept. ONIITEKhIM, Cherkassy*, 05.04.89, No. 353-KhP89
36. D Yu Maiorov, A A Blokhin V P Taushkanov, et al. *Khimiya i Tekhnologiya Redkikh i Rasseyannykh Elementov* (Chemistry and Technology of the Rare and Trace Elements), Leningrad, 1989, p. 164
37. L I Evdokimova, E S Boichinova, Yu N Kukushkin, et al. *Zh. Prikl. Khim.*, 1979, **52** 1479
38. L I Evdokimova, E S Boichinova, S A Simanova *Zh. Prikl. Khim.*, 1981, **54** 1292
39. E S Boichinova, N Ya Kryukova, S A Simanov *Zh. Prikl. Khim.*, 1981, **54** 1694
40. M M Kolosova, S A Simanova, E S Boichinova *Zh. Prikl. Khim.*, 1983, **56** 1159
41. M M Kolosova, S A Simanova, E S Boichinova *Zh. Prikl. Khim.*, 1985, **58** 67
42. L V Nikol'skaya, N Ya Kryuchkova, E S Boichinova *Zh. Prikl. Khim.*, 1984, **57** 1498
43. L V Nikol'skaya, N Ya Kryuchkova, E S Boichinova *Zh. Prikl. Khim.*, 1986, **59** 979
44. L V Nikol'skaya, E S Boichinova, S A Simanova *Zh. Prikl. Khim.*, 1985, **58** 1448
45. L V Nikol'skaya, E S Boichinova, S A Simanova *Zh. Prikl. Khim.*, 1986, **59** 949
46. L V Nikol'skaya, E S Boichinova, S A Simanova *Zh. Prikl. Khim.*, 1987, **60** 735
47. N V Abovskaya, E S Boichinova, S A Simanova, V N Pak *Zh. Prikl. Khim.*, 1986, **59** 278
48. N V Abovskaya, E S Boichinoa, S A Simanoa, V N Pak *Zh. Prikl. Khim.*, 1988, **61** 747, 2220
49. N V Abovskaya, S A Simanova, E S Boichinoa, V I Bashmakov *Zh. Prikl. Khim.*, 1989, **62** 298
50. S A Simanov, E S Boichinoa *Ionnyi Obmen i Ionometriya* (Ion Exchange and Ionometry), Izd. Leningrad. Univ., No. 6, 1988, p. 3
51. L S Kravchuk, T V Kharlashina, S V Markevich, V N Anan'in *Izv. Akad. Nauk BelorussSSR, Ser. Khim. Nauk*, 1978, (5) 51
52. L S Kravchuk, A S Kozlov, S V Sinyakova, T V Yankova *Zh. Fiz. Khim.*, 1983, **57**(11) 2794 [English translation in *Russ. J. Phys. Chem.*, 1983(11)]
53. J P Brunelle, A Sugier *Compt. Rend., C*, 1973, **276** 1545
54. E Santacesaria, S Carra, J Adami *Ind. Eng. Chem. Prod. Res. Dev.*, 1977, **16** 41
55. S I Pechenyuk, Thesis, Apatity, 1989, 415 pp.
56. S I Pechenyuk *Zh. Neorg. Khim.*, 1979, **24**(2) 437 [English translation in *Russ. J. Inorg. Chem.*, 1979(2)]
57. S I Pechenyuk *Issledovaniya v Oblasti Khimii i Tekhnologii Mineral'nogo Syr'ya Kol'skogo Poluostrova* (Studies of the Chemistry and Technology of the Mineral Deposits of the Kola Peninsula), Nauka, Leningrad, 1986, p. 3
58. S I Pechenyuk *Zh. Fiz. Khim.*, 1989, **63**(9) 2155 [English translation in *Russ. J. Phys. Chem.*, 1989(9)]
59. S I Pechenyuk, L F Kuz'mich, Z S Klemenkova, B V Lokshin *Dep. VINITI* 23.03.1988, No. 2235, Apatity, 1988 24 pp.
60. S I Pechenyuk, A G Kasikov, L F Kuz'mich *Zh. Prikl. Khim.*, 1984 **57** 748
61. S I Pechenyuk *Zh. Prikl. Khim.*, 1981, **54** 1712
62. S I Pechenyuk *Zh. Prikl. Khim.*, 1982, **55** 751
63. S I Pechenyuk, A G Kasikov, E S Boichinova *Zh. Prikl. Khim.*, 1989, **62** 309, 315

64. S I Pechenyuk *Dep. VINITI* 03.06.1981, No. 2653, Apatity, 1981, 13 pp
65. S I Pechenyuk, L F Kuz'mich *Zh. Prikl. Khim.*, 1986, **59** 764
66. S I Pechenyuk *Koord. Khim.*, 1989, **15** 673
67. S I Pechenyuk *Issledovaniya po Fiziko-khimicheskim Osnovam Tekhnologii Pererabotki Mineral'nogo Syr'ya* (Studies of the Physicochemical Foundations of the Processing of Mineral Raw Materials), Nauka, Leningrad, 1983, p. 38
68. S I Pechenyuk *Dep. VINITI* 03.02.1983, No. 612, Apatity, 1983, 17 pp
69. S I Pechenyuk, A G Kasikov, L F Kuz'mich *Zh. Prikl. Khim.*, 1986, **59** 32
70. S I Pechenyuk, L F Kuz'mich *Fiziko-khimicheskie Issledovaniya Redkikh Elementov i Protsessy Ikh Vydeleniya iz Redkometal'nogo Syr'ya* (Physicochemical Studies of the Rare Elements and Processes for their Extraction from Rare-metal Minerals), Kol'sk. Filial Akad. Nauk SSSR, Apatity, 1980, p. 55
71. S I Pechenyuk *Problemy Sovremennoi Khimii Koordinatsionnykh Soedinenii* (Problems in Modern Coodination Compound Chemistry), Izd. Leningrad. Univ., 1989, p. 81
72. S I Pechenyuk, L F Kuz'mich, E V Kalinkina *Zh. Neorg. Khim.*, 1990, **35** (6) 1409 [English translation in *Russ. J. Inorg. Chem.*, 1990(6)]
73. S I Pechenyuk *Zh. Fiz. Khim.*, 1987, **61**(1) 165 [English translation in *Russ. J. Phys. Chem.*, 1987(10)]
74. S I Pechenyuk, L F Kuz'mich, E V Kalinkina *Khimiko-tekhnologicheskie Issledovaniya Syr'ya Kol'skogo Poluostrova* (Chemical and Technological Study of the Kola Peninsula Raw Materials), Nauka, Leningrad, 1987, p. 79
75. S I Pechenyuk, E V Kalinkina *Kolloidn. Zh.*, 1990, **52** 716
76. *Adsorption from Solutions on Solid Surfaces* (Translated into Russian), Mir, Moscow, 1986, 488 pp
77. K A Bol'shakov, V V Borisov, S E Godzhiev, N M Sinitsyn *Zh. Neorg. Khim.*, 1981, **26**(9) 2515 [English translation in *Russ. J. Inorg. Chem.*, 1981(9)]
78. K A Bol'shakov, N M Sinitsyn, V V Borisov, S E Godzhiev *Dep. ONIITEKhIM*, Cherkassy, 05.10.1981, No. 9088P
79. K A Bol'shakov, N M Sinitsyn, V V Borisov, et al. *Zh. Neorg. Khim.*, 1985, **30**(8) 2065 [English translation in *Russ. J. Inorg. Chem.*, 1985(8)]
80. N M Sinitsyn, S E Godzhiev, A A Delektorskii, Yu V Blagodatin *Zh. Neorg. Khim.*, 1985, **30**(8) 2069 [English translation in *Russ. J. Inorg. Chem.*, 1985(8)]
81. S E Godzhiev, Yu V Blagodatin, A V Ryabtsev, et al. *Trinadtsatoe Vsesoyuznoe Soveshchanie po Khimii, Analizu, i Tekhnologii Platinovykh Metallov. Tezisy Dokladov* (Abstracts of Papers Presented to the Thirteenth All-Union Conference on the Chemistry, Analysis, and Technology of the Platinum Metals), Sverdlovsk, 1986, Vol. 1, p. 174
82. E A Nechaev, G V Zvonareva *Kolloidn. Zh.*, 1983, **45** 908
83. E A Nechaev, N V Nikolenko *Kolloidn. Zh.*, 1986, **48** 1196
84. E A Nechaev, N V Nikolenko *Izv. Vyssh. Uchebn. Zaved., Ser. Khim. i Khim. Tekhnol.*, 1987, **30** 89
85. N V Nikolenko, Thesis, 1987, 15 pp
86. C S Brooks *Proc. and Eng. Found. Conf. Adsorpt. Santa Barbara,* California, New York, 1987, p. 109
87. J Sipalo-Zuljevic, R H H Wolf *Mikrochim. Acta*, 1973, **2** 315
88. B B Damaskin, O A Petrii *Vvedenie v Elektrokhimicheskuyu Kinetiku* (Introduction to Electrochemical Kinetics), Vysshaya Shkola, Moscow, 1982, 400 pp
89. G A Parks, P L de Bruyn *J. Phys. Chem.*, 1962, **66** 967
90. S M Ahmed *Can. J. Chem.*, 1966, **44** 1663
91. S M Ahmed, D Maksimov *Can. J. Chem.*, 1968, **46** 3841
92. A Breeuwsma, J Lyklema *J. Colloid. Interface Sci.*, 1973, **43** 437
93. G A Parks *Chem. Rev.*, 1965, **65** 177
94. N H G Penner, L K Koopal, J Lyklema *Colloids and Surfaces*, 1986, **21** 457
95. R H Joon, F Salman, G Donnay *J. Colloid Interface Sci.*, 1979, **70** 483
96. S Ardizzone, A Daghetti, L Franceschi, S Trassatti *Colloids and Surfaces*, 1989, **35** 85
97. H Watanabe, J Seto *Bull. Chem. Soc. Jpn*, 1986, **59** 2683
98. R Paterson, H Rahman *J. Colloid Interface Sci.*, 1984, **97** 423
99. M Sasaki, M Morlya, T Yasunaga, K D Astumian *J. Phys. Chem.*, 1983, **87** 1449
100. F J Hingston, P J Atkinson, A M Posner, J P Quirk *Nature (London)*, 1967, **215** 1459
101. S Music, M Gessner, R H H Wolf *Radiochim. Acta*, 1974, **26** 51
102. J A Davis, O A Leckie *J. Colloid Interface Sci.*, 1987, **67** 90
103. S Music, M Gessner, R H H Wolf *J. Radioanal. Nucl. Chem.*, 1979, **50** 91
104. E A Forbes, A M Posner, I P Quirk *J. Soil. Sci.*, 1976, **27** 154
105. M M Benjamin, J O Leckie *J. Colloid Interface Sci.*, 1981, **79** 209
106. D A Dzombak, F M M Morel *J. Colloid. Interface Sci.*, 1986, **112** 588
107. R Paterson, H Rahman *J. Colloid. Interface Sci.*, 1983, **94** 60
108. D E Jates, T W healy *J. Colloid. Interface Sci.*, 1975, **52** 222
109. J C Ryden, I R McLaughlin, J R Syers *J. Soil Sci.*, 1977, **28** 72
110. L Lyklema *Environ. Sci. Technol.*, 1980, **14** 537
111. S H Crosby, G A Millward, E J Butler, et al. *Estuarine, Coastal and Shelf Sci.*, 1984, **19** 257
112. P J Atkinson, A M Posner, J P Quirk *J. Phys. Chem.*, 1967, **71** 550
113. K M Parida *Adsorpt. Sci. Technol.*, 1987, **3**(2) 89
114. E Tipping *Geochim. Cosmochim. Acta*, 1981, **45** 191
115. S Ardizzone, L Formaro *Ann. Chim. (Ital.)*, 1987, **77** 463
116. P H Tewari, A B Campbell, J Lee Woon *Can. J. Chem.*, 1972, **50** 1642
117. C L Wu, M N Jang, C C Liu *Radiochim. Acta*, 1983, **33** 57
118. D T Harvey, J E Fulgham, R W Linton *J. Colloid. Interface Sci.*, 1983, **94** 276
119. S K Milonijc, M M Kopecni, Z E Iric *J. Radioanal. Nucl. Chem.*, 1983, **78** 15
120. W H van Riemsdijk, J C M de Wit, L K Koopal, G H Bolt *J. Colloid. Interface Sci.*, 1987, **116** 511
121. R E Khaimina, B S Balapanova *Tr. Akad. Nauk KazSSR, Inst. Khim. Nauk*, 1981, **54** 90
122. F R Mirzayan, V A Urikh *Izv. Akad. Nauk KazSSR, Ser. Khim.*, 1982, (2) 16
123. H S Mahal, K S Vemkateswarlu *Indian J. Chem., Sect. A*, 1978, **16** 712
124. L G J Fokkink, A de Keizer, J Lyklema *J. Colloid. Interface Sci.*, 1989, **127** 116
125. J S Kim, H Zeitlin *anal. Chem. Acta*, 1969, **46** 1
126. T Hiemstra, J C M de Wit, W H van Riemsdijk *J. Colloid. Interface Sci.*, 1989, **133** 105
127. R Paterson, H Rahman *J. Colloid. Interface Sci.*, 1983, **94** 60
128. R Paterson, H Rahman *J. Colloid. Interface Sci.*, 1984, **98** 494

129. H S Mahal, B Venkataramani, K S Wenkateswarlu *J. Inorg. Nucl. Chem.*, 1981, **43** 3335
130. F Inoue, H Yamasaki *Bull. Chem. Soc. Jpn.*, 1987, **60** 891
131. W Janucz *J. Radioanal. Nucl. Chem.*, 1988, **125** 393
132. E Yu Chardymskaya, M P Sidorova, O V Semenova, V E Shubin *Kolloidn. Zh.*, 1990, **32** 547
133. K S Akratopulu, L Vordonis, A Lycourghiotis *J. Chem. Soc. Faraday Trans.*, 1986, **82** 3697
134. R Vigano, J Taraszewski, A Dagnetti, S Trassatti *Colloids and Surfaces*, 1989, **35** 85
135. M M Blesa, N M Figliolia, A J G Maroto, A E Regazzoni *J. Colloid Interface Sci.*, 1989, **101** 410
136. J A Mieth, J A Schwarz, Y-J Huang, S C Fang *J. Catal.*, 1990, **122** 202
137. S Subramanian, J S Noh, J A Schwarz *J. Catal.*, 1988, **114** 433
138. P Mulvaney, V Swayambunathan, F Frieser, D Meisel *J. Phys. Chem.*, 1988, **92** 6732
139. N J Barrow, J W Bowden *J. Colloid. Interface Sci.*, 1987, **119** 236
140. J Dousma, P L de Bruyn *J. Colloid. Interface Sci.*, 1976, **56** 527
141. A N Christensen, P Convert, M S Lehmann *Acta Chem. Scand., Ser. A*, 1980, **34** 777
142. A N Christensen, M S Lehman, A Wright *Acta Chem. Scand., Ser. A*, 1983, **37** 63
143. B Venkataramani, A R Gupta *Indian J. Chem., A*, 1988, **27** 290
144. J Carrizosa, J A Odriozola, J M Trillo *Inorg. Chim. Acta*, 1984, **94** 114
145. R Alvero, J A Odriozola, J M Trillo *J. Chem. Soc., Dalton Trans.*, 1984, 87
146. J W Perram *J. Chem. Soc., Faraday Trans.*, 1973, **69** 993
147. R Grauer, W Stumm *Colloid Polymer Sci.*, 1982, **260** 459
148. W Schindler *Osterreich Chem. Z.*, 1985, **86** 141
149. A Gupta, B Venkataramani *Bull. Chem. Soc. Jpn.*, 1988, **61** 1357
150. G Sposito *Chimiia*, 1989, **43** 169
151. Yu a Bulevich, A Yu Zubarev *Kolloidn. Zh.*, 1986, **48** 1119
152. T Hiemstra, W H van Riemsdijk, G H Bolt *J. Colloid Interface Sci.*, 1989, **133** 91
153. J Westall, H Hohl *Adv. Colloid Interface Sci.*, 1980, **12** 265
154. V V Rudin, I V Melikhov *Dept. VINITI* 25.0877, No. 3432
155. R N Spitz, J E Barton, M A Barteau, et al. *J. Phys. Chem.*, 1986, **90** 4067
156. B Venkataramani, K S Vemkateswarlu, J Shankar *J. Colloid Interface Sci.*, 1978, **67** 117
157. A K Mukherje *J. Indian Chem. Soc.*, 1983, **60** 659
158. Y Inoue, O Tochiyama, H Yamazaki, A Sakurada *J. Radioanal Nucl. Chem.*, 1988, **124** 361
159. C B Amphlett *Inorganic Ion Exchangers* (Translated into Russian), Mir, Moscow, 1966, 183 pp.
160. M Y Fuller *Chromatogr. Rev.*, 1971, **14** 45
161. A Ya Rozovskii *Geterogennye Khimicheskie Reaktsii. Kinetika i Makrokinetika* (Heterogeneous Chemical Reactions. Kinetics and Macrokinetics), Nauka, Moscow, 1980, 323 pp
162. S L Kiperman *Osnovy Khimicheskoi Kinetiki v Geterogennom katalize* (Fundamentals of Chemical Kinetics in Heterogeneous Catalysis), Khimiya, Moscow, 1979, 349 pp
163. V P Khvostova, G V Pichugina *Nauchnye Trudy Gosudarstvennogo Instituta Redkikh Metallov* (Scientific Reports of the State Rare Metals Instiute), Moscow, 1979, Vol. 30, p. 109
164. G Micera, C Gessa, P Melis, et al. *Colloids and Surfaces*, 1986, **17** 389
165. D Dobos *Electrochemical Tables* (Translated into Russian), Mir, Moscow, 1980, 365 pp
166. A Auroux, A Gervasini *J. Phys. Chem.*, 1990, **94** 6371

Translated from *Uspekhi Khimii* **61** 734–764 (1992) U.D.C. 541.138

Electrochemistry of transition metal single crystals with well defined surfaces

G V Khaldeev, T A Syur
Gor'kii Perm' State University

ABSTRACT. The effect of extended defects of the surface of metallic single crystals on the electrochemical processes of dissolution and formation of a new phase has been analysed. Theoretical ideas on the rearrangement of a crystal surface (phase transitions of the second kind) during the adsorption of surface-active substances are presented. The reconstruction (faceting) of the surface under the influence of electrochemical processes and the adsorption of nucleophilic species (hydrogen, oxygen, halogen ions) from the gas phase and from electrolytes on a well defined metal single crystal surface have been evaluated.

The bibliography contains 94 references.

Contents

I. Introduction 399
II. Surface defects. The discrete metal lattice model 399
III. Orientation dependence of the dissolution of a metal during phase transitions of the first kind (corrosion, electrocrystallisation) 400
IV. Adsorption of chalcophilic particles and phase transitions of the second kind in the near-surface layers of monocrystals. 402
V. Reconstruction of monocrystal surfaces during the adsorption of hydrogen, oxygen, and halogens 404
VI. Conclusions 415

I. Introduction

Expermental studies of the electrochemistry of well defined metal single crystal surfaces have stimulated the development of new theoretical models. The use of methods having a local resolution better than 0.1 nm provides information on the reconstruction of near-surface layers of the crystal, which usually have a stepped structure with a range of surface-active centres.

The flat condenser model (the boundary between an infinite defect-free crystal and an isotropic liquid medium) does not give a strictly quantitative description of the mechanism of the electrochemical corrosion process. The metal surface (M) contains surface defects which create adsorption centres of various types and which have different energy levels. These centres generate fields associated with deformation displacements. The description of the discrete structure of the interface must allow for the formation of complex electrical double layers (EDL) on both the metal and the electrolyte side: electrons from the metal penetrate into the active part of the fixed EDL forming electron tails. The components of the electrolyte adsorbed on the metal experience the action of the electron tails; this produces long-range order in the film, which acquires a quasi-crystalline structure.[1]

In this review we shall examine recently published data on the effect of the reconstruction of the first few near-surface layers by the adsorption-chemical interaction with the electrolyte particles upon the conditions of formation of a new phase during an electrochemical process. Often the interaction on an M/electrolyte interface does not produce a phase transition of the first kind (corrosion) but is limited to a transition of the second kind which changes the short-range order of the hierarchical structures of the EDL both in the electrolyte and in the metal. Unfortunately only a few electrochemists have paid sufficient attention to the characterisation of the surface and to the analysis of changes in the structure of near-surface layers of monocrystalline samples. Our analysis of experimental information on crystal surfaces must therefore be limited to data for surfaces having reliably determined crystallographic characteristics.

II. Surface defects. The discrete metal lattice model

The first model to succeed the parallel plate condenser model was the "jelly" model, in which the near-surface layer consists of an ensemble of uniformly charged spherically symmetrical atoms. Each pair of atoms in the first near-surface layer was characterised by a defined binding energy E_b, decreasing with increasing distance (r_{ij}) between the atoms. Because of the periodicity of the structure of a metallic crystal the E_b values are crystallographically related, and periodic bond chains (PBC) can be delineated in the first near-surface layers.

According to the generally adopted Franck–Cabrera classification[2] solid surfaces are divided into singular, near-singular (vicinal), and non-singular (diffuse), usually called *F*, *S*, and *K* faces. The *F* faces are the surfaces parallel to the two PBC systems with the largest E_b. Atomically smooth singular surfaces coincide with the low-index crystallographic planes and have a different packing density S_{hkl} of the surface atoms. The atomically rough (slightly inclined to the *F* faces) vicinal *S* faces deviate by a small angle from the singular orientation and have a stepped structure (Table 1): the length *L* exceeds the height *h* of the steps (low-index planes). The vicinal *S* faces can be stabilised by the reconstruction of the terraces between the steps. This has been observed expermentally for planes close to (100) and (111) in Au.[4] At certain "magic" angles, defining the deviation of (*khl*) from the low-index face, and for which the distances between steps are multiples of the period of the superstructure, the energy of the surface is substantially decreased.[5] Surfaces with different orientations, characterised by large step heights (β_0), are non-singular *K* faces (in which the step length *L* is

commensurate with the step height h). Examples of stepped surfaces of the $n(110)-(0\bar{1}1)-(0\bar{1}1)$, $n(110)-(1\bar{1}0)$, and $n(110)-(001)$ type are shown in Fig. 1 (where n is the number of rows of atoms in the terrace).

Table 1. Types of stepped surface (S faces) in the cubic system.[8]

Symbol of the stepped face	Miller indices	Angles between flat terraces and steps
$n(111)-(111)$	$(n, n, n-2)$	$\mathrm{tg}^{-1}(\frac{2\sqrt{2}}{3n-2})$
Sample: 9(111)–(111)	(997)	6.45°
$n(111)-(100)$	$(n+1, n-1, n-1)$	$\mathrm{tg}^{-1}(\frac{2\sqrt{2}}{3n-1})$
Sample: 10(111)–(100)	(11, 9, 9)	5.57°
$n(100)-(111)$	$(2n-1, 1, 1)$	$\mathrm{tg}^{-1}(\frac{\sqrt{2}}{2n-1})$
Sample: 10(100)–(111)	(19, 1, 1)	4.25°
$n(100)-(110)$	$(n, 1, 0)$	$\mathrm{tg}^{-1}(\frac{1}{n})$
Sample: 9(100)–(110)	(910)	6.34°
$n(110)-(111)$	$(2n-1, 2n-1, 1)$	$\mathrm{tg}^{-1}(\frac{\sqrt{2}}{2(2n-1)})$
Sample: 5(110)–(111)	(991)	4.49°
$n(110)-(100)$	$(n, n-1, 0)$	$\mathrm{tg}^{-1}(\frac{1}{2n-1})$
Sample: 9(110)–(100)	(980)	3.37°

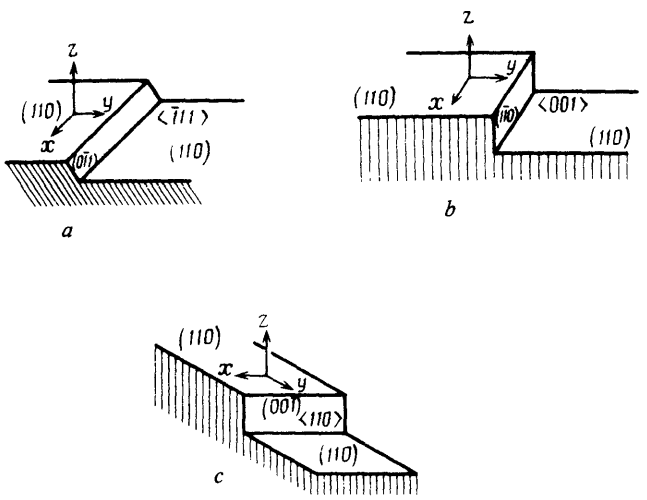


Figure 1. Geometry of the stepped surfaces; *a*, $n(110)-(0\bar{1}1)$; *b*, $n(110)-(1\bar{1}0)$; *c*, $n(110)-(001)$; n is the number of atomic rows in the terrace.

Singular surfaces have sites of a single type for capturing adsorbed species, but both one-centre adsorption and stronger multicentre adsorption can take place. According to Horiuti[6] the latter are called s states and the one-centre adsorption centres are called r states. For cubic crystals the width (r_{hkl}) and the depth (h_{hkl}) of the strong adsorption centres (s states) are calculated by the formula

$$r_{110} = a/2 - R_M,\ h_{110} = a\sqrt{2}/2 - R_M, \quad (1)$$

$$r_{100} = a\sqrt{2}/2 - R_M,\ h_{100} = a/2 - R_M, \quad (2)$$

$$r_{111} = (a/\sqrt{2})/2 \cos 30° - R_M,\ h_{111} = a\cos(\widehat{[100][111]}) - R_M, \quad (3)$$

where a is the lattice parameter of M, and R_M is the radius of the M atom, which corresponds most closely to the Zacharaisen radius $R_{M,z}$. The latter is calculated by the model of the ideal h.c.p. structure constructed from spherically symmetrical elements of radius $R_{M,z} = \Omega^{1/3}/2^{5/6}$, where Ω is the atomic volume of M at room temperature.[7]

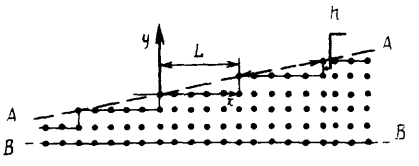


Figure 2. Square lattice with an $[lk]$ ($k = 5$) surface;[8] L is the length of the step, h is its height.

Atomically flat ideal singular F faces of M contain regular defects of the broken bond type having densities (for example, in the diamond lattice) of $\sqrt{3}/4a^2$ for the (111) face, $3/4a_2$ for the (001) face, and $3\sqrt{2}/8a^2$ for the (011) face. A simple square lattice with a single index [like the $\{lk\}$, $k = 5$ lattice surface shown in Fig. 2] is usually stepped with a step height h. Planes with the smallest number of broken bonds are energetially the most favourable for the formation of the equilibrium forms of crystals during dissolution (or corrosion). Therefore the morphology of the surface corresponds to the direction of the corrosion process which lowers the total surface energy of the system.[8]

The packing densities of the atoms are different for different S_{hkl} surfaces. Thus, the low-index (111), (001), and (011) faces of nickel crystals contain the following numbers of surface atoms (N_s) per 1 m^2 of surface area; 1.87×10^{19}, 1.61×10^{19}, and 1.14×10^{19}, and those of silver monocrystals 1.38×10^{19}, 1.20×10^{19}, and 0.84×10^{19}. Calculations of the packing densities show that the nonsingular terraced faces have the loosest surfaces. These faces, with a well defined angle of deviation from the low-index faces, are most often met in the surfaces of polycrystals.

III. Orientation dependence of the dissolution of a metal during phase transitions of the first kind (corrosion, electrocrystallisation)

Unfortunately, reliable experimental data are few, because in most cases experimental electrochemists have used monocrystals with S faces while claiming them to be singular low-index F faces. Working

surfaces are usually prepared by cutting the monocrystal by the spark erosion method, which produces the required *hkl* orientation to within 1–3°: the working surfaces are therefore invariably stepped. The best surfaces, closest to the low-index *F* faces, have a deviation of ~1° in the noble meals. A slight improvement can be achieved[9] by including a final ion etching stage (Ar^+) in the surface preparation programme (mechanical polishing with diamond pastes, electropolishing, chemical polishing). Clavilier and co-workers[10] used a special sample preparation programme in their electrochemical investigation, including a surface cleaning stage by vacuum annealing and cooling, and they claim a precision of 1–3′ in their control of *hkl*.

Another weakness of many experimental studies is a casual approach to the preparation of the electrode and to the general experimental technique; oxides, adsorbed particles, and other contaminants are removed carelessly from the surface, and mechanical lapping and polishing methods are used though they are known to perturb the structure of the near-surface layer. The most reliable electrochemical data were obtained on the equilibrium faces of single-crystal whiskers, whose working *F* faces are very close to singular surfaces.

The physical methods used to characterise and to control experimentally the surface *ex situ* and *in situ* include X-ray diffraction (XRD), high-energy and low-energy electron diffraction (HEED and LEED), secondary ion mass spectroscopy (SIMS), Auger electron spectroscopy (AES), X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS), elastic and inelastic neutron scattering (ENS and INS), elastic and inelastic scattering of helium atoms (EHS and IHS), and electron beam microanalysis (EBMA),[11] as well as other methods. Further developments in high-resolution electron microscopy (0.1–0.3 nm) have been achieved, with chemical analysis of the near-surface layer and new methods of exploiting the resonant scattering of X-rays[12] in interpreting the fine structure of the extended X-ray absorption spectra (EXAFS). By using these methods the distance between the absorbing atom and the atoms of the first coordination sphere can be determined to within 0.001 nm, and to within 0.01 nm for the next three spheres. Information on the local chemical composition and on the atomic and electronic structure of the surface is important for determining the electrochemical characteristics of metals. Auger electron spectroscopy can be used to calculate (from the energy of the Auger electrons) the local density of states in the valence band for the M surface. Several of the methods listed above are usually combined within the same experiment. The analytical possibilities of the methods are summarised in Table 2.

The interactive combination of these methods with electrochemical methods, which allow the degree of excitation of the particles in the near-surface layers of the metal and of the electrolyte to be controlled, makes it possible to re-examine the phase transitions of the first and second kind in the metal corrosion process and in the deposition of a new phase on the surface. The phase transition of the first kind during the dissolution of the crystal is preceded by a relaxation and rearrangement of the surface layers (phase transition of the second kind).

The dissolution of the crystal leads to the disappearance of some faces and the retention of others; in the surface layers of polycrystals the grains contacting the solution in given orientations dissolve fastest. The crystal in the solvent medium behaves so as to retain its mass by rearrangement of the near-surface layer, and the surface tension γ_{ji}^0 decreases according to the expression

$$\partial\gamma_{ij}^0/\partial r_{ij} = 0, \quad (4)$$

where r_{ij} is the distance between interacting particles.

The positions of the individual atoms in the near-surface layer of M are jointly described by the index (*hkl*). Sites for the adsorption of surface-active substances are considered to be equivalent. The expression (4) reflects the decrease in the area of the solid surface, which must be accompanied by an increased chemical resistance of the metallic crystal in the liquid medium. The decrease in the true area of the electrode surface is reflected by the decrease in the rate of corrosion (K) as the dissolution time increases. K can be increased by special methods (stirring, the application of an anodic potential), but the maximum rate (observed at the beginning of the dissolution

Table 2. Characteristics of the different methods of studying the surface and near-surface layers of metals.[11]

Parameter	UPS	XPS	AES	LEED	EBMA	SIMS	ESCA	XDS	EHS IHS	ENS, INS
Probe Emitted particle	$h\nu$ $\bar{e}$	γ $\bar{e}$	$\bar{e}$ $\bar{e}$	$\bar{e}$ $\bar{e}$	$\bar{e}$ γ	I I	$\bar{e}$ $h\nu$	γ $\bar{e}$	He	n
Analysed areas, mm^2	5	5	$5\cdot10^{-8}$	5	1	3–10	1–50	1–50	1–50	10^6
Lateral resolution, nm	$\sim10^3$	10^2–10^3	<0.1	<0.05	0.5–10	<1	0.1	10^{-2}–10^{-3}	20	100
Depth resolution, nm	0.5–5	0.5–5	0.5–5	0.5–5	$>1\cdot10^4$	>0.3	1–10^2	0.5–5	0.3	≥0.3
Detectable amount of substance, at.%	0.1	0.1	0.1	0.1	0.1	<0.001	0.1	0.1	<0.001	<0.001
ditto, g cm^{-2}	10^{-10}	10^{-10}	10^{-10}	10^{-10}	10^{-10}	10^{-13}	10^{-10}	10^{-10}	10^{-13}	10^{-13}

Symbols. I, ions; γ, X-ray quanta; $\bar{e}$, electrons; $h\nu$, light quanta; n, neutrons; He, helium atoms.

process) cannot be re-established without changing the nature of the solution.

A description of the effect of the roughness (or curvature) of the surface K_M on the chemical activity of its different regions is implicit in the well known Gibbs–Thomson equation, according to which the difference $\Delta\mu$ between the chemical potentials of the particles in the solid located on a projection or in a groove is proportional to the curvature K_M of the surface:

$$\Delta\mu = \gamma^0_{ij}\Omega K_M.$$

The curvature can be defined as

$$K_M \simeq d^2y/dx^2$$

where x, y are the coordinates. For $x \to 0$ the difference $\Delta\mu$ is a maximum, and therefore atoms tend to be transferred from projections to the flat surface. In this way the surface tension γ^0_{ij} of the crystal grain can minimise its surface area.

The kinetics of the dissolution of M are described by the Arrhenius expression[13]

$$i = k\theta\exp(-E_a/RT),$$

where k is the rate constant, θ is the coverage of the surface by the products of the dissolution reaction E_a is the activation energy of the dissolution, R is the gas constant, and T is the absolute temperature. In practice the ratio of the rates of dissolution (i) on portions of the surface of types r and s is the most useful parameter. The rate of dissolution of projections (i_p) on the M surface is greater than the rate of dissolution of hollows (i_h). If the projections and the hollows are approximated by hemispheres of atomic dimensions ($\sim$0.01 nm) the ratio of i_p to i_h can be written

$$i_p/i_h = \exp(2\gamma^0_{ij}\Omega/R_S RT), \quad (5)$$

where $R_S = K_M^{-1}$ is the radius of curvature of the surface ($R_S > 0$ for a projection, $R_S < 0$ for a hollow).

It has been pointed out[14] that hollows and projections (of curvature $K_{M,h}$ and $K_{M,p}$ respectively) will function as microanodes and microcathodes with a potential difference

$$\Delta E = (2\gamma^0_{ij}\Omega/zF)(K_{M,p} + K_{M,h}). \quad (6)$$

where F is the Faraday and z is the valency of the electrode reaction.

ΔE decreases with the square of the distance from the projection to the hollow, and the energy term (the dependence of ΔE on R_S) becomes a curve with a minimum at the distance $0.5\,R_S$.

For a flat boundary at $R_S \to \infty$ the Gibbs absorpton equation becomes

$$d\gamma^0_{ij} = -q_{S,0}dE_0 - \sum_i \Gamma_i d\mu_i\,, \quad (7)$$

where $q_{S,0}$ is the surface charge for an electrode potential E_0, $\Gamma_i = N_i/A_S$ is the number of adsorbed i particles (the Gibbs adsorption), N_i is the number of moles of the i-th component, and A_S is the surface area of the crystal. This equation cannot be used, since for T = const the system is invariant. However, when $K_M \neq 0$ we can write

$$d\gamma^0_{ij}/dR_S = -\Gamma_i(d\mu/dR_S) \quad (8)$$

and after some substitutions arrive at the Tolman equation[15]

$$\gamma^0_{ij}/\gamma^0_{ij\infty} = (1 + 2\delta/R_S)^{-1}\,. \quad (9)$$

For a flat surface $\delta/R_S \to 0$ and $\Gamma_i/\Delta\rho \to \delta$ (the distance from the interface); $\Delta\rho$ is the difference between the densities of the crystal and of the liquid phase. It is clear that the increase in Γ_i (i.e. the decrease in γ^0_{ij}) depends on the curvature of the corroding surface.

In a macroscopic analysis of the increments $\Delta\gamma^0_{ij}/\gamma^0_{ij}$ we must allow for a possible increase (as well as a decrease) in the surface area A_S. Gokhshtein[16] introduced the differential factor

$$\beta = \Delta A_S/A_S = \Delta\gamma^0_{ij}/\gamma^0_{ij},$$

related to the curvature of the surface K_M by the expression

$$\beta = 1/2[(1 - \nu)K_M + (1 + \nu)K_M^{-1},$$

where ν is the Poisson ratio for the metal ($\nu \cong 0.25$). The curvature of the surface K_M can be altered by the adsorption of species from the solution (with charge transfer) at the electrochemical contact. Faceting of the surface (to give S and K faces) is possible, including, as a first stage, the rearrangement of the near-surface layers of the crystal. The coherence of the coupling of the EDL with the metal and the electrolyte plays an essential role in the rearrangement of the first few surface layers of the crystal.

IV. Adsorption of chalcophilic particles and phase transitions of the second kind in the near-surface layers of monocrystals

An ideal crystal surface has the unique property of a stretched skin, i.e. an elastic surface tension γ_{ij} which compresses the inner part of the crystal. When a metallic crystal is cut to produce a new surface in transition metals, which contain electronic surface states of the Tamm or of the Shockley type, the atoms in the first near-surface layers are regrouped (rearranged, reconstructed), and γ_{ij} decreases. The radii of the first, second, and third coordination spheres on the newly formed surface of transition metals are greater than in the bulk (for example, for Fe the increase is $> 3\%$).

A strict thermodynamic description of the reconstruction of the near-surface layers can be based on Landau's theory of phase transitions.[17] Large displacements (Δd) of the atoms in the metal lattice are characterised by a nonlinear function for the deviation of the atoms from the given equilibrium positions (the nonlinear order parameter) in this theory. This function is exactly equivalent to a density wave in the metallic crystal.[18]

In the surface layers of very pure monocrystals the distance between the first and the second layer (Δd_{12}) at right angles to the surface is less than the corresponding distances in the bulk (Table 3), i.e. we observe a perturbation of the translational invariance and an alternation of the sign (with decreasing amplitude), which is more marked for the stepped nonsingular K faces [for example, (997), (991), (311), see Table 1]. This change in Δd, not related to the adsorption of particles from the solution, is a fundamental property of the first few near-surface layers of metallic crytals.

The reconstruction of the near-surface layer of a crystal was first described in terms of the charge model. The infringement of the translational invariance produces effectively localised electronic states

which give rise to surface energy bands from closely placed energy levels. The formation of surface charge and of an EDL of thickness comparable to that of the Debeye screening radius leads to the filling of the conduction band. An electric field normal to the surface and a bending of the energy bands are produced. A relaxation (a change in the displacement Δd) takes place under the influence of the surface tension forces, and the surface layer is reconstructed as a result of the difference in energy between the electronic states produced by small deformations of the surface structure. In diamond-like structures [for example, (111)Si] the relaxation can be as high as 30%.[19]

Table 3. Changes in the interplanar spacings of metals in the first near-surface layers, %.

(*hkl*)M	Δd_{12}	Δd_{23}	Δd_{34}	Refs.
(001)Ti	~ -2.0			[21]
(011)V	-0.3			
(001)V	-6.7	1.0		
(001)Fe	~ -1.5			
(211)Fe	-10.0	5.0		[20]
(310)Fe	-16.0	12.0	-4.0	
(001)Co	~ -4.0			
(111)Ni	-1.2±1.2			
(001)Ni	-3.2±0.5			[22]
(011)Ni	-8.7	3.0	-0.5	[20]
(011)Ni	-9.6	4.3		
(011)Ni	-4.8±1.6	2.4		
(011)Ni	-9.8±1.6	3.8±1.8		[22]
(011)Ni	-8.4	3.1		
(311)Ni	-15.9	4.1	-1.6	[20]
(111)Cu	-4.1±0.6	2.4		
(011)Cu	-7.9	2.3	-0.9	[21]
(011)Cu	-8.5	2.6		[20]
(011)Cu	-9.5			
(011)Cu	-10.0	3.3		
(001)Cu	~ -1.1			
(001)Mo	~ -11.5			[21]
(001)Mo	-9.5±2.0			
(110)Rh	-6.9±1.0	1.9±1.0		[23]
(011)Ag	~ -7.0±2.0	1.5	-2.0	
(011)Ag	~ -10.0			[21]
(011)Ag	-5.7	2.2		
(001)W	-2.0			[24]
(001)W	~ -6.0			[20]
(011)Re	-17.0	1.0		[21]
(111)Al	0.9			[20]
(111)Al	~ 5.0			
(111)Al	2.2	5.5	+2.2	
(011)Al	-8.5	5.2±0.2	-1.6	[21]
(011)Al	~ -10.0			
(011)Al	~ -4.0			
(311)Al	-13.0	9.0		[24]
(311)Al	-11.7±2.3	-4.1±3.1	10.3±2.7	[25]

During the reconstruction of the surface layers of the crystal we observe transverse and longitudinal displacements in the first rows of atoms in addition to the displacements Δd normal to the surface. Transverse relaxation is found on singular, low-index F faces, such as the (111), (110), and (100) faces of b.c.c. crystals of the transition metals. Both longitudinal and transverse displacements of the atoms in the first layers of atoms are possible on nonsingular S faces [for example (210), (310), and (211)].[20]

The compressive stresses in the first near-surface layers of crystals are always replaced in the deeper layers by compensating expansion stresses produced by the action of the *sp* electron gas and by the short-range repulsive pair interactions between the atoms. The tangential displacements (Δd_r) of the atoms in the first layers are expressed[26] as

$$\Delta d_r = -\frac{1}{2G_c}\int_0^\infty f_1(tr)[\nu t^2\varphi + (1-\nu)\frac{\partial^2\varphi}{\partial z^2}]dt, \qquad (10)$$

where G_c is Young's modulus, φ and r are the spherical coordinates, f_1 is a Bessel function, and the z axis is directed towards the bulk of the crystal.

A test of formula (10) by computer calculations shows that these stresses have a variable sign. The adsorption of particles from the solution produces a rearrangement which stabilises the surface layer: a phase transition of the second kind takes place in a thin layer of the crystal. Obviously, two mechanisms can be suggested for the effect of adsorbed SAS on the reconstruction of the surface:[27] (*i*) in some metals the symmetry of the atomic arrangement is modified by the adsorption of SAS, approaching the symmetry found in the bulk, and (*ii*) the adsorption of the SAS produces a reconstruction of the surface which stabilises it. These are usually the least close packed F faces in the f.c.c. (011) and the b.c.c. lattices [(001) and (111)].

According to Benneman and Tomanek[28] the reconstruction of the surface is the result of the minimisation of the surface free energy (which at $T = 0$ K is the half-sum of E_b for the two free surfaces) associated with the surface tension:

$$\gamma_{ij}^0 = \frac{1}{N_S}\sum_{i=1}^{N_A}(E_{b,k} - E_{b,i}), \qquad (11)$$

where $E_{b,k}$ and $E_{b,i}$ are the binding energies of the atoms in the bulk and on the surface of the crystal, and N_A is Avogadro's number. Acording to Rusanov[29] the tangential forces Δd_r act in a near-surface layer of thickness l, and therefore Eqn. (11) should be re-written

$$\gamma_{ij}^0 = \int_0^l(\sigma(z) - \sigma^0)dz,$$

where $\sigma(z)$ and σ^0 are the stress tensors in the bulk and on the surface of the crystal.

The heat of reconstruction of the clean surface $\Delta\gamma_R^0$ is the difference between the surface tensions of the rearranged (γ_R^0) and the nonrearranged surfaces (γ_u^0):

$$\Delta\gamma_R^0 = \gamma_R^0 - \gamma_u^0. \qquad (12)$$

The changes in d produced by the reconstruction of the surface are entirely different in the presence of an adsorbed SAS. There are a few crystals whose clean surfaces do not become reconstructed, and also some crystals in which the amplitude of the atomic vibrations in the first layers is comparable with the amplitude of the vibration of the adsorbed SAS particles, and the rearrangement proceeds as a cooperative resonance process. When SAS species are adsorbed the heat of reconstruction [according to (12)] becomes:

$$\Delta\gamma_R = \Delta\gamma_R^0 - \Delta\gamma_{ads}. \qquad (13)$$

In this expression

$$\Delta\gamma_{ads} = \theta_{SAS}(E_{ads,R} - E_{ads,u}), \quad (14)$$

where E_{ads} is the energy of the adsorbate–adsorbent bond and the difference $E_{ads,R} - E_{ads,u}$ is determined by calculation or experimentally. From Eqn (14) we obtain the main diagnostic criterion for the supression or the initiation of the reconstruction:

$$\Delta\gamma_R = \Delta\gamma_R^0 - \Delta\gamma_{ads} < 0, \quad (15)$$

which can be determined by a simple method (Fig. 3).

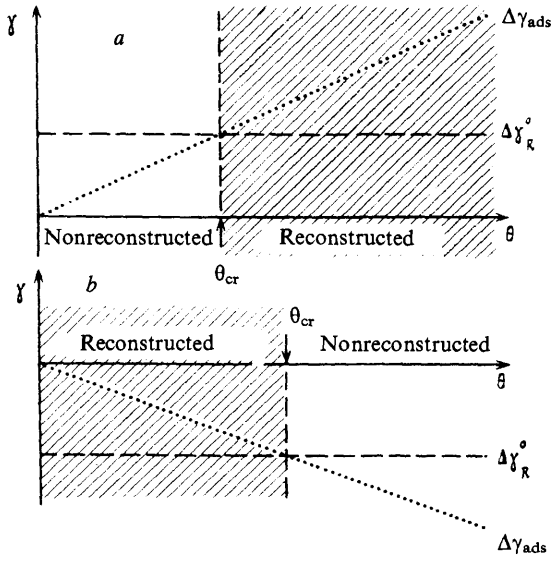


Figure 3. Changes in surface energy during the reconstruction of the near-surface layer of the metal:[24] *a*, onset of reconstruction; *b*, suppression of reconstruction.

In order to obtain the surface tension γ_{ij}^0 by Eqn. (11) we must expand $E_{b,i}$ into two terms:

$$E_L(x) = \Delta E_{rep}(z) + \Delta E_b(z), \quad (16)$$

where $\Delta E_{rep}(z)$ is the Born–Mayer phenomenological short-range repulsive potential: $\Delta E_{rep} = \Sigma A_S exp(-pR_{a,i})$, $R_{a,i}$ is the length of the bond along the z axis between the adsorbed particle and the M(i) surface atom, p is the damping coefficint, and $\Delta E_b(z)$ is the contribution from the adsorbate–adsorbent interaction. Eqn. (16) shows that the driving forces of the rearrangement are the elastic forces in the near-surface layer. The rearrangement induces a change in the chemical composition of alloys. A LEED study of the enrichment of the first surface layer in the close-packed (111) face of a monocrystal of the $Pt_{0.1}Ni_{0.9}$ alloy by platinum atoms[30] showed that the degree of enrichment can reach 30 ± 4% while the second layer is depleted of platinum by 5 ± 3%. Therefore we must allow for the ennobling of the surface even before the contact with the electrolyte when calculating the corrosion resistance of binary alloys containing a noble metal component. The ennobling of the surface layer is a well known phenomenon in corrosion or anodic dissolution studies, but it is usually attributed to the transport of alloy components into the solution and their subsequent reprecipitation.

In electrochemical dissolution processes of M taking place at low speed the rearrangement of the surface layer is undoubtedly an active factor. The ionisation of the metal during dissolution $M^0 \rightarrow M^{+n} + ne^-$, produced by the breaking of the M–M bond followed by charge transfer, should lead to periodic pulsations of the atoms in the first layer associated with the formation of metastable states. This effect will be reflected in the magnitude of the current flowing through the electrochemical system. Instability of the surface structure is mainly seen in the *d* metals with a half-filled *d* band. The mechanical instability (reconstruction) stimulates a rearrangement of the force and energy distributions on the surface, leading to electrical instability.

This type of electrical instability, accompanied by current pulsations (oscillations), is often observed in electrochemical processes on solid electrodes under conditions of pre-phase (adsorptional) evolution of material on the surface at relatively low overvoltages (η = 0.02–0.03 V) in the cathodic or the anodic region. Current oscillations may result in periodic mechanical vibrations in the M/electrolyte system, whose amplitude depends on the shape of the electrode and on the electrolysis parameters.[31]

V. Reconstruction of monocrystal surfaces during the adsorption of hydrogen, oxygen, and halogens

The adsorption of light chalcophilic species (hydrogen, oxygen, haloens) produces the highest activity in the reconstruction of the near-surface layers of metals.

Hydrogen

An analysis of the interaction of hydrogen with the near-surface layers of transition metal monocrystals is of practical value in the chemistry of catalysis and in the assessment of corrosion and brittleness in constructional materials. The reversible absorption of hydrogen in a metal plays an important role in hydrogen energetics. We shall discuss the structural effects resulting from the adsorption of hydrogen on the surface of the transition metals of Groups IB, VIB, and VIII of the Periodic Table, beginning with the adsorption of hydrogen from the gas phase, because this information is invariably used in the analysis of the contact between a metal and an electrolyte. The studies were carried out by LEED, AES, IRS, and other methods.

Adsorption from the gas phase. Most of the experimental work was done with well characterised nickel monocrystal surfaces. The adsorption parameters depend on (*hkl*), but it has been shown that the nickel (100) and (111) faces are affected similarly by the adsorption of hydrogen.[22] There are two sequentially filled β states, with activation energies for desorption of ~0.84 (β_1) and 1.00 eV (β_2). The number of hydrogen atoms in the adsorbed monolayer (*ML*) varies between $\sim 3 \times 10^{18}$ and 1.5×10^{19} atoms m^{-2}, i.e. it is slightly lower than N_S for these faces. The work function of the electron (Φ_M) from the surface of the metal M increases in proportion to the filling of the nickel surface by hydrogen (θ_H) up to saturation (state β_2), reaching ~0.2 eV at saturation (θ_H = 1 *ML*,

5×10^{-2} Pa, 298 K). LEED measurements indicate the formation of a disordered adsorbed layer of hydrogen on nickel at 298 K.

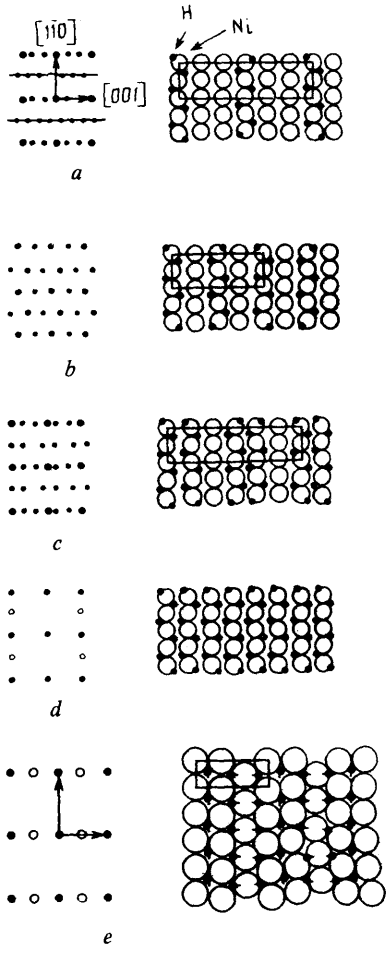


Figure 4. Superstructures formed on the (110)Ni face for different θ_H (*ML*): *a*, 0.33; *b*, 0.50; *c*, 0.67; *d*, 1.00; *e*, 1.50; on the left, LEED diffraction pattern, on the right, model.[32]

The adsorption of hydrogen on the least close packed (110) face of nickel shows some special features.[32–35] In particular, it has been shown that at the θ_H values for which $\Phi_m \cong 0.06$ eV a one-dimensional structure with the same periodicity (1×2) as the nickel lattice is formed as a result of the attraction of the adsorbed hydrogen atoms in the [1$\bar{1}$0] direction along the rows of nickel atoms of the first near-surface layer. This phase transition of the second kind is accompanied by an increase in the binding energy of the hydrogen to the nickel E_{Ni-H}, but the interactions of the adsorbed atoms in the [001] direction, across the above rows, are much weaker. The periodicity of the structures produced by the adsorption are strongly dependent on θ_H:[32] at $\theta_H = 0.33$ *ML* the first disordered (2×6) superstructure is formed, the (2×4) superstructure at $\theta_H = 0.5$ *ML*, a second (2×6) at $\theta_H = 0.67$ *ML*, and at still higher coverages we find the (2×1)–2H at $\theta_H = 1.0$ *ML* and finally the (1×2)–3H at $\theta_H = 1.5$ *ML* (i.e. at saturation) (Fig. 4). Hydrogenation of the (110) nickel face ($T \geqslant 220$ K) produces "stripes" with a (1×2)–3H structure in the [001] direction. The surface is reconstructed and consists of paired and of extended rows of nickel atoms. The hydrogen aotms are adsorbed on two (*r* and *s*) positions with a low and a high Ni–H bond energy respectively,[33] i.e. in the triple vacancies between the first two nickel layers parallel to the paired rows of the first layer in the [1$\bar{1}$0] direction, forming saw-like chains, and in the triple vacancies normal to the rows of nickel atoms in the [001] direction. The length of the Ni–H bond becomes 1.72 ± 0.01 nm, and the nickel atoms of the second layer are displaced alternately and mutually at right angles by ± 0.02 nm. The density of the adsorbed hydrogen atoms is 1.71×10^{19} atoms m^{-2}, and $E_{Ni-h} \simeq 2.75$ eV. There are reports[34,35] that at $T = 298$ K the chemisorption of hydrogen on (110)Ni–(1×1)H rearranges the surface into (110)Ni–(5×2)H, so that the nickel atoms of the first layer are shifted by 0.05 nm in the direction of dimerisation (Fig. 5), forming tetramers, which can also be interpreted as a combination of paired and extended rows (every fifth row in the [001] direction is extended).

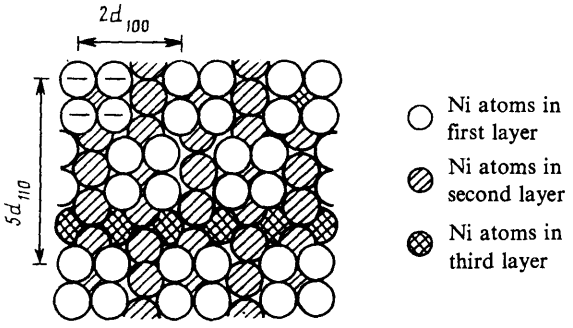


Figure 5. (5×2) Superstructure formed on (110)Ni by the adsorption of 0.5 *ML* of hydrogen at $T = 298$ K.[34]

In the high-index nickel *S* faces [for example, (997)Ni, (510)Ni, etc.] the presence of steps and terraces plays an important role, as was pointed out above. Thus, on the (510)Ni face at $T \simeq 100$K and coverages up to $\theta_H \leqslant 0.9$ *ML* hydrogen is adsorbed both on the terraces and on the steps (with preferential coverage of the steps),[36] and at $\theta_H > 0.9$ *ML* even molecular hydrogen is adsorbed, but only on the step edges.

The stepped (997)Ni *S* face, which is a combination of monoatomic (111) steps and nine-atom (111) terraces (Table 1), has a hydrogen capture probability at $T = 298$ K 10 times higher than the singular (111)Ni *F* face.[37] At low temperatures ($T \leqslant 250$ K) hydrogen adsorption takes place mainly on the step edges, but at high temperatures it extends over the terraces (according to LEED and HEED studies). The predominant adsorption of hydrogen on the steps can be demonstrated by the dependence of the sticking coefficient on the angle of incidence (Fig. 6). We can see that at $T = 90$ K the function $s_0(\theta_H)$ is determined exclusively by the presence of steps. Conversely, at $T = 800$ K only the terraces affect the kinetics of adsorption, and the plot of the $s_0(\theta_H)$ function is identical to that obtained for the (111) plane, inclined at 6.4° to the (997) plane.

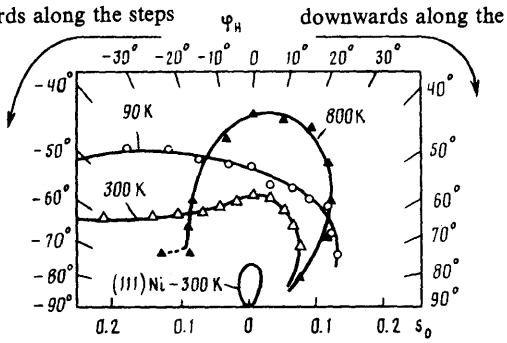


Figure 6. Dependence of the sticking coefficient s_0 on the angle of incidence of the molecular beam of hydrogen φ_H on the (997) and (111) nickel faces at different temperatures.[36]

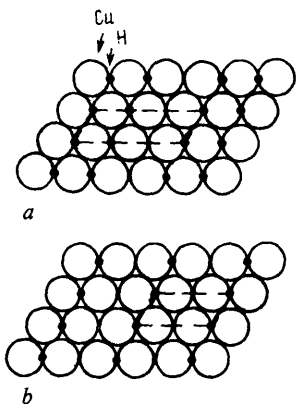


Figure 7. Superstructures formed on the (111)Cu face:[39] *a*, (3 × 1); *b*, (2 × 1).

Copper

On the (110)Cu face the adsorption of hydrogen is mainly in the atomic form,[32] with low values of E_a (0.18–0.20 eV), denoting a low probability of attachment of hydrogen molecules. It has been shown by LEED measurements that subsurface reconstruction with formation of a specific (1 ×2)* phase takes place at 300 K. The octahedral surface position of the hydrogen atoms is more favourable than the interstitial position in the bulk of the metal, but it is less stable (by 0.3 eV) than the normal chemisorption position.[38] Under these conditions a substantial contribution to the stabilisation is provided by the change in the relaxation of the near-surface layer of atoms (Δd_{12} = 4–9.6% at θ_h = 0.5 *ML*). Of course, so far we have no definite model of the resulting structure, because of the difficulty of correlating the LEED results variously obtained for the (110)Cu surface covered with hydrogen.

A study of the temperature dependence of the adsorption of hydrogen on the (111)Cu surface by IR spectroscopy has shown[39] the presence of two superstructures (3 × 3) at 150 K and (2 × 2), into which the (3 × 3) phase is converted when heated to 186 K (Fig. 7). The structures are combinations of domains with (3 × 1) and (2 × 1) orientations. The adsorbed hydrogen atoms are accommodated in (111)Cu double vacancies parallel to the rows, so that every third row is extended for the (3 × 1) structure and every second for the (2 × 1) structure. The filling with hydrogen of the double vacancies is confirmed by studies of the electron energy loss spectra (ν_1 = 1040 cm^{-1}, whereas a ν_1 frequency of 1000 cm^{-1} is calculated for the filling of triple vacancies).

Ruthenium

Like the (110)Ni–H system, the (100)Ru–H system forms a wide spectrum of superstructures at low temperatures, depending on θ_H. At θ_H = 2.0 *ML* we find the (1 × 1)–2H structure (Fig. 8), in which the chains of adsorbed hydrogen atoms are arranged only in the [$\bar{1}$20] direction, unlike the (1 × 2) structure obtained for nickel.[32] A reversible surface reconstruction takes place at θ_H = 1.5 *ML*: in this state alternate ruthenium atoms are raised above the plane of the surface, and form a (2 × 2) structure. The density of adsorbed hydrogen atoms at θ_H = 2.0 *ML* is 1.73 × 10^{19} atoms m^{-2}, with E_{Ru-h} = 2.7 eV, which is comparable with the N–H bond energy. According to the desorption spectra hydrogen can be adsorbed in the α_1, β_1, and β_3 states, which exist at 220, 260, and 350 K respectively. The α_1 state corresponds to the formation of a (1 × 1)–2h structure (θ_H = 2.0 *ML*), the β_1 (probably) to the formation of a (2 × 2) structure (θ_H = 1.5 *ML*), and the β_3 state to the (1 × 2) structure. As in the case of nickel the sticking coefficient s_0 initially has very high values ($s_0 \simeq 1$), so that a coverage of only 0.3–0.4 *ML* of hydrogen is sufficient to saturate this state. However, s_0 rapidly falls to ~0.1 for the filling of the β_1 state at θ_H = 1.5 *ML*, and the rate of adsorption also falls.

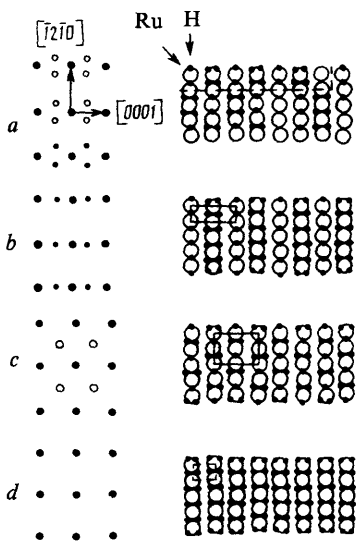


Figure 8. Superstructures formed on the (100)Ru face for different θ_H (*ML*):[32] *a*, 1.0; *b*, 1.4; *c*, 1.5; *d*, 2.0.

Rhodium

The structures obtained in the adsorption of hydrogen on the (110)Rh face (Fig. 9) are similar to those found on ruthenium.[32] At θ_H = 2.0 *ML* a structure with a periodicity of (1 × 1) is formed,

with two hydrogen atoms in the unit cell. The hydrogen occupies triple vacancies, forming linear chains in the [1$\bar{1}$0] direction, but in this arrangement it produces stronger changes in the surface relaxation of the rhodium atoms than it does in ruthenium.[40] As in other *d* metals, we find a compression at right angles to the surface (a decrease in Δd, Table 3). The distance between the layers is 0.132 nm, and the length of the Rh–H bond is 0.184 nm.

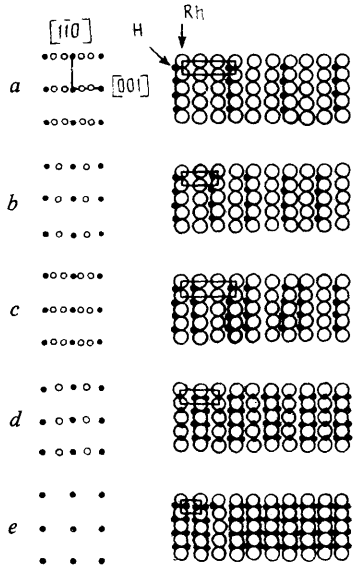


Figure 9. Superstructures formed on the (110)Rh face for different θ_H (*ML*):[32] *a*, 0.33; *b*, 0.50; *c*, 0.67; *d*, 1.60; *e*, 2.00.

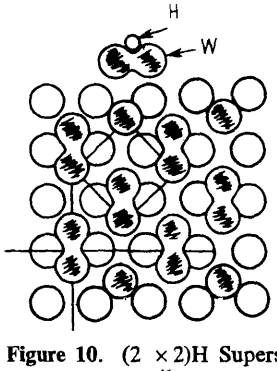


Figure 10. (2 × 2)H Superstructure formed on the (100)W face for θ_H = 0.25 *ML*.[41]

Under these conditions the density of the hydrogen atoms is ~2 × 10^{19} atoms m^{-2}. The high bond energy E_{Rh-H} = 5.7 eV [unlike E_{Ni-H} = 2.7 eV for (110)Ni] can account for the lack of surface reconstruction in rhodium even after the adsorption of large amounts of hydrogen. The hydrogen desorption spectra show that two states are being filled: α_1 (at 138 K), corresponding to the (1 × 1)–2H structure (θ_H = 2.0 *ML*), and α_2 ($T \simeq$ 250 K), corresponding to the (1 × 2) structure (θ_H = 1.5 *ML*). As was subsequently pointed out,[25] at θ_H = 0.5 *ML* a reconstruction takes place, yielding a (1 × 2)–2H structure in which the hydrogen atoms occupy three-coordinated positions between two atoms of the upper layer and one atom of the second layer, and are arranged along rows of rhodium atoms in the [1$\bar{1}$0] direction. The surface relaxation changes so as to maintain a distance of 0.127 nm between the first and the second layer, which is comparable with the results obtained for the (1 × 1) structure. The electronic work function Φ_M reaches 0.930 eV for $\theta_H \to 1$ *ML*, but the increase in Φ_H is not affected by an increase in p_{H_2}.[42] This effect is attributed[42] to the preferred orientation of the hydrogen dipole with its negative end towards the gas phase.

Tungsten

At $T \simeq$ 300 K and low surface coverages of the (100)W surface flash desorption reveals one adsorbed β_2 state whose formation is completed at θ_H = 0.16–0.25 *ML*. At higher surface loadings we observe a second (β_1) state in which the density of adsorbate is 2.0 × 10^{18} molecules m^{-2}.[22] The ratio of the concentrations corresponding to saturation in each of the states is σ_1/σ_2 = 2. The adsorption of hydrogen in the β_1 state producs a diffraction pattern corresponding to the (2 × 2) structure, which reduces to the ordered (1 × 1) structure at θ_H = 1 *ML* (Fig. 10), with molecules and atoms accommodated in tetrapores. The adsorption of hydrogen on the (100)W *F* face at θ_H < 0.25 *ML* produces a reconstruction with the surface tungsten atoms in pairs in the [100] direction, forming dimers, and the adsorbed hydrogen atoms are accommodated on the surface atoms as saw-tooth chains.[41]

Flash desorption studies of the (100) and (110) tungsten faces gave similar results.[22] When the adsorption has taken place at 300 K we observe two peaks for β_1 and β_2 states with E_{W-H} bond energies of 1.2 and 1.4 eV respectively. When saturated these states contain approximately the same number of particles, formed by dissociative adsorption; at θ_H = 0.5 *ML*, when the β_2 state is filled, a (2 × 1) structure is formed and the hydrogen is again accommodated in tetrapores. the density of adsorbate in the β_2 state is 1.42 × 10^{19} atoms m^{-2}. The electronic work function decreases with increasing coverage during the adsorption in this state, reaching Φ_M = 0–(–0.5) eV at θ_H = 1.0 *ML*. There are reports that multilayer coverage (θ_H = 8 *ML*, 300 K) produces a reconstruction of the less closely packed (110)W face in which the tungsten atoms are shifted relative to each other in a [1$\bar{1}$0] direction and the hydrogen atoms occupy triple vacancies.[43]

In the b.c.c. tungsten lattice the (211)W is the simplest *S* face, containing atoms having two coordinations: in close-packed rows, forming the first or the surface layer respectively, or in the channels between rows.[9] Though the latter are in the second layer they are accessible to adsorption. This nonuniformity of the face is reflected by the hydrogen adsorption. We observe two adsorption states, β_1 and β_2, which are filled sequentially at $T \simeq$ 100 K. They correspond to atomic states with approximately equal contents of adsorbate at saturation. The sticking probability is $s_0 \simeq 1$, and the decrease in s_0 produced by an increase in Φ_H is proportional to $(1-\theta_H)$. The LEED method failed to detect the formation of a structure with a (1 × 1) periodicity. The electronic work function Φ_M increases by ~0.6 eV for β_2 but falls when the β_1 state is filled. This is explained by the structual properties of the (211)W face towards the adsorbed hydrogen (the adsorbed β_1 state is above the

plane of the surface, and the β_2 state is below it). If a hydrogen atom is adsorbed in a β_1 state (in the uppermost close-packed rows) its dipole is oriented with its positive end towards the metal, resulting in a decrease of Φ_M.

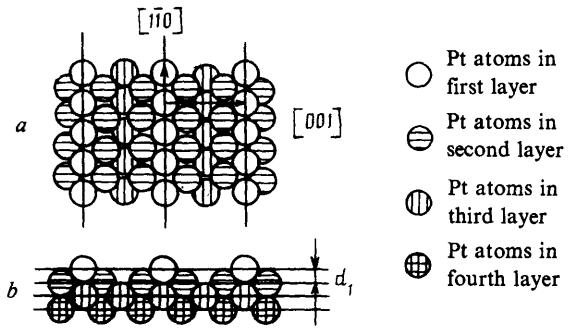


Figure 11. (110)−(1 × 2)Pt Superstructure formed after treating the (110)Pt surface in ultra-high vacuum:[32] *a*, plan view; *b*, side view.

Platinum

As we know, the clean surface of the "loose" (110)Pt face (unlike that of nickel or rhodium) is unstable and is spontaneously reconstructed into a (1 × 2) structure when treated in a high vacuum, so that each row is extended in the [001] direction.[32] In this way the third layer of platinum atoms becomes accessible to the adsorption of hydrogen as well as the second. The surface of the (110)Pt face can be represented as an assembly of (110) micro-facets inclined at 109.5° relative to each other, containing various types of triple or double vacancies between the first and the second layer. The hydrogen adsorbed on these sites does not affect the initial reconstruction (Fig. 11). Of course, the faceted (110)Pt surface is relatively rough and therefore can hold more hydrogen atoms than other faces [$\theta_H = (2.2 \pm 0.2) \times 10^{19}$ atoms m^{-2}]. The hydrogen is adsorbed in two states [β_1 and β_2, for $\theta_H = (0.4-0.6)$ *ML*, 300 K].

The β_1 state formed at $T \simeq 200$ K requires longer exposures to reach saturation. Initially the sticking probability is $s_0 \simeq 1$, but during the filling of the β_1 state $s_0 = 0.022$ and $E_{Pt-H} \simeq 2.8$ eV. The electronic work function initially increases with the coverage ($\Phi_M = 0.170$ eV for $\theta_H = 0.3$ *ML*), but at $\theta_H = 1$ *ML* Φ_M falls to 0.05 eV (Fig. 12). This is explained by the difference between the dipole moments of the β_1 and the β_2 state ($\mu_2 = +0.12$ D for β_2 and $\mu_1 = -0.17$ D for β_1, where 1 D = 10^{-2} C m[44]), which depend on the topology of the adsorbed hydrogen. The filling of the β_1 state corresponds to the adsorption of hydrogen on the (111) micro-facets, when the negative ends of the dipoles of the hydrogen adatoms are directed towards the upper row of platinum atoms. The adatoms themselves lie below the plane of the image charge, i.e. in the triple vacancies, and this lowers the dipole moment of the metal.

Two adsorption states have been observed by the thermal desorption of hydrogen from the close packed (111)Pt face, but at 300 K the β_1 state is absent because of the low energy of the Pt−H bond, and the β_2 state is only partially filled.[9] It has been shown that in the β_1 and the β_2 state the hydrogen is atomically bound to the platinum and that at $\theta_H = 1$ *ML* the amounts of these two states are approximately equal. The hydrogen is adsorbed in triple vacancies between the atoms of the first and the second platinum layer without perturbing the ordered (1 × 1) structure, so that the length of the Pt−H bond is 0.058 nm,[45,46] and $E_{Pt-H} \simeq 2.6$ eV.

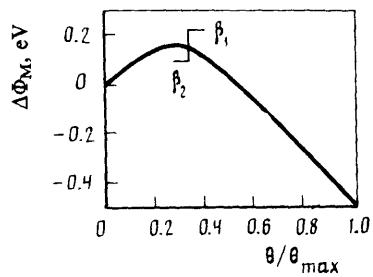


Figure 12. Dependence of the electronic work function Φ_M on the surface coverage θ_H for the (110)Pt face;[44] β_1 and β_2 are the adsorption states.

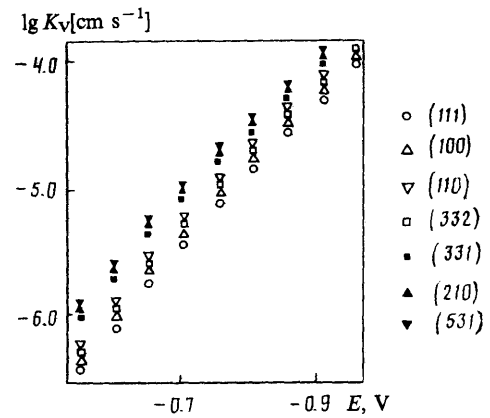


Figure 13. Dependence of the rate of the hydrogen evolution reaction on the potential for different *F* and *S* faces of a gold monocrystal (0.1 M $HClO_4$).[47]

Interesting results have been obtained on the stepped (997)Pt face [a combination of monoatomic steps and nine-atom terraces, oriented in the [111] direction]. As on the (997)Ni face, the sticking probability s_0 was found to be very high [~4 times greater than on the singular (111)Pt face.[32,34]]. At high coverages $\theta \geqslant ML$ the s_0 values for (997)Pt (like the Φ_M values) are comparable with those obtained for (111)Ni. However, at low saturations the "loose" steps of the (997)Pt *S* face act as centres on which the hydrogen is adsorbed most rapidly, is held most strongly, and has a dipole of opposite sign to that of hydrogen adsorbed on (111)Pt. There is evidence of the presence of a second break in the dependence of s_0 and $\Delta\Phi_M$ on θ_H at $\theta_H = 0.15$ *ML*: 9 hydrogen atoms are adsorbed

on each terrace at saturation. Therefore the two centres at the ends of each terrace have a stronger Pt–H bond energy than the others, and are the first to be filled. It is experimentally established that these centres are geometrically different from the others, and that the hydrogen atoms adsorbed on them have dipoles different from the rest.

Adsorption in solutions of electrolytes

The adsorption of electrochemically reduced hydrogen (during which the pressure of the gas on the metal surface is much higher than p_{H_2} = 1 GPa) has been adequately studied on well characterised faces of gold, platinum, nickel, and niobium monocrystals.[47–60]

Thus the hydrogen evolution reaction (HER) has been studied not only on the low-index gold faces, but also on the (311), (210), (332), and (531) *S* faces, consisting of sets of steps and terraces.[47] It was found that both in $HClO_4$ solutions and in electrolytes with specifically adsorbed halogen ions (Hal^- = F^-, Cl^-, Br^-, I^-) the HER is slower on the close-packed faces, but faster when the faces contain steps and breaks. The rate of the HER increased with the concentration β_0 of monoatomic steps; for example, in a solution of NaF the rate of the HER on the (210) gold face was ~3.5 times higher than on the (111) face (Fig. 13). This is due mainly to the decrease of Φ_M on the atomically rough *S* and *K* faces. Obviously, the low-coordinated *r* states on the crystal surface have a catalytic effect on the adsorption of hydrogen. When in contact with the surface the hydrogen fills the tetrapores on the steps, forming bonds.

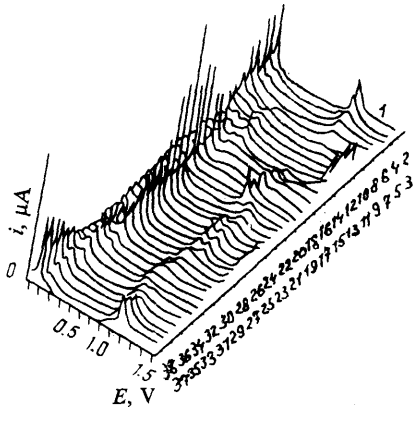


Figure 14. Current–voltage diagrams for Pt faces of different crystalline orientation.[49] Face indices: *1*, (110); *2*, (551); *3*, (331); *4*, (227); *5*, (332); *6*, (554); *7*, (10109); *8*, (202019); *9*, (111); *10*, (201919); *11*, (1099); *12*, (544); *13*, (355); *14*, (322); *15*, (513); *16*, (211); *17*, (311); *18*, (511); *19*, (211); *20*, (911); *21*, (1711); *22*, (3111); *23*, (100); *24*, (2110); *25*, (1510); *26*, (1210); *27*, (910); *28*, (610); *29*, (510); *30*, (410); *31*, (310); *32*, (210); *33*, (530); *34*, (320); *35*, (430); *36*, (620); *37*, (12110); *38*, (110).

These pores offer strong bond positions (*s* state) which are energetically more favourable to adsorption. The difference in E_{M-H} energies between the weakly bound (*r*) and the strongly bound states (*s*) is determined essentially by the crystallographic parameters of the hydrogen adsorption. This has been experimentally demonstrated, for example, for the (881), (771), and (661) *k* faces of an Fe + 3% Si crystal,[48] which are combinations of 8-, 7-, and 6-atom terraces, consisting of (110) planes and of loose monoatomic (100) steps. The radii of the tetrapores (*s* state) on the (110)Fe and (100)Fe faces are r_{110} = 0.00173 and r_{100} = 0.0766 nm. Therefore, since the radius of a hydrogen atom is r_h = 0.046 nm, the adsorbed hydrogen can easily penetrate into the pores in the steps afer being discharged, but the process is suppressed in the close-packed terraces.

The form of the cyclic potentiodynamic potential–current curves depends on the density of β_0 and (*hkl*) steps in the platinum *S* faces.[49] As β_0 decreases, i.e. as the packing density S_{hkl} is increased, the characteristic hydrogen adsorption peak moves into the region of positive potentials (Fig. 14), due to the increase in Φ_M and to the corresponding shift of the zero charge potential $E_{q=0}$. it can also be seen that, as the less densely packed steps become saturated, hydrogen begins to be evolved on the terraces and the intensity of the corresponding peak is increased. Cyclic potentiodynamic curves can be used for a quantitative as well as a qualitative assessment of the adsorption on the *K* faces of monocrytals, and in particular for determining the structural characteristics of these faces, as was demonstrated[50] for the [*n*(111) × (100)] platinum surfaces (*n* = 2–9, 12, 14, 20, 26, and 40).

High-sensitivity optical methods[51] are now widely used to determine the changes in structure of monocrystal surface at the contact with electrolytes. We know that the form of the electroreflectance (ER) spectra depends on the crystallographic orientation of the faces; the $\Delta R/R$ effect (where *R* is the Fresnel reflection coefficient) is smaller when the lattice is most closely packd [for an f.c.c. lattice, of copper (say), the sharpest peaks are found in the spectrum of the (311) *S* faces, and the weakest in the spectrum of the (111) face[52]]. Furthermore the presence of steps and of terraces with different crystallographic orientations is also reflected by the shape of the spectral lines.

The structure of the interface between monocrystalline gold [(111), (100), (110), and (210) faces] or silver electrodes [(111) and (100) faces] and an aqueous solution of 0.01 M NaF has been studied ellipsometrically.[53] As before, a strong dependence of the optical spectra near $E_{q=0}$ on the crystallographic orientation of the electrodes was noted [though the spectra of the reconstructed and of the nonreconstructed (100)Au faces do not differ very markedly]. The effect of the charge density *q* on the polarisation angle Δ depends on the sign of the charge; for $q < 0$ only a small $q = f(\Delta)$ response is observed. This is consistent with the assumption of a weak metal–solvent interaction. The sharp change in the level of the optical signals for $q > 0$, largely determined by the crystallographic orientation of the sample, can be attributed to the onset of specific adsorption of the anions and to a strong $M-H_2O$ interaction. Information on the surface structure was obtained by calculating the relaxation time of the free electrons τ: the greater is τ, the smaller is the difference in structure between the surface and the bulk. As expected, the highest value of τ was found for the most closely packed (111)Au face.

Subsurface defects (dislocations, vacancies, and their combinations) have a marked influence on the electrochemical characteristics of a monocrystal suface. The walls of the etch pits formed on defects can be described as a combination of terraces (*F* faces) and steps with breaks (*k* faces). This produces new adsorption–desorption peaks, not seen on the potential–current curves of well ordered surfaces of perfect monocrystals.[54] The application of a relatively small number of oxidation–reduction

cycles, or of a high-temperature anneal, eliminates the defect portions of the electrochemical process and finally yields an improved potential–current curve.

However, it hs been reported[55] that extending the range of applied potentials can produce irreversible changes in the potential–current curve as a result of a far-reaching breakdown in the initial structure of the metal. The same situation is found when the scan rate of the potential is increased (>0.1 V s^{-1}); fast cycling "strikes" the metal atoms in the near-surface layer from their equilibrium positions. This results in microfaceting, i.e. in a change in surface structure accompanied by the formation of highly coordinated adsorption s states. Fig. 15 shows, as an example, the cyclic potentiodynamic E, i curves for the (111)Au and (111)Pt faces for different scan rates and different ranges of the applied potential. The structure of the (111)Pt and (100)Pt surfaces has been studied by transmission electron microscopy (TEM) after various cycles of electrochemical treatment.[56,57]

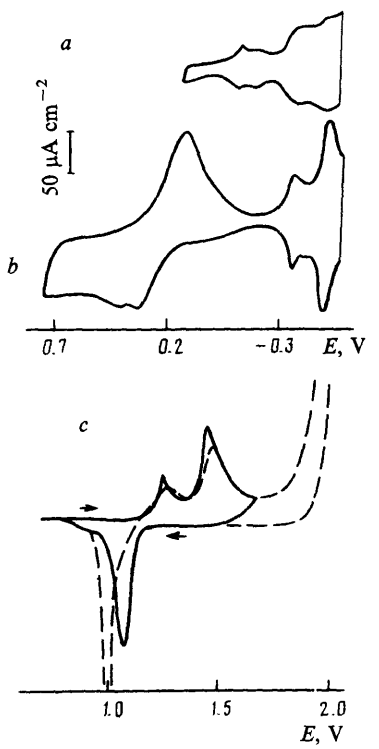


Figure 15. Current–voltage curves of the (111)Pt and (111)Au faces for different potential scan rates and different applied potentials: *a*, (111)Pt, 0.5 M H_2SO_4, V_E = 0.5 V s^{-1}, E = 0.15–(–0.48) V; *b* (111)Pt, 0.5 M H_2SO_4, V_E = 0.2 v s^{-1}, E = 0.70–(–0.5) V;[58] *c*, (111)Au, 0.1 M $HClO_4$, V_E = 0.02 V s^{-1}, E = 0.7–1.7 V (full line), E = 0.7–2.0 V (broken line).[93]

Let us examine more closely the electrochemical faceting process. The (111)Pt and (100)Pt faces were subjected to the so-called (100) treatment in a solution of 0.5 M H_2SO_4, consisting in the application of rectangular potential pulses (0.23–1.23 V) at a frequency of 3.5 kHz. Under these conditions the potential E varied cyclically between the hydrogen evolution region and the oxide formation region (–0.5–0.7 V) for a short time (0.5–5 s). This treatment had a radical influence on the morphology of the (111)Pt face [while the (100)Pt face was not significantly affected], and the results were comparable with the application of several hundred single pulses of the potential. After 5 s of this treatment the (111)Pt face showed an increased roughness K_M, the steps became flat and well defined, and the outline of the terraces was markedly altered by the formation of K faces (with atomic projections and hollows), seen in the TEM pictures as small kinks on the terrace surfaces. The monocrystallinity of the (111)Pt steps after the electrochemical treatment is explained by the ability of the steps to act as recesses for Pt adatoms, leading to cluster formation and thus being self-perpetuating. After 50 cycles of applied potential (0.77–0.53 V) with a scan rate of 0.2 V s^{-1} less than 10% of the surface has escaped the phase transition of the second kind (faceting).[58] In this case the shape of the E, i curve is similar to that obtained for polycrystalline platinum. Thus the parameters of the electrochemical treatment (E and V_E values, frequency of the applied pulses, etc.) have a strong influence on the morphology and on the crystallographic orientation of the experimenal faces. These effects explain the large differences in the published results.[59]

In the electrochemical reactions, as in the adsorption of hydrogen from the gas phase, the surface of metal monocrystals becomes reconstructed.[60] Homa, et al.[61] described the transition of the (100)–(5 × 20)Pt structure into the (100)–(1 × 1)Pt structure after contact with the 0.1 M HF + CO electrolyte while cycling E between 0.05 and 0.50 V or without an applied potential. These workers conclude[61] that the instability of the surface is due to the adsorption of small quantities of CO during the preparation of the electrode for the experiment, which suppresses the reconstruction. The reverse transition from the (100)–(1 × 1)Pt to the (100)–(5 × 20)Pt structure during the contact of platinum monocrytals with 0.5 M H_2SO_4 + 0.1 M $H_2C_2O_4$ was observed by Orts, et al.[62] This reconstruction is typical not only of the (100)Pt surface but also of the (310), (610), and (211) platinum K faces, which contain terraces with a (100) orientation. As suggested,[62] the reconstruction process is due to the specific adsorption of the $HC_2O_4^-$ ions. There are reports[63] of the reconstruction of the (110)Pt surface at the contact with 1 M H_3PO_4 [transition of the (1 × 1) into the (1 × 2) superstructure by cycling E between 0.065 and 0.750 V with V_E = 0.05 s^{-1}]. The reconstruction of the (111)Au surface in a dilute solution of HF and $HClO_4$ has also been studied.[64] The (111)Au surface was pretreated in ultra-high vacuum by Ar^+ ion bombardment followed by heat treatment. The two-dimensional (111)–($\sqrt{3}$ × 22)Au structure, unstable at any applied potential, was formed on the close packed (111)Au surface. This was followed by the structural transition of (111)–($\sqrt{3}$ × 22)Au into the ordered (111)–(1 × 1)Au structure, which survived 10 cycles of potential scanning (0.2–1.75 V, V_E = 0.05 V s^{-1}).

Reports on the stability of the (100)Au face reconstructed by a similar vacuum treatment are contradictory. Thus, it was shown[52] that the resulting (100)–(5 × 20)Au structure (a hexagonal close packed upper layer on a square sublattice) is stabilised by immersion in 0.01 M solutions of $HClO_4$ and H_2SO_4 over the whole range of applied potential, which excludes specific adsorption (up to 0.31 V in $HClO_4$ and up to 0.11 V in H_2SO_4). This reconstruction is suppressed only by the adsorption of ClO_4^- and SO_4^{2-} anions. However, other works[64,65] find that the (100)–(5 × 20)Au structure, like the (111)–($\sqrt{3}$ × 22)Au structure, is converted into the

ordered (111)−(1 × 1)Au structure at any applied poential. The difference in surface tension $\Delta\gamma_{ij}$ between these structures is only 0.06−0.09 eV, and therefore a phase transition of the second kind can take place even in the physisorption region with $E_b \simeq 0.1$ eV. The stability of the (100)−(5 × 20)Au structure in contact with an electrolyte is attributed[65] to contamination of the surface during the preparation of the gold monocrystals by silicon and alkali metals, which stabilise the reconstructed surfaces of the 3*d* transition elements.

The (110)Au surface is reconstructed after being annealed and cleaned in an ultra-high vacuum. It forms a (1 × 2) superstructure which survive cyclic changes in potential (−0.35−0.45 V) when immersed in 0.01 M $HClO_4$. Contamination of the clean (110)Au surface by small quantities of calcium induced the formation of a (1 × 3) structure, which was again transformed into a (1 × 2) structure by the application of a variable potential in the same electrolyte.[66] This is inconsistent with Hamelin's results.[65]

The reconstruction of the (100)Au face in 0.005 M H_2SO_4 during cyclic changes in E (−0.1−1.3 V) was studied by electroreflectance spectroscopy.[67] The difference between the optical spectra of reconstructed and of nonreconstructed surfaces was attributed[67] to the presence of surface Tamm states, suppressed by the adsorption of SAS during phase transitions of the second kind. From the increase (or decease) in the height of the characteristic peaks for the optical transitions from the *d* band to the empty surface states in the ER spectrum the kinetics of the reconstruction of the (100)Au face were determined.

Oxygen

In an electrochemical corrosion process it is important to allow for the surface relaxation of the oxygen adsorbed on the metal surface, which has a high chemical affinity for the transition metals. The chemisorption of oxygen (like the chemisorption of halide ions) at 298−2300 k increases the distance between the uppermost near-surface layers: $\Delta d_{12} = 2.0 \pm 1.0\%$ in the case of the $p(2 \times 2)$ surface structure observed for coverages $\theta_0 < 0.4$ *ML*, and $\Delta d_{12} = 5.2 \pm 1.5\%$ in the case of the $c(2 \times 2)$ for 0.4 *ML* $< \theta_0 <$ 0.46 *ML* (*p* and *c* refer to the cell types: *p* for primitive and *c* for centred). The particles adsorbed from the solution usually stabilise (freeze) both the normal and the tangential vibrations of the atoms in the surface layer of the metal.

The study of these vibrations was begun by Germer, et al.,[68] who examined the "loose" (110)Ni faces. In the first two layers the amplitudes of the vibrations in the mutually perpendicular <001> and <110> directions differed by a factor of ~1.5, and in the deeper layer (beyond the sixth) the amplitudes were comparable. The amplitude of the vibration of the surface layers normal to the surface (0.0117−0.0001 nm) is much greater than the amplitude of the atomic vibrations in the bulk (0.0080 nm); this ratio of the amplitudes, which is very important in corrosion studies, is not affected by the adsorption of oxygen. An important structural feature of the oxidation is the negligibly small effect of the relaxation of the surface layer of the crystal on the Coulombic barrier opposing the penetration of the adsorbed oxygen into the metal. Thus, for the (111)Cu face Bauschicher[69] showed that the reconstruction of the near-surface layer, which begins after the adsorption of the first three oxygen atoms (at $\theta_0 = 0.5$ *ML*), lowers the energy barrier to the penetration of additional oxygen atoms from 8.2 to 5.3 eV. This process initiates the reconstruction of the surface, since the chemical bond for the incorporation of additional oxygen atoms is strengthened.[70]

The reconstruction of the low-index faces of monocrystals as θ_0 is increased has long been recognised.[71] The work function Φ_M increases at first during the adsorption of the first portions of oxygen on the (001)Ni surface, and then decreases (due to the reconstruction of the first layer of the crystal). The kinetics of the reconstruction of the (2 × 4) into the (2 × 1) structure on the (011)Ni face during the adsorption of oxygen are described by the well known Avrami−Kolmogorov equation, which assumes an initial induction period:

$$V_t/V = 1 - \exp(-K_t t^m), \tag{17}$$

where V and V_t are the rate of reconstruction of the surface without and with oxygen respectively, K_t and m are coefficients and $m \simeq 0.3$. The height of the activation energy barrier is 0.23 eV. On the (001)Ni and (011)Ni faces the charge transfer from the nickel to the oxygen atoms increases with θ_0, and the energy of the Ni−O bond decreases,[70] as does also the number of holes in the 3*d* sub-band (as a result of the hybridisation of the 3*d* states of nickel and of the 2*p* states of the adsorbed oxygen).[72] The "fit" of the oxygen on the ideal surface of the *F* crystal face is improved by a decrease in Φ_M (and therefore also in S_{hkl}).[73]

The adsorption of oxygen on the metal surface is followed by the formation of oxide (which usually has semiconductor properties). For layer thicknesses smaller than the Debye length $l_D = [2\varepsilon_{D,Ox}\varepsilon_{D,V}(\Phi_M - \Phi_{ox})/e^2 n_{Ox}]^{1/2}$ the band bending in the oxide (the shift by E_0 from the Fermi level E_F) is described by the equation[74]

$$E_F - E_C = E_{C0} \pm [en^2_{Ox}(\Phi_M - \Phi_{Ox})(l_{Ox} - l_D)2\varepsilon_{D,Ox}\varepsilon_{D,V}], \tag{18}$$

where Φ_{Ox} is the electronic work function of the oxide, l_{Ox} is the thickness of the oxide layer, $\bar{n}_{Ox}$ is the average concentration of free electrons in the oxide, E_C is the energy of the bottom of the conduction band, E_{C_0} is the position of the bottom of the conduction band of the oxide for $l_{ox} > l_D$; $\varepsilon_{D,Ox}$ is the dielectric permittivity of the medium and $\varepsilon_{D,C}$ is the dielectric permittivity of free space ($\varepsilon_V = 8.854 \times 10^{-12}$ F m^{-1}). According to Eqn. (18) $E_F - E_C$ varies as the oxide thickness l_{ox} increases. The surface energy E_C is determined by the ratio of Φ_m to Φ_{Ox}, decreasing steeply at first when the adsorption layer of oxygen is formed and then stabilising as l_{ox} continues to increase. A decrease in γ^0_{ij} [and therefore also in ΔE, see Eqn. (6)] suppresses the electrochemical dissolution of the metal.

The ionic conductivity of the oxide films is exponentially dependent on the electric field within the oxide E_{Ox}, and can be calculated by the Günterschultz−Betz equation

$$i_+ = A_+ \exp(B_+ E_{Ox}), \tag{19}$$

where A_+ and B_+ are empirical constants of dimensions A m^{-2} and m V^{-1} respectively. The formation of these films on the *d* metals is made possible by the reconstruction of the first few layers of the crystals. Thus, in the $p(2 \times 2)0/(111)$Ni surface structure the length of the Ni−Ni bonds is increased by ~1.5 nm (sic., Ed. of Translation),[75] which helps the fitting of the next portions of oxygen and their clustering. According to LEED and AES data[76] at surface coverages of the (001)Ni surface by adsorbed oxygen $\theta_0 \leqslant 0.25$ *ML* ($T = 500$ K) we observe a $p(2 \times 2)$ structure, at 0.25 *ML* $\leqslant \theta_0 \leqslant$ 0.35 *ML* a $c(2 \times 2)$ as well as the $p(2 \times 20$ structure, and at $\theta_0 \geqslant$ 0.35 *ML* only the $c(2 \times 2)$ structure. Reiudle, et al.[76] assume that a $p(1 \times 1)$ structure is also possible. The most stable is the $p(2 \times 2)$

structure, in which the oxygen atom is in a highly coordinated state in the tetrapore.

In the least densely packed (110)Ni plane (as shown by some early experiments[77]) the oxygen successively forms the (3 × 1), (2 × 1), and (3 × 1) surface structures at $\theta_0 \leqslant 0.3$ *ML*. The oxygen occupies long bridging positions in a strongly coordinated state with a 3 nm Ni–O distance, forming rows in the [001] direction (Fig. 16). A decrease in the activation energy of 0.03–0.05 eV (at θ_0 = 0.5 *ML*) is produced by the rearrangement (faceting) of only the first three near-surface layers (Fig. 16*d*).

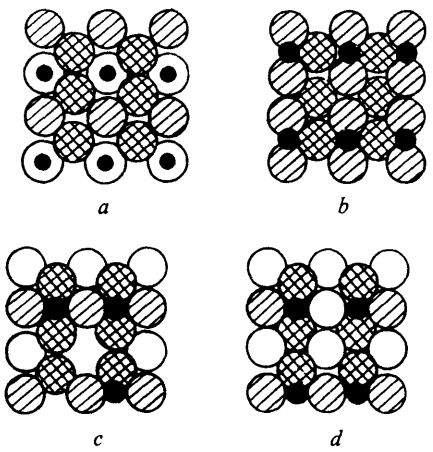


Figure 16. Structure of the (2 × 1) oxygen adsorption phase on the (110)Ni face: *a*, weakly coordinated adsorption of oxygen without reconstruction of the near-surface layer; *b*, reconstruction of the face through the replacement of Ni by O atoms; *c*, reconstruction of the face with displacement of the Ni atoms; *d*, faceting of the face during the adsorption of O ("tooth separation" model[77]).

Comparing the chemical compositions of oxygen layers prepared from the gas phase (10^{-4} Pa, 500 nm) and by electrochemical oxidation at a constant potential *E* (0.01 M $HClO_4$, 1.05 V) shows that in the latter case the NiO layer (l_{Ox} = 85 nm) is covered with a hydroxide layer (l_{HOx} = 25 nm).[78] The structures of the oxide layers are also different: the (100)NiO face is formed from the gas phase and a disordered phase with local inclusions of (111)NiO from the electrolyte.

The energy of the M–O bond is quite high (4.0–14.0 eV), and the dissolution of the oxide at the corrosion potential E_{cor} in pure water according to Purbaix' data[79] seems thermodynamically improbable for many *d* metals. The breakdown of the oxide in aqueous media is accompanied by the penetration of anions (A^-) into the oxide with simultaneous adsorption of water molecules. Some comments by Vijh on these processes[80] are based on the relative values of the dielectric constants of water (ε_{D,H_2O}) and of the oxide ($\varepsilon_{D,Ox}$), and of the electric fields E_{H_2O}, E_{ox}. For an anodic potential of 1 V a field $E_V = 10^{10}\,\varepsilon_{D,V}$ V m^{-1} normal to the electrode surface is produced, in a vacuum, in an oxide layer 10 nm thick.

Table 4. Dielectric constants of the oxides.

Oxide	$10^8 E_{Ox}$, V m^{-1}	ε_{Ox}	$10^{10} D$, V m^{-1}	$10^3(1/\varepsilon_{Ox})$	l_D, nm
Bi_2O_3	2.2	40	0.88	25.0	30.0
UO_3	3.6	25(UO_2)	0.90	40.0	11.9
Y_2O_3	4.4	18	0.79	55.5	23.9
Nb_2O_5	4.6	41	1.92	24.1	11.8
ZrO_2	5.1	22–25	1.02–1.35	40.0	16.0
TiO_2	5.0	15–40	0.75–2.00	25.0	6.4
WO_3	5.5	42(WO_2)	2.31	23.8	5.5
Ta_2O_5	6.2	27	1.71	36.2	7.3
Al_2O_3	7.9	8–10	6.32–8.29	95.2	12.7
SiO_2	26.0	3	0.91	285.7	4.2

In an aqueous solution (unlike a vacuum) we must allow for the adsorption of water and for the formation of an electrical double layer. The normal field at the anode–electrolyte contact is $E_{H_2O} = E_V/\varepsilon_{D,H_2O}$; for an anodic oxide it is $E_{ox} = E_V/\varepsilon_{D,Ox}$. Therefore we can write $E_V = E_{H_2O}\varepsilon_{D,H_2O} = E_{Ox}\varepsilon_{D,Ox} = 1 \times 10^{10}$ V m^{-1} and characterise the changes in the oxide in terms of the dielectric displacement vector. Indeed, for many oxides we find that $E_V \equiv D$ = const (Table 4). By using the universal constant *D* we can explain the formation of thick layers on the valve metals and of thin layers on the noble metals. The width of the tunnelling barrier l_D of the oxides is smaller in the metals which have a high chemical resistance. We can lower l_D and improve the electronic conductivity of the oxides of the valve metals (Nb, Ti, Zr) by anodic treatment in very concentrated alkaline solutions with anodic current densities $i_a = (2.5–4.0) \times 10^4$ A m^{-2}, E = 35 v, T = 303 K, t = 10–20 s.[81]

The thermodynamic description of the simultaneous adsorption of A^- anions and of water molecules on the metal surface:

$$A^-(H_2O)_n + (H_2O)_{ads}(M) \rightleftarrows A^-(M) + (H_2O)_{n+1},$$

requires a knowledge of the hydrophilicity or hydrophobicity ΔG°_{hydr} of the adsorbent.[82] The change in Gibbs free energy is

$$\Delta G^\circ_{ads} = \Delta G^\circ_{hydr} + \Delta G^\circ_{M-A^-} - \Delta G^\circ_{M-H_2O}, \qquad (20)$$

where $\Delta G^\circ_{M-A^-}$ and $\Delta G^\circ_{M-H_2O}$ are the parts of the free energy responsible for the adsorption of the anion and of water, and $\Delta G^\circ_{hydr} = \Delta G^\circ_{A^--H_2O}$ is the chemical energy of hydration of the anion. According to Trasatti's calculations[82] the linear increase in the zero-charge potential $E_{q=0}$ with increasing reticular density of

the monocrystal surface S_{hkl} is responsible for a decrease in ΔG°_{ads}. For two corroding metals in contact with the solution Eqn. (20) becomes

$$\Delta(\Delta G^\circ_{ads}) = -\Delta(\Delta G^\circ_{M-H_2O}). \quad (21)$$

Halide ions

Experimental determinations of ΔG° have been carried out for systems composed of halide ions and well characterised low-index faces of noble metals.[83] Depending on the reticular density S_{hkl} the values of the second term in Eqn. (20) can be arranged in the sequence

$$-\Delta G^\circ[(111)M\text{–}Hal^-] > -\Delta G^\circ[(001)M\text{–}Hal^-] > -\Delta G^\circ[(011)M\text{–}Hal^-].$$

The specifically adsorbed Hal^- anions weaken the bond in the $M-H_2O$ complex. In crystals with a covalent bond and *s, p* metals (Cd, Sn, Bi) the relationship (21) was tested by studying the adsorption of aliphatic alcohols,[84] assuming that the interactions of $R-OH$ (where $R \equiv nCH_2$ denotes the methyl groups in the SAS) with the surface are negligible (for $nCH_2 = 0$, $\Delta G^\circ = 0$), i.e. the change in free energy per methyl group should be zero. The ability of the SAS to become adsorbed on two corroding metals in ohmic contact (often met in practice) is determined by the properties of the water in the EDL and in the bulk of the solution:

$$\frac{\Delta(\Delta G^\circ_0)}{\Delta n} = \frac{\Delta(\Delta G_S)}{\Delta n} - \frac{\Delta(\Delta G_V)}{\Delta n}. \quad (22)$$

The change in the energy of hydrophobic hydration in the bulk (ΔG_V) and in the EDL (ΔG_S) for aliphatic alcohols, calculated by Eqn (21), shows that the contribution of the interaction energy of the water molecules to the energy of adsorpion is insignificant and approximately the same for different *s, p* metals.[84]

Water on a metal surface has a low-entropy structure; the entropy factor is determined by the *(hkl)* of the surface. In the case of chemisorbed halide ions incorporated in the interstitial sites between the surface metal atoms the energy term is characterised, as for $H_{ads}(M)$ and $O_{ads}(M)$, by two maxima, i.e. we have states of strong and of weak specific adsorption. It is believed that the transfer of charge from the halide ion to the metal is accompanied by a change in the orientation of the water molecules in the $Hal(H_2O)_6^-$ cluster being discharged (from the orientation with the oxygen atoms towards the surface to the orientation with the hydrogen atoms towards the surface[85]). The formation of adsorption cluster structures on the metal surface strengthens the charge transfer as compared with the single atom: the charge transfer coefficient (the Esin–Markov coefficient K_{EM}) is greater for the cluster than for the single Hal atom.

In the strong specific adsorption the Hal^- ion is accommodated in a many-centre adsorption site on the metal surface, but if the adsorption is weak and the transfer of charge is only partial the reconstruction of the hydration shell of the ion is not substantial. Crystallographic factors have a large influence on the standard thermodynamic parameters of the adsorption of halide ions. On platinum electrodes, and on electrodes of the other *d* metals, we observe an increase in the entropy of adsorpion and a decrease in the Gibbs free energy and in the enthalpy. The standard thermodynamic parameters for the adsorption of Cl^- ions on Pt and on Hg (kJ mol^{-1}) are:[86]

	ΔG	ΔH	$T\Delta S$
Hg	–2.06	–10	7.9
Pt	–6.10	–30	23.8

The "charging" of the metal surface by halide ions suppresses the formation of passivating oxygen compound: the thickness of the passivating layer l_{Ox} decreases with increasing concentration c_{Hal^-} in the solution and with increasing time of immersion of the electrode in the medium containing halogen. The halide ions can be arranged in the following series with respect to their effectiveness in the dissolution of the 3*d* transition metals: $F^- > Cl^- > Br^- > I^-$. The electrically negative halide ions adsorbed on the metal surface weaken the $d-\pi^*$ interaction with the passivating chalcophilic particles, and they assist the desorption of adsorbed hydrogen from the surface of the transition metals. The desorbing action of the halide ions can be adequately explained in terms of formal kinetics. For the Volmer–Heyrovsky mechanism of the hydrogen evolution reaction (HER), realised as two consecutive one-electron transfers to the M_k active centres:

$$H_9O_4^+ + M_k + e^- \rightarrow M_kH_{ads} + 4H_2O, \quad (23)$$

$$M_kH_{ads} + H_9O_4^+ + e^- \rightarrow M_k + 4H_2O + H_2, \quad (24)$$

the conjugated competing process

$$Hal^- + M_k \rightarrow M_kHal_{ads} + e^-, \quad (25)$$

$$M_kHal_{ads} + Hal^- \rightarrow M_k + Hal_2 + e^-, \quad (26)$$

leads to the generation of very mobile charge carriers which are free to tunnel. Reactions (23)–(26) on metal surfaces completely or partially covered with an oxide phase improve the electronic conduction in the solid phase and lower the chemical resistance of the metal.

Data on the coherence of the contacting phases and on the structure of halogen ad-layers on the well characterised surfaces of noble-metal monocrystals have been obtained in recent years.

Platinum

Structural studies by LEED and AES methods of the (111)Pt face in contact with aqueous solutions of KBr or $CaBr_2$ at different pH have shown that the adsorbed halide ion forms an ordered (111)Pt–(3 × 3)Br structure on the metal surface,[87] similar to the structure obtained by exposing platinum to HBr vapour in a vacuum.[88] This structure can exist at positive potentials, but it is reconstructed by the incipient reduction (with desorption) of the bromine atoms at –0.1 V by the scheme

$$(111)Pt\text{–}(3\times3)Br[\theta_{Br} = 4/9ML] + $$

$$+ xe^- \rightleftarrows (111)Pt(4\times4)[\theta_{Br} = 7/16ML] + xBr^-,$$

where x corresponds to only $4/9 - 7/16 = 0.007$ electron per Br^- anion on one surface Pt atom. This means that the adsorption of bromide (like that of other halide ions) is a redox process with partial charge transfer. The adsorption of halide ions is more marked in acid solutions than in alkaline solutions, mainly because

of the competition with adsorbates containing oxygen [see Eqn. (20)], which interact strongly with the surface. The ordered (1 × 1) structure and the diffuse oxygen surface layer with $\theta_0 = 0.5$ *ML* are retained during the initial stages of oxidation of the platinum, but in the second stage (as was pointed out above) the ordering is perturbed in both the platinum and the oxygen.

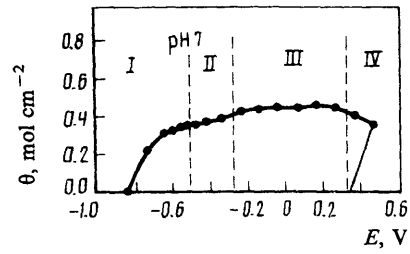


Figure 17. Dependence of the packing density of the iodine atoms on the (111)Pt face upon the electrode potential:[87] *I*, region of existence of the $(\sqrt{3} \times \sqrt{3})R30°-I$ superstructure; *II*, region of simultaneous existence of the $(\sqrt{3} \times \sqrt{3})R30°-I$ and $(\sqrt{7} \times \sqrt{7})R19°-I$ superstructures; *III*, region of existence of the $(\sqrt{7} \times \sqrt{7})R19°-I$ superstructure; *IV*, region of existence of the (3 × 3)−I superstructure.

Immersing the (111)Pt face in aqueous solutions containing iodine produces an ordered ad-layer of iodine atoms[87] whose packing density and structure depend on the potential (Fig. 17). The (111)Pt−(3 × 3)I[θ_I = 4.9 *ML*] structure exists at moderately high positive potentials (~0.5 V), the (111)Pt−$(\sqrt{7} \times \sqrt{7})R19°$−I[$\theta_i$ = 3/7 *ML*] at intermediate potentials (~0.1 V), and the (111)Pt−$(\sqrt{3} \times \sqrt{3})R30°$−I[$\theta_I$ = 1/3 *ML*] at negative potentials (< −0.5 V).

The reductive desorption of I^- anions takes place at very high negative potentials (< −0.8 V). All these structures are observed also after treating (111)Pt with HI and I_2 vapour in a vacuum.[89] The adsorption of iodine vapour on the stepped [6(111) × (111)]Pt(*s*) platinum surface failed to reveal even a partial affinity of the iodine atoms for the stepped formations on the surface.[90] Instead, the presence of steps (kinks) produced several phase domains with a local (3 × 3) or $(\sqrt{3} \times \sqrt{3})R30°$ geometry, and a structural correspondence of the adjoining terraces [6(111) × (111)]Pt−(3 × 1*T*)−I, [6(111) × (111)]Pt−(8 × 1*T*)−I, and [6(111) × (111)]Pt−(20 × 2*T*)−I.

As could have been expected, the chemosorption of chlorine anions on a platinum electrode is much weaker than the chemisorption of bromide or iodide. HCl species in a vacuum do not form an ordered layer on the (111)Pt face.[87] The peak on the *E*, *i* curve produced by the adsorption and desorption of chlorine can be distinguished from the hydrogen peak only because the former process [see reaction (25)] is independent of pH.[91] For $c_{HCl} \leqslant 0.01$ mol dm^{-3} the adsorption of chlorine becomes stronger, and produces an ordered (111)Pt−(3 × 3)Cl (τ_{Cl} = 0.33 *ML*) layer. The packing density of the chlorine is close to 0.5, which corresponds to the h.c.p. lattice.

Silver

The adsorption of halide ions on the (111)Ag face is an active process of the oxidation−reduction type,[87] as in the case of platinum. The reductive desorption of chlorine and bromine takes place almost entirely at negative potentials (< −0.8 V), and the iodine remains adsorbed over a wide range of potential (−0.6 to + 0.6 V). Chlorine and bromine atoms form simple (111)Ag−$(\sqrt{3} \times \sqrt{3})R30°-x$ structures, with θ_x = 1/3 *ML*, whereas iodine gives the structures which are also obtained in the electrodeposition of the silver on a (111)Pt face previously treated with iodine (Fig. 18). Thus the silver surface is reconstructed in solutions containing iodine.

Studies of the adsorption of halide ions by thermal desorption and UPS have shown that the adsorption−desorption characteristics are independent of the nature of the halogen.[92] Comparing the results for (110)Ag and (111)Ag confirms the strong topological dependence of the adsorpion of the halogens.

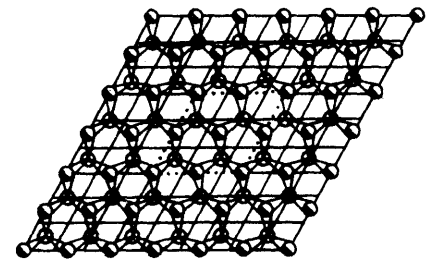


Figure 18. Structure of the (111)Pt−(3 × 3)Ag, I face; (θ_{Ag} = θ_I) = 4/9 *ML*.[87]

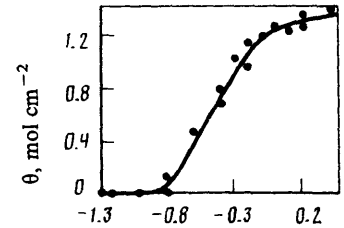


Figure 19. Dependence of the packing density of the bromine atoms on the (100)Au face upon the electrode potential.[93]

Gold

For the other noble metals only a few data on adsorption and surface reconstruction are available so far. The adsorption of bromine on the (100)Au face from aqueous solutions produces the (5 × 20)→(1 × 1) structural transition.[93] The dependence of the bromine packing density on the electrode potential (Fig. 19) can be described by the Avrami−Kolmogorov equation (17) with a long induction period and a potential < −0.5 V.

Copper

Chlorine adsorbed from a 10^{-3} M solution of HCl on the (100)Cu face forms the (100)Cu$-(\sqrt{2} \times \sqrt{2})R45°-$Cl structure with $\theta_{Cl} = 0.5$ *ML*, almost irrespective of the applied potential and of the concentration of chloride ions.[94] Desorption of the adsorbed chlorine is observed by immersing the electrode in 10^{-3} M H_2SO_4 at $E < -0.11$ V.

VI. Conclusions

Our analysis of the metastable states of the near-surface layer of metallic crystals in contact with a condensed (liquid) or a noncondensed (gas) medium suggests new approaches to corrosion-electrochemical processes (phase transitions of the first kind, accompanied by the evolution of adsorbed gases and by the adsorption and penetration of light chalcophilic species). Unique properties are found in the hydrogenated metal–electrolyte system. since hydrogen has an anomalously high diffusion coefficient in metals it is easly redistributed in the lattice and interacts with surface and subsurface defects, altering their concentration, topology, and energy state. Other outstanding aspects of the behaviour of hydrogen in condensed media are the ease with which it can lose (or gain) an electron, the ability of protons to generate heavier species dissolved in the metal, the contribution of H^- and H^+ to the deprotonation of adsorbed water structures, and the formation of new compounds in the adsorbed layers.

A new topic in electrochemistry has been created: the electrochemistry of monocrystals with well characterised surfaces. The possibility of analysing surface rearrangements by a whole group of high-resolution physical methods not only creates a new situation in this field of knowledge but also forces us to reconsider the traditional electrochemical approaches, which relied exclusively on an analysis of integral kinetic information on the transfer of charge across the metal–electrolyte interface

References

1. A A Lopatkin *Teoreticheskie Osnovy Fizicheskoi Adsorbtsii* (Theoretical Foundations of Physisorption), Izd. Moskov. Univ., 1983, 339 pp.
2. M Hentzer *Dynamic Phenomena on Surfaces, Interfaces, and Superlattices* (Proceedings of the International Summer School at Erice, July 1984), Berlin, 1985, p. 14
3. A Hamelin *Modern Aspects of Electrochemistry*, Plenum Press, New York, 1985, No. 16, p. 1
4. A Bartolini, F Ercolessi, E Tosatti *Helv. Phys. Acta*, 1989, **62** 820
5. J P Bourdin *J. Phys. F*, 1988, **18** 1801
6. P Horiuti *Z. Phys. Chem. (BRD)*, 1958, **15** 162
7. C T Campbell *Surf. Sci.*, 1986, **167** 181
8. V I Zubov *Zh. Fiz. Khim.*, 1988, **62**(4) 1026 [English translation in *Russ. J. Phys. Chem.*, 1988(4)]
9. E B Bezlepkina, Z V Kasatkin, V S Tsoi *Elektrokhimiya*, 1988, **24** 226
10. J Clavilier, D Armand, S G Sun, M J Petit *J. Electroanal. Chem.*, 1986, **205** 267
11. D Woodruff, T Delchar *Modern Methods of Studying Surfaces* (Translated into Russian), Mir, Moscow, 1989, 496 pp.
12. F N Chukhnovskii, V N Ol'tsev *Itogi Nauki i Tekhniki. Seriya Metallovedenie i Termicheskaya Obrabotka* (Advances in Science and Technology. Metal Science and Heat Treatment Series), VINITI, Moscow, 1988, Vol. 22, p. 125
13. V S Bagotskii *Osnovy Elektrokhimii* (Foundations of Electrochemistry), Khimiya, Moscow, 1988, 400 pp.
14. M Parlapanski *Proceedings of the Eleventh International Corrosion Congress*, Florence, April 1990, Vol. 3, p. 517
15. M Jaycock, J Parfitt *Chemistry of Interfaces* (Translated into Russian), Mir, Moscow, 1988, 400 pp.
16. A Ya Gokhshtein *Poverkhnostnoe Natyazhenie Tverdykh Tel i Adsorbtsiya* (The Surface Tension of Solids and Adsorption), Nauka, Moscow, 1976, 399 pp.
17. L D Landau, E M Lifshits *Statistichskaya Fizika* (Statistical Physics), Fizmatgiz, Moscow, 1967, 415 pp.
18. B Horovitz, R J Gooding, J A Krumhansl *Phys. Rev. Lett.*, 1989, **62** 843
19. J Bénard (Editor) *Adsorption on Metal Surfaces*, Elsevier, Amsterdam, 1983, p. 337
20. J S Luo, B Legrand *Phys. Rev. B*, 1988, **38** 1728
21. K Müller *Ber. Bunsenges. Phys. Chem.*, 1986, **90**(3) 184
22. M W Roberts, C S McKee *Chemistry of the Metal–Gas Interface* (Translated into Russian), Mir, Moscow, 1981, 539 pp.
23. W Ruchta, W Nichtl, W Oed, N Bickel *Phys. Rev. B*, 1989, **39** 1020
24. M Jo, M Onchi, M Nishjina *Surf. Sci.*, 1985, **154** 417
25. D L Adams, C S Sprensen *Surf. Sci.*, 1986, **166** 495
26. T V Berenshtein, A M D'yachenko *Ukr. Fiz. Khim.*, 1986, **31** 905
27. V P Zhdanov *Elementarnye Fiziko-khimicheskie Yavleniya na Poverkhnosti* (Elementary Physicochemicl Phenomena on Surfaces), Nauka, Moscow, 1989, 373 pp.
28. K H Benneman, D Tomanek *Phys. Rev. Lett.*, 1986, **5/7** 2594
29. A I Rusanov *Fazovye Ravnovesiya i Poverkhnostnye Yavleniya* (Phase Equilibria and Surface Phenomenon), Khimiya, Leningrad, 1967, 388 pp.
30. R Bandoing, Y Gauthier, M Lundberg, T Rundgren *J. Phys. C.: Solid Phys.*, 1986, **19** 2825
31. O Teschke, D M Soares, F Galembeck *J. Electrochem. Soc.*, 1985, **132** 1284
32. K Christmann *Mol. Phys.*, 1989, **66**(1) 1
33. B Voigtländer, S Lehwald, H Ibach *Surf. Sci.*, 1989, **208**(1/2) 1
34. Y Kuk, P J Silverman, H Q Nguyen *J. Vac. Sci. Technol. A*, 1988, **6**(3) Pt. 1 576
35. D A Harrington, P R Norton *J. Vac. Sci. Technol. A*, 1988, **6**(3) Pt. 1 778
36. A-S Martensson *Surf. Sci.*, 1989, **215**(1/2) 55
37. K D Rendulic *Appl. Phys. A*, 1988, **47**(1) 55
38. K W Jacobsen, J K Norskov *Phys. Rev. Lett.*, 1987, **59**(24) 2764
39. E M McCash, S F Parker, Jh Pritchard *Surf. Sci.*, 1989, **215**(3) 363
40. W Nichtle, N Bickel, L Hammer *Surf. Sci.*, 1987, **188**(8) 279
41. D King *Phys. World*, 1989, (3) 45
42. T V Kalish, M E Belyaeva, S I Sergeev *Elektrokhimiya*, 1987, **23**(1) 126
43. D Chauveau, C Guillot, B Villette *Solid State Commun.*, 1989, **69**(11) 1015
44. J R Engstron, W Tsai, W H Weinberg *J. Chem. Phys.*, 1987, **87** 3104

45. K Mortensen, F Besenbacher, I Stensgaard *Surf. Sci.*, 1989, **211–212** 813
46. P J Feibelman, D R Hamann *Surf. Sci.*, 1987, **182**(3) 411
47. A Hamelin *Modern Aspects of Electrochemistry*, Plenum Press, New York, 1985, No. 16, p. 123
48. G V Khaldeev, T F Borisova *Elektrokhimiya*, 1988, **24**(5) 618
49. N Furuya *Inf. Mater. Energy Theory Life*, 1988, **56**(3) 166
50. A Rodes, K Elachi, M A Zamakhchari, J Clavilier *J. Electroanal. Chem.*, 1990, **284**(1) 245
51. J E Fulghum, G E McGuire, L M Musselman, R J Nemanich *Anal. Chem.*, 1989, **61**(12) 243
52. D M Kolb *Phys. Chem.*, 1988, **92** 1175
53. F Chao, M Costa, J Lecoeur, J P Bellier *Electrochim. Acta*, 1989, **34**(12) 1627
54. E B Bezlepkina, Z V Kasatkin, V S Tsoi *Elektrokhimiya*, 1987, **23**(10) 1419
55. A Hamelin *Portug. Electochim. Acta*, 1987, **5** 77
56. D M Kolb *J. Vac. Sci. Technol.*, 1986, **4**(3) 1294
57. T Twomey, Y Uchida *Z. Phys. Chem. (BRD)*, 1988, **160**(1/2) 1
58. S Sugawara, K Itaya *J. Chem. Soc. Faraday Trans.*, 1989, **85**(6) Pt. 1 1351
59. A Visintin, J C Canullo, W E Triaca, A J Arvia *J. Electroanal. Chem.*, 1988, **239**(1/2) 67
60. A M Brodskii, L I Daikhin *Elektrokhimiya*, 1988, **23**(8) 1095
61. A S Homa, E Yeager, B Cahan *J. Electroanal. Chem.*, 1982, **150** 181
62. J M Orts, J M Feliu, A Aldaz, J Clavilier *J. Electroanal. Chem.*, 1990, **281**(1/2) 199
63. F Cases, E Morallon, J L Vazquez *Portug. Electrochim. Acta*, 1989, **7** 131
64. A T D'Agostino, P N Ross *Surf. Sci.*, 1987, **185**(1/2) 88
65. A Hamelin *J. Electroanal. Chem.*, 1988, **255**(1/2) 281
66. R Michaelis, D M Kolb *Surf. Sci.*, 1990, **234**(3) 281
67. D M Kolb, C Franke *Appl. Phys. A*, 1989, **49**(4) 379
68. A U McRae, L H Germer *Surf. Sci.*, 1964, **2** 522
69. Ch W Bauschicher *Chem. Phys. Lett.*, 1985, **118** 544
70. W Ravenek, F M M Geurts *J. Chem. Phys.*, 1986, **84** 1613
71. H Farnsworth *The Gas–Solid Interface* (Translated into Russian), Mir, Moscow, 1970, p. 359
72. A Seiter, C S Feigerle, I L Pena, R J Celotta *Phys. Rev. B.: Condensed Matter.*, 1985, **32** 7776
73. H Niehus, G Comsa *Surf. Sci.*, 1985, **151** 171
74. G P Peka *Fizicheskie Yavleniya na Poverkhnosti Poluprovodnikov* (Physical Phenomena on Semiconductor Surfaces), Vischcha Shkola, Kiev, 1984, 214 pp.
75. I S Caputi, S Holloway, I K Nirskov *Surf. Sci.*, 1986, **152/153** 660
76. S Reiudle, G M Pastor, K H Benneman *Surf. Sci.*, 1989, **211/212** 912
77. T Engel, K H Reider, I P Batra *Surf. Sci.*, 1984, **148** 321
78. F T Wagner, Th E Moylan *J. Electrochem. Sci.*, 1989, **136** 2498
79. M Pourbaix *Atlas d'EquilibresElectrochimiques*, Gauthier-Villars, Paris, 1963, p. 415
80. A K Vijh *React. Solids*, 1988, **4** 341
81. L P Bicelli, P Pedeferri, G Razzini *Int. J. Hydrogen Energy*, 1986, **11** 647
82. S Trasatti *Electrochim. Acta*, 1983, **28** 1083
83. G Valette *J. Electroanal. Chem.*, 1988, **255** 215
84. F I Danilov, V I Grishchuk, S A Panasenko *Ukr. Khim. Zh. (Russ. Ed.)*, 1989, **55** 830
85. A M Kusnetsov, R R Nazmutdinov, M S Shapnik *Elektrokhimiya*, 986, **22** 836
86. S Minc, M Jurkiewicz-Herbich *J. Electroanal. Chem.*, 1972, **34** 351
87. A T Hubbard *Chem. Rev.*, 1988, **88**(4) 633
88. G A Garwood, A T Hubbard *Surf. Sci.*, 1982, **112** 281
89. F Lu, G N Salaita, X Baltruschat, A T Hubbard *J. Electroanal. Chem. Interfacial Electrochem.*, 1987, **222** 305
90. A Wieckowski, B C Schardt, S D Rosasco, J L Stickney *Surf. Sci.*, 1984, **146** 115
91. T Solomun, A Wieckowski, S D Rosasco, A T Hubbard *Surf. Sci.*, 1984, **147** 211
92. H Hinzert, K K Kleinherbers, E Janssen, A Goldmann *Appl. Phys. A*, 1989, **49** 313
93. D Trevor, C E D Chidsey, D N Loiacono *Phys. Rev. Lett.*, 1989, **62** 929
94. C B Elers, I Villegas, J L Stickney *J. Electroanal. Chem.*, 1990, **284**(2) 403

Translated from *Uspekhi Khimii* **61** 765–791 (1992) U.D.C. 541.128.13

Mechanism of the interaction between Group VIII metals and oxides of transition elements

O S Alekseev, Yu A Ryndin
Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk

ABSTRACT. The results of research into the chemisorptive and catalytic properties of Group VIII metals supported on oxides of transition elements are reviewed. The mechanisms put forward to account for the effects of a strong interaction between metal and support are discussed. The causes of the strong interaction between metal and support are analysed using the results of studies on the properties of $(M + E^{IV})/SiO_2$ model systems.

The bibliography includes 187 references.

Contents

I. Introduction 417
II. Properties of Group VIII metals supported on oxides of transition elements 418
III. Models of the interaction between metals and oxides of transition elements 419
IV. Study of the mechanism of the interaction between Group VIII metals and oxides of transition elements using $(M + E^{IV})/SiO_2$ model systems 424

I. Introduction

Supported metal catalysts are being used to an increasing extent in large-tonnage industrial processes involving the chemical treatment of hydrocarbon raw materials (reforming, hydrogenation, dehydrogenation, etc.), and in the future they may also be used for the synthesis of a wide range of hydrocarbons and oxygen-containing compounds from CO and H_2. Therefore, extending the range of control over their catalytic properties is a vital task. Variation of the dispersity, the use of promoters, and varying the nature of the support constitute effective methods of controlling the activity and selectivity of a supported metal.

In the 1960s Schwab and Solymosi[1,2] called into question the generally held view at the time that an oxide support that prevented the sintering of a metal was inert. In 1978 Tauster et al.[3] discovered the effects of a strong metal–support interaction (SMSI) for metals that were supported on oxides of transition elements (TE). After publication of this pioneering work the number of studies in this area started to increase at an exponential rate (Fig. 1), and in 1982 an international conference devoted to the effect of supports and additives on the catalytic properties of metals was organised. It is worth noting that even at that time there was an intuitive understanding of the common nature of the mechanisms of the action of TE oxides as supports and promoters of active metals (also reflected in the name of the conference). To date more than 1000 studies on the problem of SMI have appeared in the literature. In correlating these studies it may be noted that the consequences of SMSI are: a) a reduction in specific chemisorption of CO and H_2 on a metal; b) a sharp decrease in specific catalytic activity of the metal in reactions involving hydrocarbons; c) an increase in specific catalytic activity and a change in selectivity in the hydrogenation of CO; d) an intensification of these effects with an increase in the temperature of reduction of the catalyst and their reversible disappearance after oxidation followed by treatment with hydrogen at a moderate temperature.

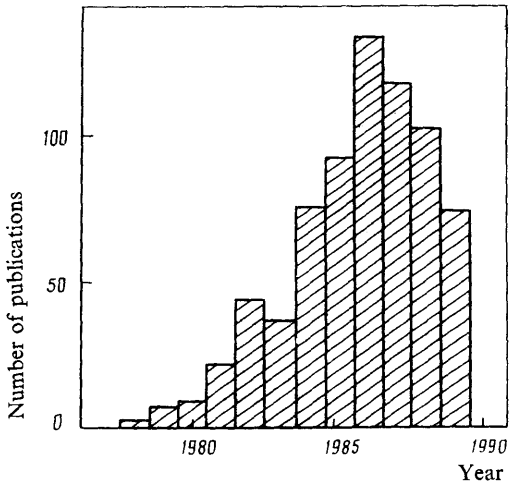


Figure 1. Growth trend for the number of publications on the problem of SMSI.[179]

It should be noted that effects similar to those of SMSI had previously been detected by Ermakov et al.[4–8] in catalysts prepared by fixing highly dispersed particles of Pd and Pt on low-valent surface Mo, W, or Re ions. In these studies the idea that the effect of the addition of an element that is difficult to reduce on the properties of Pd and Pt is caused by an interaction between the metal clusters and the surface ions of the promoter was first developed and confirmed experimentally. This interaction increases the stability of the dispersed metal towards sintering and is responsible for a change in its electronic properties, resulting in a change in its chemisorptive and hence its catalytic properties.

Despite the fact that at the present time a very large amount of experimental material on research into the properties of catalysts with SMSI has been collected, reviews concerned with classification

of the accumulated data are virtually absent from the literature. In the present review there is the task of analysing the results obtained by different research workers in the field of SMSI. At the same time particular attention is given to an analysis of models put forward to explain the effects of SMSI.

II. Properties of Group VIII metals supported on oxides of transition elements

1. Chemisorptive properties

The first systematic study of the adsorption of CO and H_2 on different Group VIII metals supported on TiO_2 was undertaken by Tauster et al.[3] It was as a result of this investigation that the unusual phenomenon known as "a strong metal–support interaction" was observed. In fact, the reduction of Group VIII metals supported on TiO_2 at a low temperature (473 K) results in the formation of dispersed catalysts that are capable of the chemisorption of considerable quantities of CO and H_2. At the same time when the reduction temperature is increased to 773 K the quantity of chemisorbed CO and H_2 on all systems decreases almost to zero, while according to the data of electron microscopy and X-ray phase analysis such a significant change in the chemisorptive properties as this is not due to sintering of the supported metal.[3]

The range of supports on which the chemisorptive properties of metals are altered was considerably extended in subsequent studies.[9–12] Thus, on increasing the reduction temperature to 773 K for Ir supported on Nb_2O_5, V_2O_3, Ta_2O_5, almost complete suppression of the chemisorptive properties towards CO and H_2 was observed. It should be noted that treatment with oxygen followed by reduction at a moderate temperature (573 K) almost completely restores the chemisorptive capacity of the supported metals.

Water has a similar influence on the SMSI effect. It was shown by Duprez and Miloudi[13] that treatment of Pt, Ni, and Rh supported on TiO_2 with water vapour at 773 K completely eliminates the phenomenon of a decrease in chemisorption of H_2. At the same time, on a number of supports such as SiO_2, Al_2O_3, Se_2O_3, MgO, ZrO_2, V_2O_3, no perceptible changes in the chemisorptive properties of supported metals were observed over a wide range of reduction temperatures. On the basis of these results the authors[9–12] assumed that the SMSI effect is characteristic of readily reducible oxides of transition elements. In fact, it was demonstrated by Loye et al.[14] in a study of the chemisorption of H_2 on Ni/Ti_nO_{2n-1} that the ratio of H : Ni decreases substantially on increasing the degree of reduction of the support. Beringhelli et al.[15] reported a decrease in chemisorption of H_2 on Rh/ZrO_2, although this had not previously been found for Ir/ZrO_2.[9] The patterns of variation in chemisorptive properties of Group VIII metals found by Tauster et al.[3] were confirmed in the studies of other authors.[16–22]

An interesting correlation between the chemisorptive properties of Pt and the heats of adsorption of H_2 and CO was found by Vannice et al.[23–25] It was shown that the heats of adsorption of CO and H_2 on Pt deposited on different supports (SiO_2, Al_2O_3, TiO_2) with low-temperature reduction of the catalysts did not depend on the nature of the oxide but were governed by the dispersity of the supported metal, being equal to 28 and 30 kcal mol^{-1} for CO and H_2 respectively. However, the high-temperature reduction of Pt/TiO_2 in hydrogen (773 K) resulted in a substantial decrease in the heats of adsorption for CO to 10 kcal mol^{-1} and for H_2 to 6–10 kcal mol^{-1}. Thus, for Pt/TiO_2 when the degree of covering the surface of Pt with CO and H_2 decreases, there is a reduction in the heats of chemisorption of these gases. Apart from that for Pt/TiO_2 no other similar correlations were found.[22] Despite the contradictory nature of the results of Vannice et al.,[22–25] a decrease in the heats of adsorption of CO and H_2 on the surface of the metal, resulting in a decrease in strength of the metal–adsorbate bond may be regarded as one of the causes of a reduction in the degree of covering the surface of the supported metal with a high reduction temperature.

2. Catalytic properties

a) Conversions of hydrocarbons

A change in the chemisorptive properties of metals supported on oxides of transition elements at high reduction temperatures must have a considerable effect on the properties of M/E_xO_y systems. Thus, the activity of Pt/TiO_2 in the hydrogenation of benzene decreases after high-temperature reduction (793 K) by a factor of $10^{1.5}$ compared with a catalyst reduced at 473 K.[26] In the dehydrogenation of cyclohexane and the hydrogenation of ethylene the activity of Pt/TiO_2 decreases by a factor of 10. After reduction of Ir/TiO_2 and Rh/TiO_2 at 793 K a similar dependence occurs: in the hydrogenation of benzene the activity decreases by a factor of 10–100, in the dehydrogenation of cyclohexane it decreases by a factor of 5, and in the hydrogenation of ethylene it decreases by a factor of 10–100.[26] Oxidative treatment followed by reduction at a low temperature restores 80% of the original activity of these catalysts. A similar decrease in activity in the hydrogenation of benzene at a high reduction temperature (773 K) was observed for Pt/TiO_2,[27] (Ni, Pd, Ir)$/TiO_2$,[16] Pt/TiO_2,[28] and Rh/TiO_2 and Pt/TiO_2.[29]

In the hydrogenolysis of paraffins the activity of the catalysts is significantly affected by the temperature of their initial treatment in hydrogen. On increasing the reduction temperature from 523 to 773 K, Burch[30] observed a thousandfold decrease in the specific catalytic activity of Ni/TiO_2 in the hydrogenolysis of n-hexane. A similar dependence was found for (Ni, Pt, Pd/TiO_2) [16,31] and for Rh/TiO_2 [28] in the hydrogenolysis of ethane. At a reduction temperature of 773 K complete deactivation of the catalyst occurred in the same reaction for Ir/TiO_2.[26] Data on the effect of the reduction temperature on the properties of M/TiO_2 are given in five studies.[32–36] For all the Group VIII metals, except for Ru, when the reduction temperature is increased in the hydrogenolysis of ethane there is a sharp decrease in specific catalytic activity. At the same time, as for the hydrogenation of hydrocarbons, oxidative treatment followed by reduction under mild conditions restores the initial activity of the catalysts.[18,26,28,33,35]

It is interesting to note that the effect of the temperature of treatment does not manifest itself to an equal extent for all oxides of transition elements. Thus, in the hydrogenation of benzene on Pt/CeO_2 the activity decreases by a factor of 5 when the reduction temperature is increased, while in the hydrogenolysis of n-hexane there is no decrease in activity at all,[37] although the activity of Pt/TiO_2 in these reactions decreases by a factor of $10^{1.5}$–10^2.

b) Hydrogenation of carbon monoxide

An indication of the effect of the nature of the support on the properties of Group VIII metals in the hydogenation of CO was first given by Ichikawa et al.[38–40] In studying the synthesis of CH_3OH on Rh, Pd, Ir, and Pt catalysts at atmospheric pressure, the authors[38–40] showed that the activity and selectivity of the catalysts

depended not only on the nature of the metal itself but also on the composition of the supported compound and the acid-base properties of the support. Thus, in the hydrogenation of CO on oxides with weakly defined basic properties such as MgO, La_2O_3, and V_2O_3, methanol is mainly formed, while on oxides with pronounced basic or acidic properties (Li_2O, SiO_2, TiO_2), methane is formed. A similar effect from the support on the properties of supported palladium in the hydrogenation of CO at a high pressure was observed by Ryndin et al.[41] However, in these studies[38–41] there is no analysis of the effect of dispersity on the activity and selectivity of the process. At the same time the dispersity of supported metal particles plays a significant role in this reaction. Thus, it was shown in two studies[42,43] that the specific catalytic activity of Pd/SiO_2 in the hydrogenation of CO to methane increases with an increase in dispersity of Pd, but it was found by Hicks and Bell[44] that the specific catalytic activity of Pd/SiO_2 in the synthesis of methane does not depend on the dispersity of Pd while the specific catalytic activity of Pd/La_2O_3 decreases with an increase in dispersity of Pd. In two other studies[45,46] it was shown that in the synthesis of methanol from CO the specific catalytic activity of Pd/SiO_2 and Pd/La_2O_3 catalysts increases with a decrease in dispersity of the supported metal. It was shown by Arkawa et al.[47] that for Rh catalysts the selectivity of the reaction with respect to oxygen-containing products increases with an increase in dispersity of Rh. On the whole the results given in the literature concerning the effect of dispersity on the activity of supported metals in the hydogenation of CO are quite contradictory.

The nature of the support affects the properties of a supported metal more significantly than a change in its dispersity.[48] It was shown in several studies[16,30,49–53] that at a reduction temperature of 723 K the specific catalytic activity of Ni/TiO_2 is higher than that of Ni/SiO_2, Ni/Al_2O_3, and Ni/C by a factor of 10–100. At the same time there was an increase in selectivity towards the formation of higher hydrocarbons.

Similar trends were found for other Group VIII metals.[54,55] Thus, Vannice[56,57] showed that the specific catalytic activity of platinum catalysts in the synthesis of methane was unchanged over a wide range of particle size (from 12 to 1000 Å), while the nature of the support had a considerable effect on their specific activity, which in Pt/TiO_2 was 10 times higher than in Pt/Al_2O_3 and $Pt/(SiO_2-Al_2O_3)$ and 100 times higher than in Pt/SiO_2. A constant value of the specific catalytic activity over a wide range of change in particle size of Pd in the hydrogenation of CO to CH_4 was established by Vannice et al.[58] However, as for Pt, the specific catalytic activity of Pd changed by a factor of 100 on varying the support (at the same time the activation energy of the reaction does not depend on the nature of the oxide).

An increase in activity of the supported metal also takes place on changing from SiO_2 and Al_2O_3 to oxides of transition elements. For example, the activity of Ni/Nb_2O_5 and Ni/ZrO_2 is considerably higher than the activity of Ni/SiO_2 and Ni/Al_2O_3,[59,60] and at the same time the selectivity towards higher hydrocarbons reaches 55%. It was shown by Szymanski et al.[61] that the specific catalytic activity of Pt/ZrO_2 in the synthesis of methanol at atmospheric pressure is higher than that of Pt/SiO_2 and Pt/C by a factor of $10^{1.5}$, and the selectivity with respect to CH_3OH reaches 50%.

The effect of the reduction temperature on the properties of nickel catalysts in the synthesis of CH_4 from CO and H_2 was investigated in two studies.[59,62] When the reduction temperature of Ni/ZrO_2 and Ni/TiO_2 was increased from 543 to 973 K the activity per unit weight of nickel decreased more than ten times while the dispersity of the nickel did not alter significantly.[59] Fang[62] showed that on increasing the reduction temperature from 523 to 723 K the specific catalytic activity of Ni/TiO_2 decreased by a factor of 2, which was due to a decrease in strength of the Ni–CO bond, since there is a direct correlation between the decrease in activity and the reduction in strength of the Ni–CO bond. The reverse dependence occurs for Pt and Pd supported on TiO_2. At a reduction temperature of 773 K the specific catalytic activity of Pd/TiO_2 and Pt/TiO_2 is higher than at 573 K.[56,58,63]

An increase in the reduction temperature of M/E_xO_y has only a slight effect on the selectivity for hydrogenation of CO to methane. It was shown by Turlier et al.[59] that the selectivity towards CH_4 for Ni/TiO_2 and Ni/ZrO_2 when the reduction temperature is changed from 523 to 923 K is virtually unchanged. It was shown by Anderson et al.[16] that the selectivity of a Pd/TiO_2 catalyst in the synthesis of CH_4 is virtually independent of the reduction temperature, but it is 20% higher than the selectivity of Pd/SiO_2.

Interesting results were reported by Kunimori et al.[21] in a comparison of the catalytic properties of Pd and Rh supported on TiO_2 and Nb_2O_5. When the reduction temperature for Rh/Nb_2O_5 and Pd/Nb_2O_5 was increased from 573 to 773 K, in addition to a decrease in chemisorption of CO by a factor of more than 10, there was a decrease in the specific catalytic activity of these catalysts in the synthesis of CH_4—by a factor of 100 for Rh/Nb_2O_5 and by a factor of 10 for Pd/Nb_2O_5. At the same time the activity of Rh/TiO_2 and Pd/TiO_2 remained constant on increasing the reduction temperature. However, prolonged experiments on the hydrogenation of CO on Rh/Nb_2O_5 and Pd/Nb_2O_5 catalysts showed that with the passage of time their activity increases to a value that is typical for samples reduced at 573 K. In the opinion of Kunimori et al.,[21] the increase in activity of M/Nb_2O_5 is due to disruption of SMSI by oxygen formed through dissociation of CO or by water formed as a result of reaction. At the same time the higher activity of M/TiO_2 catalysts compared to M/Nb_2O_5 (whatever the reduction temperature) is due to the readier disruption of the interaction between metal and support.[21] The true activity of M/TiO_2 catalysts at high reduction temperatures, according to Kunimori et al.,[21] must be lower than the observed value by a factor of 10–100.

It was found by Jackson et al.[64] that the specific catalytic activity of Ru/TiO_2 catalysts prepared from supported Ru carbonyl clusters decreased with an increase in reduction temperature, while raising the reduction temperature from 523 to 873 K had no effect on the activity of Rh/ZrO_2 catalysts.[65]

Thus, the data reported in the literature concerning the effect of the reduction temperature on the activity of Group VIII metals supported on TiO_2 and other oxides of transition elements in the hydrogenation of CO are contradictory in nature. However, the increase in specific catalytic activity of metals supported on TiO_2 or other oxides of transition elements compared to that of the same metals supported on SiO_2 or Al_2O_3 is not in doubt.[66]

III. Models of the interaction between metals and oxides of transition elements

1. Direct interaction between metal atoms and low-valent ions of a support

A model which assumes direct interaction between the atoms of a supported metal and low-valent ions of the support was put forward by Horsley.[67] This model was based on theoretic calculations using

the method of the self-consistent field of dispersed waves of models of molecular clusters for a Pt/TiO_2 catalyst. Two different models were considered (Fig. 2). According to model (A) (Fig. 2*A*) a platinum atom interacts with an octahedral $(TiO_6)^{8-}$ cluster, while the metal atom is situated outside the octahedron. Model (B) (Fig. 2*B*) assumes that there is an oxygen vacancy in the $(TiO_6)^{8-}$ cluster that is occupied by a Pt atom. While in model (A) the closest neighbours of the Pt atom are oxygen ions, in model (B) direct coordination between the Pt atom and the titanium cation is assumed.

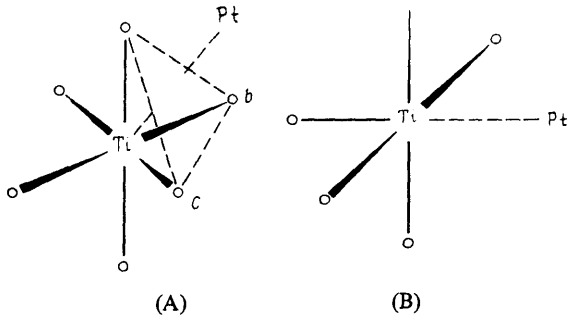


Figure 2. Models of clusters in a Pt/TiO_2 catalyst.[67]

Theoretical calculations show that for model (A) the platinum atom cannot lie sufficiently close to the $(TiO_6)^{8-}$ cluster because of strong repulsion between the Pt atoms and the adjacent oxygen ions, and the formation of a Pt–Ti bond is impossible.[67] For model (B) the Pt atom and Ti cation can lie sufficiently close to each other and the formation of a $Pt-Ti^{3+}$ bond is possible.[67] This bond is probably partly ionic with electron transfer from Ti^{3+} to the platinum atom. According to the authors,[67–69] even a small transfer of electron density to platinum will produce a change in hybridisation of the metal–metal bonds, which assumes considerable changes in metal–metal distances. This may affect the population or change in symmetry of *d* orbitals in such a manner that they will not be able to interact with the molecular orbitals of H_2 and CO. As a result, a decrease in chemisorption and strength of the bond between metal and CO and H_2 will occur. It is clear that the interaction between metal atoms and Ti^{3+} atoms is of a specific type and only occurs at the metal–support phase boundary, since the metal atoms and cations of the support are restricted in movement at the limits of the crystal lattice.[70]

The hypothesis put forward by Horsley was later supported experimentally in a number of studies. For example, Golodets et al.[71–73] observed a reduction in strength of the Ni–CO and Ni–H bonds on a Ni/TiO_2 catalyst as a result of the electronic interaction of $Ni-Ti^{3+}$. A similar trend was observed for a Pd/La_2O_3 catalyst.[74] However, the data from studies on the electronic state of metals are contradictory. Thus, in two studies[17,75] no significant changes occurred in E_{bind} of the core levels of Rh and Pt supported on TiO_2 (X-ray photoelectron spectroscopy method), so the authors were able to conclude that electron transfer from Ti^{3+} to the Rh and Pt atoms was negligible. At the same time, it was shown in several other studies[28,69,76–82] that reduction of (Rh, Ni, Pt)/TiO_2 catalysts with hydrogen at 873 K results in a decrease in E_{bind} of the core levels of the metals, which suggests an increase in electron density on the metal atoms.

Experimental confirmation of an interaction occurring between Ti^{3+} cations and Group VIII metals constituted important evidence in favour of the Horsley mechanism. A series of phyiscal methods (X-ray photoelectron spectroscopy, high-resolution electron energy loss spectroscopy, and UV photoelectron spectroscopy) were used to establish that when Ni,[76,83] Pt,[84] Pd,[85] and Rh [70] are deposited on the surface of a support containing Ti^{3+} cations, the spectroscopic parameters that are characteristic of Ti^{3+} cations either decrease or disappear. It was shown by means of Auger spectroscopy[70] that deposition of Rh on TiO_2 is accompanied by oxidation of the surface, and the changes in the UV photoelectron spectra are similar to those that occur when oxygen is adsorbed.

Direct experimental confirmation of the existence of a Rh–Ti bond was first obtained by Shpiro.[28,79] In a study of a Rh/TiO_2 catalyst reduced at 773 K using secondary ion mass spectrometry, mixed $RhTi^+$ clusters were detected together with Rh^+ and Ti^+, while at reduction temperatures of 473 and 573 K no $RhTi^+$ clusters were observed.

At the same time there is virtually no information in the literature about detection of a metal–Ti^{n+} bond by means of the extended X-ray absorption fine structure (EXAFS). Only two examples of the detection of such bonds using the EXAFS method are known. Thus, Konigsberger[86] found the Rh–Ti^{n+} distance to be 3.4 Å in length in a Rh/TiO_2 catalyst reduced at 773 K. However, this distance is too great for the formation of a chemical bond.[70] For a similar catalyst, Haller[87,88] demonstrated the existence of a Rh–Ti^{n+} bond of length 2.55 Å, which is somewhat shorter than the length of the Rh–Ti bond in the majority of stable intermetallic compounds (2.68 Å). However, in more recent studies of Rh/TiO_2 catalysts using EXAFS it was not possible to detect a Rh–Ti^{n+} bond.[68] The difficulties in attempting direct detection of a M–Ti^{n+} bond arise because it is of a special type and is only formed at the metal–support interface. It is therefore to be expected that the coordination numbers for titanium may be low and lie outside the limit of sensitivity of this method.

2. Change in morphology of supported metal particles

The formation of flat metal particles (with a "pill-box" or "raft-like" structure) on the surface of partially reduced TiO_2 were first introduced by Baker[89] to explain the existence of SMSI. In a study of the sintering of Pt on different supports using high-resolution electron microscopy over a temperature range of 425–1075 K it was shown that the dispersity of Pt deposited on TiO_2 is higher than that on other supports. At the same time the Pt particles have a flat hexagonal form with uniform thickness, which indicates the formation of flat structures. Moreover, in the presence of Pt, TiO_2 was reduced to Ti_4O_7, being accompanied by a change in the lattice parameter (5.6 Å). In fact, Prins[90] showed by means of EPR that Pt catalyses the reduction of TiO_2. After treatment of a Pt/TiO_2 catalyst with hydrogen even at 573 K, the concentration of Ti^{3+} ions is 30 times less than in the pure support.

It was shown by Baker et al.[91] that the formation of flat metal particles in an M/TiO_2 system is reversible. Thus, high-temperature treatment of Pt/TiO_2 with water vapour or O_2 results in the formation of globular Pt crystallites, while repeated reduction leads to the formation of flat structures.

A comprehensive scheme of the formation of flat particles is depicted in Fig. 3. As a result of high-temperature reduction, hydrogen atoms, diffusing from the surface of the metal to the support, reduce the Ti^{4+} ions to Ti^{3+}. At the same time oxygen vacancies are formed in the surface layer through the elimination of lattice oxygen in the form of H_2O. The resulting oxygen vacancies can be compensated by the formation of a bond between the metal atoms and Ti^{3+} cations. In fact, it was shown by Gingerich et al.[92] that the Pt–Ti bond is stronger than Pt–Pt. Thus, in their tendency to form a $M-Ti^{n+}$ bond, the metal atoms enter oxygen vacancies, and flat structures are formed on the surface, which was recorded by means of electron microscopy.[91] On oxidation by oxygen or H_2O the $M-Ti^{n+}$ bonds are broken and Ti_4O_7 is oxidised to TiO_2. At the same time the metal particles change their structure, adopting an energetically more favourable spherical form. The metal acquires its normal chemisorptive and catalytic properties through cleavage of the $M-Ti^{3+}$ bonds.[90,91]

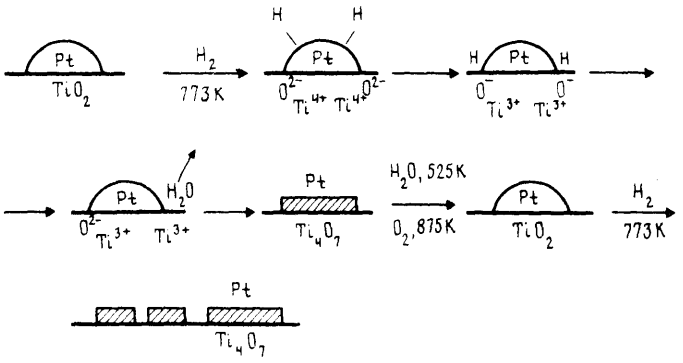


Figure 3. Scheme for the formation of flat metal structures in the system Pt/TiO_2.[90,91]

It should be noted that the unique flat structure of the Pt particles was not observed on oxides of nontransition elements (SiO_2, Al_2O_3) or on carbon. However, it was shown by Yates et al.[93] that flat Rh particles may also be obtained on Al_2O_3, while the shape of the particles does not affect the chemisorptive properties of Rh. Thus, the change in chemisorptive and catalytic properties of the metals in an SMSI state cannot be explained solely by a change in shape of the particles.

We should note that the existence of flat structures in other metals has not been clearly demonstrated. For example, the formation of flat particles of Ni in a Ni/TiO_2 catalyst was demonstrated by Mustard et al.[94] using electron microscopy, while flat structures were not detected by Baker et al.[95–97] in studies on similar catalysts. The formation of flat structures in Pd/TiO_2 was also not detected in another study.[98]

The results which suggest that partial reduction of TiO_2 occurs in the presence of Group VIII metals are not in doubt. The fact that the supported metal is localised on the reduced forms of TiO_2, namely, Ti_4O_7, suggests that the metal atoms form a chemical bond with the surface Ti^{3+} cations. A change in the chemisorptive and catalytic properties of a supported metal also occurs because of the interaction between the metal atoms and the Ti^{3+} cations.[89] The mechanism discussed in this section reiterates the assumptions made by Horsley.[67]

3. Formation of intermetallic compounds

The formation of intermetallic compounds was first proposed by Tauster as one of the mechanisms for interaction between a supported metal and a transition element oxide.[3] Experimental support for this hypothesis was obtained in two studies,[99,100] in which it was demonstrated that $Pt_{1-x}Zr_x$ intermetallic compounds are formed during the high-temperature reduction of Pt/ZrO_2 according to the reaction:

$$(1-x)Pt + xZrO_2 + 2xH_2 \longrightarrow Pt_{1-x}Zr_x + 2xH_2O.$$

In the case of $Pt/ZrO_2/C$ catalysts, intermetallic compounds are formed according to the reaction:

$$(1-x)Pt + xZrO_2 + 2xC \longrightarrow Pt_{1-x}Zr_x + 2xCO,$$

where C acts simultaneously both as a reducing agent and support. Appreciable formation of $Pt_{1-x}Zr_x$ compounds occurred at temperatures above 873 K. With an increase in temperature x increases and reaches a maximum value ($x = 0.25$) at 1273 K.

In three studies[96,101,102] the formation of compounds of the type M_3Ti was observed at 973 K for (Ni, Pt)/TiO_2. However, in two other studies[26,103] for Ni/TiO_2 there is no possibility of intermetallic compounds being formed even at 1073 K, since at this temperature TiO_2 cannot be reduced to metallic titanium.

A decrease in specific chemisorption of CO on Ni_xZr_y was observed by Tomanek et al.,[104] and it was established that above 300 K carbon monoxide is mainly adsorbed in a dissociative form. It should be noted that after treatment of the Pt_3Ti catalyst with hydrogen, the thermally programmed desorption (TPD) spectra indicated that desorption of H_2 did not occur. In the opinion of Bardi et al.,[105,106] either H_2 is not adsorbed at all on the surface or it is adsorbed sufficiently strongly for desorption not to occur up to 900 K. However, it is widely known that intermetallic compounds can form hydrides. Thus, it was shown in three studies[107–109] that Zn–Ni, Zr–Co, and Zr–Ni–Mo intermetallic compounds can dissociatively adsorb H_2 and contain it in bulk in the form of monoatomic species, which assumes that there is a high concentration of active hydrogen on the surface.

In the hydrogenolysis of ethane the activity of $Pt_{1-x}Zr_x/(ZrO_2, C)$ is 15–20 times lower than that of Pt/ZrO_2 and Pt/C catalysts.[99,100] It was shown in three studies[61,99,100] that in the hydrogenation of CO the specific catalytic activity of $Pt_{1-x}Zr_x$/support catalysts does not depend on the nature of the support, but their activity is higher than that of Pt/support catalysts by a factor of 10, and their selectivity towards CH_3OH reaches 80%.

It should be noted that intermetallic compounds are stable towards oxygen and do not decompose at room temperature.[26,110,111] However, oxidation at temperature above 573 K results in segregation of the components and a decrease in the observed changes in chemisorptive and catalytic properties.[107,109–114]

4. Electronic interaction between a metal and transition element oxide

Schwab[1] and Solymosi[2] attempted to explain the change in catalytic properties of metals on varying the nature of the support in terms of an electronic interaction between the deposited metal and

support. Interest in these ideas grew again at the end of the 1980s. For example, it was shown in two studies[115,116] that electron transfer between the metal and support can play a substantial role in the catalytic reaction. It was first suggested by Meriaudeau[26] that electron transfer between metal and support is the main cause of the change in chemisorptive and catalytic properties of metals in an SMSI state. The model put forward by Meriaudeau[26] is based on the theory of semiconductors and is depicted schematically in Fig. 4.

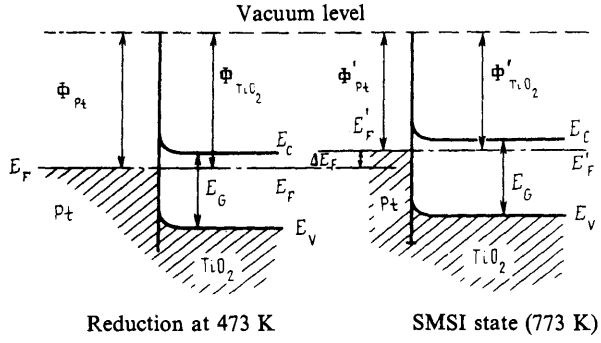


Figure 4. Schematic depiction of energy diagram for the system Pt/TiO_2.[26] E_F is Fermi level, Φ is electronic work function, E_V is top of valence band, E_C is bottom of conduction band, E_G is width of forbidden band, ΔE_F is increase in Fermi level in the SMSI state.

Since at a low reduction temperature the electronic work function (Φ) for TiO_2 is 5.5 eV while for Pt it is 5.6 eV,[26] the Fermi level (E_F) of TiO_2 lies near E_F for platinum. At high reduction temperatures, as a result of the high concentration of defects in TiO_2 (oxygen vacancies and Ti^{3+}) the electronic work function decreases to 4.6 eV, while the value of E_F becomes higher than in Pt. At the points of contact between platinum and TiO_2 the values of E_F equal out through the flow of electron density from support to platinum. The excess electron density on Pt will cause a modification of its electronic structure through a progressive filling of the d orbitals and there is a transition from a d^9 configuration to d^{10}, i.e., to the same as in gold. Gold is known not to exhibit the chemisorption of H_2 and does not catalyse reactions involving the dissociative chemisorption of hydrogen.

When oxygen is added TiO_2 undergoes reoxidation. In this case the support becomes electron-deficient, which assist a flow of electron density from platinum to support. As a result Pt acquires a normal d^9 configuration and at the same time its normal chemisorptive properties restored.

The hypothesis put forward by Meriaudeau[26] has been supported experimentally in four studies.[117–120] Thus, it was shown by Herrmann et al.[118,119] that on reduction of TiO_2 in the presence of platinum, the electrical conductivity of TiO_2 increases by a factor of 100, which suggests that platinum plays a catalytic role in the reduction of TiO_2 and it confirms the results of Huizinga and Prins.[90] It was established[119] that evacuation of TiO_2 at 673 K increases the electrical conductivity by a factor of 100, and the subsequent deposition of Pt leads to a decrease in electrical conductivity of TiO_2 by a factor of 2. A decrease in the electrical conductivity of TiO and Ti_2O_3 on deposition of Pt was also observed by Chen and White.[117] These phenomena are due to the simultaneous occurrence of two processes:[117,119] 1) formation of anion vacancies through removal of lattice oxygen and the generation of free electrons; 2) migration of the free electrons from the bulk of the support to the metal, resulting in a decrease in electron density on the support and a decrease in its electrical conductivity. As a result of the latter process the chemisorptive properties of the metal must change, according to Meriaudeau et al.[26] In fact, it was shown by Loye et al.[14] for Ni/Ti_nO_{2n-1} that with an increase in the degree of reduction of the support, a decrease in chemisorption of H_2 occurs. The change in chemisorptive properties of Ni through a change in electronic structure is supported by Longe and Stacy.[121] At the same time in a study by Fang et al.[62] on similar systems it was shown that an increase in bulk concentration of Ti^{3+} has no effect on the catalytic properties of Ni in the hydogenation of CO. Using X-ray photoelectron spectroscopy, Huizinga and Prins[122] did not detect any change in the electronic state of Pt when the reduction temperature for Pt/TiO_2 was changed from 483 to 823 K.

An alternative explanation to that put forward by Baker et al.[89] concerning the formation of flat metal particles follows from the mechanism proposed by Meriaudeau.[26] Chen and White[117] assume that when transfer of electron density occurs from the bulk of TiO_2 to the metal, the negatively charged metal particle will tend to increase its surface area in order to reduce the surface charge density. Consequently, when electron transfer occurs the formation of particles with a flat shape becomes energetically more favourable.

Despite the fact that the mechanism proposed by Meriaudeau[26] accounts for the change in chemisorptive and catalytic properties of platinum, which has a d^9 configuration, it cannot be recognised as a fundamental principle since it does not explain why Ir and Rh, which have d^7 and d^8 electron configurations respectively, when supported on oxides of transition elements exhibit properties that are characteristic of systems with SMSI.

5. Interaction at the metal–support interface

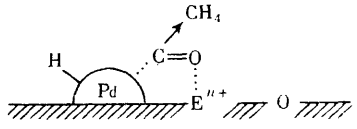
The existence of an interaction at a metal–support interface was first demonstrated by Burch and Flambard.[50] According to the model put forward by them, the formation of anion vacancies and Ti^{3+} ions at the phase boundary can produce a change in the catalytic properties of a supported metal through direct and indirect participation of the support in the catalytic process. For example, Ti^{3+} cations that are formed at the phase boundary can participate in the activation of CO molecules which undergo dissociative hydrogenation by hydrogen adsorbed on the surface. Furthermore, the support can form part of a heteroatomic adsorption site involving metal atoms and Ti^{3+} cations on the surface of the support. It has been suggested that during adsorption to these sites a CO molecule forms a bond via its carbon atom with a metal atom while the oxygen atom binds to a surface Ti^{3+} cation, resulting in a considerable loosening of the bond in the CO molecule and assisting its hydrogenation. Burch and Flambard[49,50] assume that in the interaction of metal atoms with Ti^{3+} cations through the transfer of electron density to the metal atoms the electronic properties of the supported metal are modified. When excess electron density occurs on the metal it is to be expected, on the one hand, that there will be a decrease in the activity of the catalysts in reactions involving the conversion of hydrocarbons because of a reduction in the strength of chemisorption of reactants on the surface of the metal, while on the

other hand, an increase in activity is to be expected in the hydrogenation of CO through an increase in the rate of dissociation of a CO molecule or an increase in the rate of desorption of reaction products.[49,50]

The idea that the support participates in the catalytic process and that specific active sites are formed at the phase boundary has found further confirmation in several studies.[123–128] For example, it was shown by means of angular resolved X-ray photoelectron spectroscopy[125] that on treatment of Pt/TiO_2 with hydrogen, the resulting Ti^{2+} and Ti^{3+} cation sare localised at the metal–support interface. Stadler et al.[126] found that the high activity of a Pd/TiO_2 catalyst in the hydrogenation of 1,5-hexadiene is due to coordination of the olefin on the surface Ti^3 cations and to hydrogenation of the resulting complex by hydrogen that is dissociatively adsorbed on the surface of palladium.

It was established[127] that on addition of Sb^{5+}, Ta^{5+}, W^{6+} ions to Pt/TiO_2 and Pt/Nb_2O_5, there is a decrease in chemisorption of hydrogen because of an electronic interaction at the interface between Pt and the introduced ions. When Na^+ ions were added to Ni/TiO_2, the selectivity of the catalyst increased and higher alcohols were formed from synthesis gas, which is attributed by Hayasaka et al.[128] to the participation of the Na^+ ions in the activation of CO.

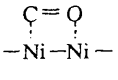
The high activity of Pd/TiO_2 and Pd/La_2O_3 catalysts in the hydrogenation of CO is attributed to participation of supports in hydrogenation.[21,45] In this case, as was suggested by Burch and Flambard,[49,50] the authors assume[21,45] that cations of the support can form part of a mixed adsorption site and participate in the activation of a CO molecule:



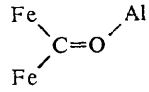
(I)

or take part in the adsorption of reaction intermediates.

Thus, the existence of active sites at the metal–support interface assumes that an unusual form of CO adsorption occurs parallel to the surface. The possibility of the planar coordination of CO simultaneously on Pt and Ti atoms was calculated theoretically by Mehandru et al.[129] According to Rice and Haller,[130] vibrations of the planar-coordinated form of CO should appear in the region below 1800 cm^{-1} in the IR spectra. In fact, it was shown in two studies[131,132] by means of IR spectroscopy that when manganese, titanium, or zirconium ions are added to a Rh/SiO_2 catalyst, a new absorption band due to CO appears in the region 1800–1600 cm^{-1}. In this case its position depends on the metal–promoter ratio. We should note that in 1965 Garland,[133] when studying the adsorption of CO on Ni films, first detected an unusual absorption band of adsorbed CO at 1620 cm^{-1}, which was provisionally attributed to the coordination of CO on two nickel atoms:



It was only progress in the chemistry of cluster compounds that demonstrated the validity of assigning the absorption bands in the region below 1700 cm^{-1} to vibrations of CO coordinated simultaneously through its carbon and oxygen atoms on metal atoms. For example, Nelson et al.[134] established the presence of



residues with a CO vibration frequency of 1527 cm^{-1} for different Fe carbonyl clusters. It was shown by Sachtler et al.[135] that for different heteronuclear Mo, Fe, and Ru complexes the absorption bands of CO in M–C–O–M residues are in the region of 1700–1500 cm^{-1}.

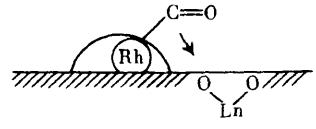
A considerable contribution towards proving that complexes exist at the metal–support interface in catalysts of the type M/E_xO_y was made by Bredikhin et al.,[136–139] who demonstrated by means of IR spectroscopy that in the adsorption of CO, complexes are only formed at the metal–support interface for catalysts prepared by deposition of metals on oxides of transition elements (TiO_2, ZrO_2, HfO_2, V_2O_5, La_2O_3). At the same time for metals supported on oxides of *p*-elements (Al, Zn, Cd, Ga, Bi) and also for bulk metals or supports without metals, the formation of these complexes does not occur. Moreover, a systematic study of the chemical and spectroscopic properties of complexes formed at the metal–support interface was undertaken by Bredikhin et al.[136–139] It was shown in this case that they have a number of characteristics:

1) a broad absorption band in the region of 1800–1600 cm^{-1}, whereby its position depends on the nature of the metal and support used;

2) a low value of the isotopic shift ($^{12}CO \rightarrow {}^{13}CO$) and a lower value of the high-frequency shift with an increase in the degree of filling the surface compared to surface carbonyls, and the heat of adsorption of CO is similar to the corresponding value for carbonyl complexes;

3) they are oxidised by oxygen, in the same way as surface carbonyls.

At the same time the question concerning the type of CO adsorption at the sites formed at the metal–support boundary remains open. While Bredikhin et al.[136] give preference to complexes of the type

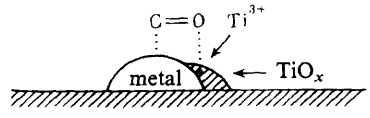


in several other studies[20,49,50,130,131,135] the authors assume that an adsorbed CO molecule forms a complex of the type (I).

Despite the difference in proposed forms for the coordination of CO at the metal–support interface, it may be assumed that the hydrogenation of CO on M/E_xO_y catalysts occurs with the participation of novel complexes of adsorbed CO, which accounts for the unusual nature of their catalytic properties in the hydrogenation of CO. There is no doubt that further studies need to be carried out in order to verify this hypothesis, but the results already reported in the literature indicate the necessity for admitting the funadmental possibility of the coordination of molecules at the metal–support interface in representing the mechanisms of the catalytic reactions.[138]

6. Diffusion of TiO_x to the surface of the metal

According to a number of published studies, one of the most widely recognised mechanisms introduced to account for the unusual properties of metals on oxides of transition elements is the diffusion of partially reduced residues of the support to the surface of the metal particles. This mechanism was first suggested by Meriaudeau et al.[37] and was further developed in three studies.[16,140,141] This mechanism essentially involves partial reduction of TiO_2 around the perimeter of the metal particles followed by migration of the TiO_x residues to the surface of the particle. As a result the surface of the metal particle is obstructed by small islets of TiO_x, resulting in a decrease in the available surface of the metal for chemisorption of hydrocarbons and hydrogen, and hence to a decrease in activity of the catalysts in the conversion of hydrocarbons.[37,140] Furthermore, the total metal–support interface increases as a result of the migration of TiO_x to the surface of a metal particle. At the same time, according to Anderson et al.,[16] there is an increase in the number of adsorption sites consisting of metal atoms and E^{n+} cations that can participate in the coordination of a CO molecule according to the scheme:



Thus, on the basis of this mechanism participation of the support in the activation of CO explains the increase in activity of M/TiO_x catalysts in the hydrogenation of CO.[16,142]

Experimental support for the mechanism involving decoration of the metal surface is provided in a number of studies.[143–160] At the same time the question regarding the migration mechanism of TiO_x to the surface of the metal remains open. For example, in two studies[16,162] distortion of the crystal lattice of platinum was observed on reduction of Pt/TiO_2 above 673 K, which was attributed to diffusion of TiO_x into the bulk of Pt. Diffusion of TiO_x into the bulk of Pt over the temperature range 700–900 K was recorded in two other studies.[163,164]

It has also been thought possible that transport of TiO_x to the surface of the metal occurs through the intermediate formation of metastable $M-TiO_x$ compounds which segregate on reduction to form TiO_x residues on the surface of the metal. For example, the formation of $Ni-TiO_x$ structures was recorded in two studies.[121,165] The formation of $LaPd_xO$ structures on reduction of a Pd/La_2O_3 catalyst was demonstrated by Fleisch et al.,[166] and at the same time an increase in electron density on Pd was detected by X-ray photoelectron spectroscopy. On addition of K^+ ions to a Pt/TiO_2 catalyst, a decrease in chemisorption of H_2 occurred, which Spencer[167] related to the participation of potassium ions in the form of K_2TiO_3 in the transport of TiO_x to the surface of Pt.

Furthermore, the counter-diffusion of metal atoms and resulting TiO_x residues at the metal–support interface is not excluded. According to Spencer,[168] the mobility of the metal atoms is governed by the Hüttig temperature (T_H), which is equal to one third of the melting point of the metal. For example, T_H = 700 K for Pt, 750 K for Rh, and 700 K for TiO_2 and TiO. It is to be expected that at reduction temperatures above 700 K the mechanism for transport of TiO_x to the surface of the metal through the mutual diffusion of metal atoms and TiO_x residues predominates.[97,168]

In order to confirm the hypothesis about decoration of the metal surface, a study was made of model systems obtained by depositing TiO_2 on the surface of different metals. It was shown by Gorte et al.[163,169] that when the content of TiO_x on the surface of Pt foil is increased, the chemisorption of CO and H_2 is almost completely suppressed. The activity of TiO_x/Pt catalysts in the synthesis of CH_4 from CO and H_2 is similar to that of Pt/TiO_2, while at the same time there is a decrease in the activation energy of reaction by 12 kcal mol^{-1}.

An increase in the activity of model TiO_x/Rh catalysts in the hydrogenation of CO with an increase in the extent of surface coverage of Rh foil with TiO_x particles was observed by Levin et al.[170] The maximum increase in activity in the synthesis of CH_4 occurred when the extent of surface coverage of the metal with TiO_x was 15%, which is attriubted to an optimum number of Rh atoms being located along the TiO_x boundary.[170]

The maximum activity for model TiO_x/Ni catalysts in the synthesis of CH_4 occurred at 8% covering.[171] It was shown[172] that the chemisorption of CO on the surface of Ni(III) decreases in the presence of MnO_x, and the quantity of chemisorbed CO decreases linearly with an increase in coverage of the nickel with MnO_x particles. Moreover, in the presence of MnO_x a novel form of adsorbed CO occurs on the surface of Ni(III) with vibration frequency 1620 cm^{-1}, the intensity of this form reaching a maximum for average degrees of coverage with MnO_x.

Thus, investigation of model TiO_x/M catalysts shows that blocking the metal surface with partially reduced residues of support (TiO_x) and modification of the electronic properties of the metal through the interaction of metal atoms with TiO_x results in a considerable loss of chemisorptive properties of these catalysts. However, the presence of residues of support on the surface of the metal leads to an expansion in the metal–support interface and an increase in the number of active sites consisting of metal atoms and support, which may be the cause of the increased activity of catalysts in the hydogenation of CO. We should note in conclusion that the model for decoration of the surface of the metal with TiO_x residues is generalised model and incorporates the models put forward by Horsley, Baker, and Burch.

IV. Study of the mechanism of the interaction between Group VIII metals and oxides of transition elements using $(M + E^{IV})/SiO_2$ model systems

It may be concluded from an analysis of the results given above that six basic mechanisms to account for the unusual properties of metals supported on transition element oxides have been discussed in the literature. However, the experimental data supporting a given mechanism are usually contradictory, and not one of these hypotheses has so far received conclusive experimental confirmation. We should note that research into the problems of SMSI is mainly being conducted in the following areas:

a) a study of real M/E_xO_y catalysts using a range of physical methods;

b) the development and study of model systems (mainly catalysts obtained by covering the metal surface with TiO_x residues);

c) theoretical calculations of the active sites in catalysts with SMSI.

It would appear that significant progress in solving the problem of SMSI could be achieved either by conducting more precise experimental studies of M/E_xO_y catalysts using a range of physical methods or by developing fundamentally new model systems. In this regard the results of studies by Ryndin et al.,[173–184] in which the directed synthesis of $M-E^{n+}$ heteroatomic active sites similar to the active sites supposedly existing in real M/E_xO_y catalysts on the surface of an inert matrix has been carried out using organometallic chemical methods, are of interest. The ideas developed by Ermakov[4–8] form the basis of the synthesis of the $(M + E^{IV})/SiO_2$ catalysts. As a result of a reaction between Group IV organometallic compounds with SiO_2, bonding of the surface hydroxide groups occurs, while treatment in H_2 results in the formation of fixed, coordinatively unsaturated E^{IV} ions. When organometallic compounds of Group VIII metals are subsequently deposited, they interact with the coordinatively unsaturated E^{IV} ions to form $M-E^{n+}$ bonds. With this method it is possible to obtain active sites directly by synthesis rather than as a result of high-temperature reduction as in the case of M/E_xO_y catalysts.

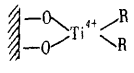
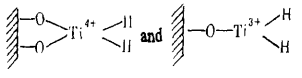
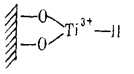
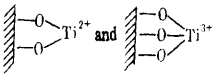
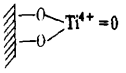
We shall briefly summarise the results obtained from the studies on model $(M + E^{IV})/SiO_2$ systems.

1. Information about the state of surface E^{IV} ions

a) State of E^{IV} before deposition of a Group VIII metal

It follows from the chemisorption and TPD data of Ryndin et al.[180] that treatment of fixed Ti and Zr organometallic complexes with hydrogen either gives surface hydride complexes or leads to the formation of low-valent ions that are not bound to hydrogen. The composition of the surface compounds depends on the treatment conditions of the samples, principally on the temperature of treatment (Table 1). The presence of low-valent ions in E^{IV}/SiO_2 samples is confirmed by the X-ray photoelectron spectroscopy data.[180]

Table 1. Composition of the surface compounds for the system 1.1% Ti/SiO_2.[180]

Activation conditions	Average degree of oxidation	H/Ti	Surface compounds
No treatment	4.0	–	
H_2, 423 K	3.4	2.3	
H_2, 573 K	3.0	1.2	
H_2, 873 K	2.7	0.1	
O_2, 673 K	4.0	–	

According to the electron microscopy data, disperse oxide phases or extended two-dimensional formations of E^{IV} compounds are not formed in reduced E^{IV}/SiO_2 samples.[180] It follows from the data of EXAFS that the reduced Zr/SiO_2 catalysts mainly contain isolated Zr ions bound to oxygen of SiO_2.[179,180]

b) State of E^{IV} in the presence of M

This information may be obtained from data on the quantity of O_2 consumed in the oxidation of $(M-E^{IV})/SiO_2$ samples at different temperatures. For all the $(M-E^{IV})/SiO_2$ systems the quantity of O_2 consumed in oxidation was higher than that corresponding to the stoichiometry of O/M = 1 that is characteristic of M/SiO_2 (Table 2). These data indicate that in the model catalysts the promoter ions occur in a low oxidation state.[173–184]

Table 2. Quantity of O_2 consumed in the oxidation of $(M + E^{IV})/SiO_2$ samples at 673 K.[176,177,183,184]

Catalyst, wt.%	M_s/M_t^*	Atomic ratio		N^{**}
		O/M	O/E^{IV}	
2.5% Pt	0.66	0.97	–	–
0.9% Ni+1.1% Ti	1.00	2.44	1.00	2.7
2.0%Pd+5.2%Zr	0.84	1.35	0.12	3.8
3.2%Pt+1.1%Ti	0.71	1.52	0.37	3.2
2.7%Pt+5.3%Zr	0.79	1.31	0.11	3.8
2.0%Pt+4.0%Hf	0.78	1.26	0.13	3.7

*Fraction of surface atoms of metal.
**Average degree of oxidation of E^{IV}.

2. Properties of the metal particles of $(M + E^{IV})/SiO_2$ catalysts

a) Dispersity of metal particles

In all cases the introduction of small quantities of E^{IV} into catalysts containing Ni, Pd, or Pt on SiO_2 results in a decrease in the metal particle size and a narrower distribution of particle size, while the stability of the metal particles towards sintering increases. This is suggested by the data of electron microscopy (Fig. 5), chemisorption (Table 2), and X-ray photoelectron spectroscopy.[176]

b) Chemisorptive properties

Palladium and platinum catalysts on TiO_2 and ZrO_2 obtained from organometallic compounds contain dispersed metal particles (15 Å after reduction at 823 K). These catalysts adsorb virtually no H_2 (H/M = 0.01) or CO (CO/M = 0.05).[176,183,184]

Modified Pd catalysts are also characterised by a reduced chemisorption of CO and H_2. It follows from a comparison of the dispersity of Pd in (Pd + Zr)/SiO_2 and (Pd + Ti)/SiO_2 catalysts with a quantity of adsorbed H_2 and CO that the degree of coverage of the surface of Pd with these molecules is less than 50%. In the presence of Ti ions on the surface of SiO_2 platinum also exhibits

decreased chemisorption of H_2 and CO (H/Pt = 0.2, CO/Pt = 0.2).[176,183,184] Thus, the introduction of E^{IV} ions on to the surface of SiO_2 leads qualitatively to the same effects relative to chemisorption on Group VIII metals as the deposition of these metals on TiO_2 or ZrO_2.

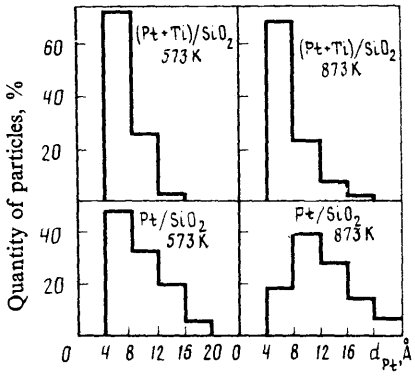


Figure 5. Dependence of the distribution of particle size on the temperature of reduction of the catalysts.[176]

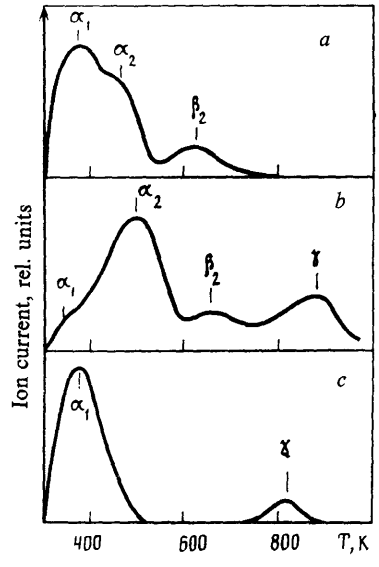
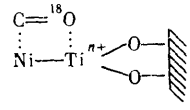


Figure 6. Thermal desorption spectra of ^{13}CO from nickel catalysts reduced at 823 K.[178] *a*, 0.72% Ni/SiO_2; *b*, (0.94% Ni + 1.1% Ti)/SiO_2; *c*, 0.47% Ni/TiO_2.

The nature of the adsorption of CO on Ni catalysts was studied by Alekseev et al.[178] by means of TPD. Three forms of adsorbed CO characterise the spectrum of the thermal desorption of CO from the surface of Ni/SiO_2 (Fig. 6). Two low-temperature molecular forms α_1 and α_2 occur with temperatures of the desorption maximum (T_{max}) at 370 and 450 K together with a medium-temperature form β_2 with T_{max} = 620 K, which results from the recombination of C and O on the surface of nickel.

The TPD spectrum of the desorption of CO from the surface of a (Ni + Ti)/SiO_2 can be represented qualitatively as the sum of the TPD spectra of desorption from the surface of Ni/SiO_2 and Ni/TiO_2 catalysts. This phenomenon suggests that Ni particles of two types are present in the modified catalyst: 1) particles with chemisorptive properties that are similar to Ni/SiO_2; 2) those with properties that are similar to Ni/TiO_2.

The spectrum of the thermal desorption of CO from the surface of Ni/TiO_2 differs from that for the thermal desorption from the surface of Ni/SiO_2 by virtue of the presence of a high-temperature dissociative γ form, which represents the dissociatively adsorbed CO at the metal–support interface. This assertion follows from the fact that for the Ni/TiO_2 catalyst the γ form plays an active part in the heteroexchange of the oxygen in $C^{18}O$ with lattice oxygen. In the case of Ni/SiO_2 this reaction does not occur. The heteroexchange of $C^{18}O$ with oxygen of the support on a (Ni + Ti)/SiO_2 catalyst suggests that Ti ions in an oxygen environment form part of the active sites on which dissociative adsorption of $C^{18}O$ occurs:[178]



For Pd catalysts the nature of the activation of CO was studied by means of IR spectroscopy. In addition to the absorption bands corresponding to the linear and bridged forms of CO adsorption on metallic palladium, in the adsorption of CO on (Pd + Zr)/SiO_2 an additional absorption band appears at 1610 cm^{-1}, whose intensity increases, and which is shifted 10 cm^{-1} to higher frequency with an increase in the CO pressure (Fig. 7).[184] From the results obtained and also the literature data the absorption band at 1600 cm^{-1} can be attributed to the adsorption of CO on mixed active sites involving Pd atoms and Zr ions.

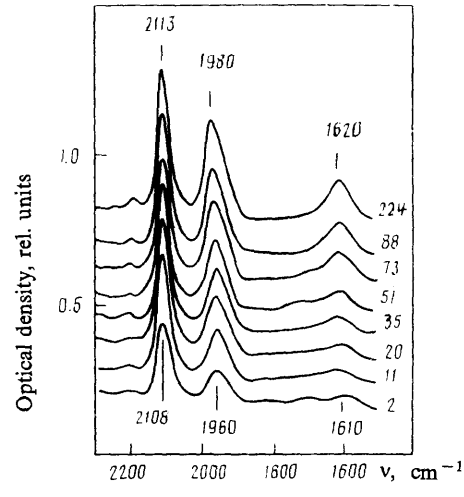


Figure 7. IR spectra of CO adsorbed on a (1.7% Pd + 5.2% Zr)/SiO_2 catalyst reduced at 573 K.[184] The figures by the curves correspond to the CO pressures (in Torr).

c) Study of the electronic state of supported elements

Information about the electronic state of Pd and (Pd + Zr)/SiO_2 systems was obtained by means of X-ray photoelectron spectroscopy. When Pd was supported on silica gel modified with Zr ions, there was an increase in E_{bind} for the $3d_{5/2}$ level of Pd by 0.6–1.0 eV compared to E_{bind} for this level in Pd/SiO_2, corresponding to a reduction in electron density on the Pd atoms in the presence of Zr ions. The electron-deficient nature of Pd in (Pd + Zr)/SiO_2 was also suggested by the IR spectroscopic data.[183,184] Since samples of similar dispersity were being compared, this positive shift could not be due to a dimensional effect but was caused by an interaction between supported components in the (Pd + Zr)/SiO_2. In the case of (Pt + Ti)/SiO_2 there was also a tendency for E_{bind} of the $4f_{7/2}$ level of Pt to increase, but these changes were of the same order as the experimental error.[176]

After deposition of Pd and Pt on samples of Zr/SiO_2 and Ti/SiO_2 it was not possible to detect changes in the binding energies of levels in Ti and Zr. However, deposition of Pd and Pt results in a decrease in the relative intensity of the spectrum of the promoting element by 20% on average. These findings suggest that a proportion of the ions of the promoting elements is shielded by the metal particles.

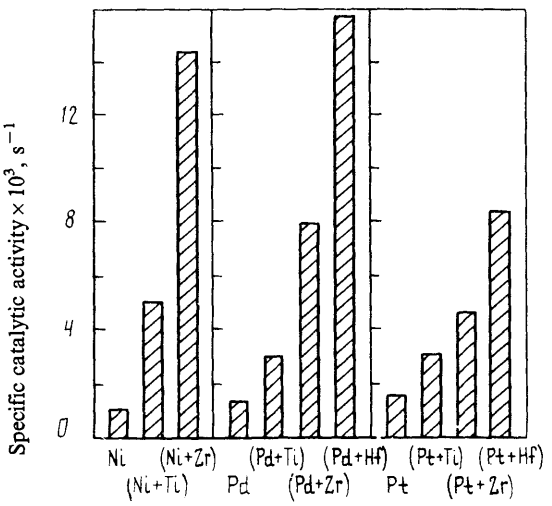


Figure 8. Effect of a Group IV element on the activity of a Group VIII metal in the hydrogenation of CO at 523 K.[176,177,183,184]

d) Catalytic properties

In all cases the presence of E^{IV} ions in Ni, Pd, and Pt catalysts causes an increase in activity of the supported metal in the hydrogenation of CO. At the same time the selectivity of the process also varies—for Ni the yield of C_2–C_3 hydrocarbons increases to 30%, while for Pd and Pt the output of hydrocarbons decreases and the yield of methanol increases, reaching 95–99% at 523 K and a pressure of 10 atm. For all the Group VIII metals the promoting effect of the E^{IV} ions increased in the series: Ti < Zr < Hf (Fig. 8).

In the hydrogenation of benzene a decrease in the activity of (M + E^{IV})/SiO_2 catalysts compared to M/SiO_2 occurred by a factor of up to 10. At the same time the activity of the model systems was similar to that of M/TiO_2 and M/ZrO_2 catalysts.[173–184]

In the hydrogenolysis of ethane the activity of (M + E^{IV})/SiO_2 systems, like that of M/E_xO_y catalysts, decreases by a factor of 100–1000 compared to MSiO_2. It should be noted that after high-temperature oxidation the inhibitory effect of E^{IV} ions on the activity of the model systems in the conversion of hydrocarbons disappears in a similar manner to that observed for M/E_xO_y systems.

We should point out that the decrease in activity of (M + E^{IV})/SiO_2 catalysts occurs even at low reduction temperatures (573 K). In this respect the model systems studied by Ryndin et al.[173–184] differ from metals on bulk oxides, where SMSI occurs after their reduction at high temperatures (above 773 K). This difference occurs because in the M/E_xO_y catalysts the active sites that are needed for SMSI to develop are only formed during high-temperature reduction. At the same time formation of the active sites for the model systems actually occurs during synthesis of the catalaysts when the second component is deposited on the silica gel modified with E^{IV} ions.[181,184] Therefore, high reduction temperatures are not needed for the effects of SMSI to be exhibited when model (M + E^{IV})/SiO_2 catalysts are used.

3. Possible causes of the effect of Group IV elements on the properties of supported metal particles

Let us examine the possible models of surface formations in supported model (M + E^{IV})/SiO_2 catalysts (Fig. 9).[179]

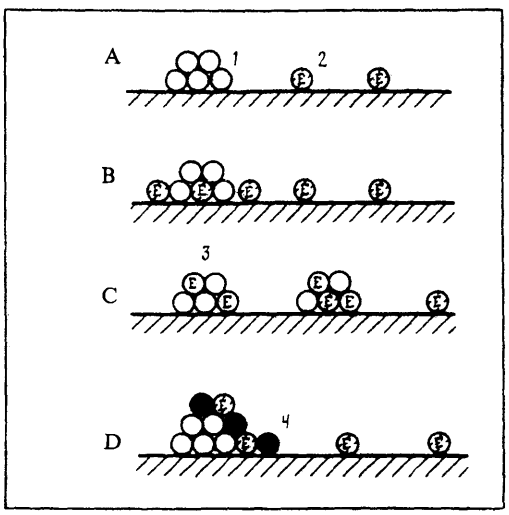


Figure 9. Possible models of surface formations in catalysts supported on SiO_2:[179] *1*, atom of Group VIII metal; *2*, surface ion of promoting element E^{IV}; *3*, atom of E^{IV} element in a zero valence state; *4*, oxygen ion.

Model A. Metal particles that are not bound to E^{IV} occur on the surface. This separate distribution of M and E^{IV} does not explain the increase in dispersity nor the decrease in catalytic activity in the

conversion of hydrocarbons. However, it cannot be excluded that a proportion of the metal particles is located on the surface of SiO_2 without interacting with E^{IV}.

Model B. In this case it is assumed that the metal particles interact directly with the surface ions of the transition element in a similar manner to that previously proposed.[8]

Model C. This model assumes the formation of particles of an alloy of modified element and metal. Theories of this type have also been advanced to explain the properties of M/E_xO_y systems.[3] However, for the model systems studied by Ryndin et al.[173-184] such a model is not consistent with the presence of E^{IV} ions in an intermediate oxidation state in the catalysts.

Model D. Adsorption of E^{IV} oxide occurs on the surface of a cluster of metal M. However, this model is at variance with the decrease in surface concentration of E^{IV}, as indicated by the data of X-ray photoelectron spectroscopy.

Thus, a model of the type B can explain the following results:

a) the increase in dispersity of metal particles in the presence of E^{IV} through the stabilisation of metal clusters on fixed E^{IV} ions;

b) the change in catalytic properties as a result of the change in electronic state of the metal cluster;

c) the effect of initial oxidation. Treatment of $(M + E^{IV})/SiO_2$ samples with oxygen at a high temperature leads to oxidation and segregation of the components (M and E^{IV}) followed by sintering of the metal;

d) the change in chemisorptive properties of the metal through a change in its electronic state.

At the same time the existence of $M-E^{IV}$ bonds was not revealed by the direct EXAFS method in these studies,[173-184] which would constitute the most important evidence in favour of model B occurring for the model systems. The absence of information about the existence of $M-E^{IV}$ bonds in the EXAFS spectra is evidently related to the reasons discussed in Section III. However, a set of evidence for the existence of an interaction between the metal and promoter in $(M + E^{IV})/SiO_2$ catalysts has been obtained.[173-184] Thus, it has been demonstrated that the following occur:

1) a change in the spectroscopic properties of Ti^{3+} ions when an active metal is deposited (EPR data);

2) a change in the electronic state of the components in model systems and also shielding of a proportion of the ions of promoter by metal clusters (IR and X-ray photoelectron spectroscopic data);

3) the presence in the model catalysts of an additional absorption band due to CO in the region of 1600 cm^{-1} (IR spectroscopic data);

4) the presence of a high-temperature γ form of adsorbed CO in the TPD spectra of model systems as well as data on the heteroexchange of $C^{18}O$ with oxygen of the support (TPD data);

5) retention of a chemical bond with the surface of silica gel for E^{IV} ions during reduction of the catalysts (IR and EXAFS spectroscopic data).

Thus, the data of TPD, EPR, EXAFS, and IR spectroscopy obtained from studies of model systems[173-184] in combination with chemisorption and catalytic electron microscopy data support the validity of model B for $(M + E^{IV})/SiO_2$ catalysts. This model does not exclude additional reasons (in addition to the change in electronic properties of a cluster of metal M) for the change in catalytic activity. For example, the increase in activity in the hydrogenation of CO may occur as a result of activation of CO on mixed active sites according to Scheme (I), as put forward in a number of studies.[18,49,130,131,135] At the same time the increase in activity of $(M + E^{IV})/SiO_2$ catalysts in the hydrogenation of CO in the promoter series Ti < Zr < Hf appears reasonable since the strength of the $E^{IV}-O$ bond increases in the same series.[185] Thus, by varying the nature of the Group IV ion in the chemisorption complex (Scheme I), the strength of the bond between the oxygen atom of the CO molecule and the E^{IV} ion will increase in the above series. This may assist the addition of hydrogen adsorbed on the metal to the carbon atom to form a formyl complex, which acts as an intermediate in the synthesis of methanol from CO and H_2.[185]

4. Mechanism of the metal–support interaction in M/E_xO_y systems

As has already been mentioned in Section III, in an examination of the effects of SMSI a considerable number of reasons have been suggested in the literature to explain the unusual properties of metals supported on TiO_2 and other oxides of transition elements. However, not one of these theories has received conclusive experimental confirmation. It is possible that for catalysts containing metal particles on transition element oxides there is no single cause of the effects of the so-called SMSI but the different characteristics of the metal properties have different causes. Let us examine the above mechanisms in terms of the results obtained by Ryndin et al.[173-184]

In one of the studies of Baker[89] it was found in a Pt/TiO_2 catalyst that Pt particles with a cross-section of several tens of Ångstroms had a flat, frequently hexagonal shape and were located on reduced sections of the surface of TiO_2 (Ti_4O_7 suboxide), which, according to Baker, gives rise to SMSI. The difference in shape and size of the metal particles in M/TiO_2 catalysts in this study[89] was due to the difference in the methods of preparing these catalysts. A study of M/TiO_2 catalysts prepared via fixed metal complexes showed that over a wide temperature range of reduction (573–823 K) the particles of supported metal retained a spherical form.[173-184] Furthermore, these catalysts exhibit all the catalytic and chemisorptive properties that are characteristic of SMSI. Consequently, the presence of flat metal particles located on the surface of suboxides such as Ti_4O_7 is not a necessary condition for the effects of SMSI to occur.

The results obtained in these studies[173-184] on $(M + E^{IV})/SiO_2$ catalysts suggest that intermetallic compounds and dispersed phases of E^{IV} oxides are not present in these catalysts. Hence the common nature of the catalytic and chemisorptive properties of M/E_xO_y and $(M + E^{IV})/SiO_2$ catalysts cannot be explained in terms of mechanisms that assume the formation of intermetallic compounds and the transfer of electron density to the metal particles from the bulk of the support.

In recent years in the literature there has been an increasing amount of publishd data to suggest that direct interaction between atoms of the active metal and low-valent surface ions of the transition element causes the SMSI effects.[67,161,186,187] Theoretical calculations of $PtTiO_5$ [67] and $Ni_3Ti_2O_5$ [187] clusters showed that in these cases a strong covalent bond exists between the metal atoms and the Ti^{n+} ion. At the same time it appears that the metal atoms are positively charged as a result of the transfer of electron density from the Ni atom to the Ti^{n+} ion. In an analysis of the properties of the model $(M + E^{IV})/SiO_2$ catalysts,[173-184] a model of the active sites involving interaction between the metal atoms and the promoter ions was put forward. Taking into account the similarity in the properties of $(M + E^{IV})/SiO_2$ and M/E_xO_y systems, this model can be extended to M/E_xO_y catalysts. In fact, $RhTi^+$ clusters were

detected in studies of a Rh/TiO_2 catalyst using secondary ion mass spectrometry[28,79] while the presence of $Rh-Ti^{n+}$ bonds in a Rh/TiO_2 catalyst was demonstrated by EXAFS in two studies.[86,87]

The idea that the reactants are activated at the boundary between the metal and support is a logical addition to the mechanism of Horsley,[67] since in its original exposition this theory[49,50] assumes that the catalytic and chemisorptive properties of M/E_xO_y catalysts change both as a result of a change in the electronic properties of the metal and through the activation of the reactants at the metal–support boundary. In the opinion of Burch et al.,[20,45] participation of cations of the support in the activation of a CO molecule will assist the hydogenation of CO and thus permit an increase in activity of M/E_xO_y catalysts. The existence of mixed active sites in M/E_xO_y catalysts has been demonstrated experimentally by Bredikhin et al.[136–139] The existence of such sites in $(M + E^{IV})/SiO_2$ catalysts has been demonstrated in the studies by Ryndin et al.[173–184]

The mechanism which assumes the diffusion of reduction products of the support to the surface of the metal particles has gained the widest recognition in the literature.[16,37,140] According to this mechanism, the reduction in chemisorptive properties of the metal and also the decrease in activity of M/E_xO_y catalysts in the conversion of hydrocarbons is due to blocking of the surface of the active metal with particles of the type TiO_x while the increase in activity of these systems in the hydrogenation of CO is due to the expansion of the metal–support interface, which results in an increase in concentration of mixed active sites incorporating metal atoms and ions of the support.[16,140] Results that would exclude this mechanism were not obtained in studies of M/E_xO_y catalysts.[173,184]

Furthermore, for the model $(M + E^{IV})/SiO_2$ catalysts the shielding of a proportion of the E^{IV} ions occurs as a result of their interaction with the metal atoms. Thus, a situation occurs for the model $(M + E^{IV})/SiO_2$ systems which is the opposite of what is proposed in the mechanism put forward by Meriaudeau[37] and Haller.[140] Consequently, when there are no E_xO_y residues on the surface of the metal (i.e., with no blocking of the surface of the metal), in the $(M + E^{IV})/SiO_2$ catalysts a reduction in chemisorption of CO and H_2 occurs as well as a decrease in activity of these catalysts in the conversion of hydrocarbons and an increase in their activity in the hydrogenation of CO. It may be assumed from these results and also the results of Burch and Flambard[50] which suggest that M/TiO_2 catalysts have high activity in the hydrogenation of CO even at low reduction temperatures, when the effect is absent that shielding of the surface of the metal with TiO_x particles is not a necessary condition for SMSI to occur.

It should be noted that the origins of SMSI in M/E_xO_y catalysts may be more complex than those in the model $(M + E^{IV})/SiO_2$ systems. Therefore, more rigorous arguments are required to prove the decoration mechanism for M/E_xO_y catalysts.

Thus, the results of a number of studies[4–8,28,79,86,136–139,173–184] suggest that SMSI in M/E_xO_y catalysts can be explained in terms of a mechanism which assumes a direct interaction between the metal atoms and low-valent ions of the support and the formation of mixed active sites involving metal atoms and support ions at the metal–support interface.

The above data show that supported metal catalysts obtained from organometallic compounds are convenient model systems for a study of the mechanism of SMSI. With the use of organometallic compounds it is possible not only to obtain highly dispersed metal catalysts but also to carry out the directed synthesis of active sites on the surface of supports and thus prepare catalytic systems with given chemical properties. From the synthesis and study of model $(M + E^{IV})/SiO_2$ catalysts obtained from organometallic compounds it is possible to make a critical investigation of the mechanisms that have been put forward in the literature to explain the effects of SMSI.

References

1. G-M Schwab *Adv. Catal.*, 1978, **27** 1
2. F Solymosi *Catal. Rev. Sci. Eng.*, 1968, **1** 233
3. S J Tauster, S C Fung, R L Garten *J. Am. Chem. Soc.*, 1978, **100**(1) 170
4. Yu I Yermakov *Catal. Rev. Sci. Eng.*, 1976, **13**(1) 77
5. Yu I Yermakov, V A Sakharov, B N Kuznetsov *Zakreplennye Kompleksy na Oksidnykh Nositelyakh v Katalize* (Fixed Complexes on Oxide Supports in Catalysis), Nauka, Novosibirsk, 1980, p. 248
6. N G Maksimov, G A Nesterov, V A Zakharov, et al. *J. Mol. Catal.*, 1978, **4**(3) 167
7. M S Ioffe, B N Kuznetsov, Yu A Ryndin, Yu I Yermakov *Proceedings of the 6th International Congress on Catalysis*, The Chemical Society, London, 1976, Vol. 1, p. 131
8. Yu I Yermakov *Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, 1981, Vol. 7A, p.57
9. S J Tauster, S C Fung, R T K Baker, J A Horsley *J. Catal.*, 1978, **55**(1) 29
10. S J Tauster, S C Fung, R T K Baker, J A Horsley *Science*, 1981, **211**(4487) 1121
11. Z Hu, K Kunimori, H Asano, T Uchijima *J. Catal.*, 1988, **112**(2) 478
12. R Burch *Hydrogen Effects in Catalysis: Fundamental and Practical Applications*, Basel, New York, 1988, p. 348
13. D Duprez, A Miloudi *Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, 1981, Vol. 11, 179
14. H-C Loye, T A Faltens, A M Stacy *J. Am. Chem. Soc.*, 1986, **108**(9) 2488
15. T Beringhelli, A Gervasini, F Morazzoni, D Strumolo *Proceedings of the 8th International Congress on Catalysis*, Dechema, Berlin, 1984, Vol. 45, p. 63
16. J B F Anderson, J Bracey, R Burch, A R Flambard *Proceedings of the 8th International Congress*, Dechema, Berlin, 1984, Vol. 5, p. 111
17. S C Fung *J. Catal.*, 1982, **76**(1) 225
18. P G Menon, G F Froment *Appl. Catal.*, 1981, **1**(1–2) 31
19. W Hongli, T Sheng, X Maosong, et al. *Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, 1982, Vol. 11, p. 19
20. J D Bracey, R Burch *J. Catal.*, 1984, **86**(2) 384
21. K Kunimori, H Abe, E Yamaguchi, et al. *Proceedings of the 8th International Congress on Catalysis*, Dechema, Berlin, 1984, Vol. 5, p. 251
22. A Vannice, P Chon *J. Chem. Soc., Chem. Commun.*, 1984, 1590
23. M A Vannice, L C Hasselbring, B Sen *J. Catal.*, 1985, **95**(1) 57
24. M A Vannice, L C Hasselbring, B Sen *J. Phys. Chem.*, 1985, **89**(14) 2972
25. M A Vannice, L C Hasselbring, B Sen *J. Catal.*, 1986, **97**(1) 66
26. P Meriaudeau, O H Ellestad, M Dufaux, C Naccache *J. Catal.*, 1982, **75**(1) 243
27. M A Vannice, P Chon *Proceedings of the 8th International Congress on Catalysis*, Dechema, Berlin, 1984, Vol. 5, p. 99
28. E S Shpiro, B B Dyusenbina, O P Tkachenko, et al. *Kinet. Katal.*, 1986, **27** 638

29. D E Resasco, R J Fenoglio, M P Suarez, O J Cechini *J. Phys. Chem.*, 1986, **90**(18) 4330
30. R Burch, A R Flambard *React. Kinet. Catal. Lett.*, 1981, **17**(1–2) 23
31. J B F Anderson, R Burch, J A Cairns *J. Catal.*, 1987, **107**(2) 364
32. E I Ko, R L Garten *J. Catal.*, 1981, **68**(1) 233
33. P A Burke, E I Ko *J. Catal.*, 1989, **116**(1) 230
34. A J Den Hartog, A G T M Bastein, V Ponec *J. Mol. Catal.*, 1989, **52**(1) 129
35. K Kunimori, H Nakamura, Z Hu, T Uchijima *Appl. Catal.*, 1989, **53**(1) L11
36. R J Fenoglio, G M Nunez, D E Resasco *J. Catal.*, 1990, **121**(1) 77
37. P Meriaudeau, J F Dutel, M Dufaux, C Naccache *Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, 1982, Vol. 11, p. 95
38. M Ichikawa *J. Chem.Soc., Chem. Commun.*, 1978, **13** 566
39. M Ichikawa *Bull. Chem. Soc. Jpn.*, 1978, **51**(8) 2268
40. M Ichikawa, K Sikakura *Shokubai*, 1979, **21**(4) 253
41. Yu A Ryndin, R F Hicks, A T Bell, Yu I Yermakov *J. Catal.*, 1981, **70**(2) 287
42. M Ichikawa, H Poppa, M Boudart *J. Catal.*, 1985, **91**(1) 1
43. D L Doering, H Poppa, J T Dickinson *J. Catal.*, 1982, **73**(1) 104
44. R F Hicks, A T Bell *J. Catal.*, 1985, **91**(1) 104
45. J S Rieck, A T Bell *J. Catal.*, 1985, **96**(1) 88
46. K P Kelly, T Tatsumi, T Uematsu, et al. *J. Catal.*, 1986, **101**(2) 396
47. M Arakawa, K Tekeuchi, T Matsuzaki, Y Sugi *Chem. Lett.*, 1984, (9) 1607
48. Y Saitoh, S Ohtsy, Y Makir, et al. *Bull. Chem. Soc. Jpn.*, 1990, **63**(1) 108
49. R Burch, A R Flambard *Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, 1982, Vol. 11, p. 193
50. R Burch, A R Flambard *J. Catal.*, 1982, **78**(2) 389
51. R Burch, A R Flambard *J. Catal.*, 1984, **85**(1) 16
52. M A Vannice, R L Garten *J. Catal.*, 1979, **56**(2) 236
53. B Song, X Jiang *J. Fuel Chem. Technol. (Chinese)*, 1988, **16**(4) 381
54. T Mori, S Taniuchi, Y Mori, et al. *Shokubai Catalyst*, 1988, **30**(6) 496
55. I Mochida, N Ikeyama, H Ishibashi, H Fujitsu *J. Catal.*, 1988, **110**(1) 159
56. M A Vannice, C C Twu, S H Moon *J. Catal.*, 1983, **79**(1) 70
57. M A Vannice, C C Twu *J. Catal.*, 1983, **82**(1) 213
58. S-Y Wang, S H Moon, M A Vannice *J. Catal.*, 1981, **71**(1) 167
59. P Turlier, J A Dalmon, G A Martin *Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, 1982, Vol. 11, p. 203
60. Z Jiang, B-H Song, Y Chen, Y-W Wang *J. Catal.*, 1986, **102**(1) 257
61. R Szymanski, H Charcosset, V Perrichon *Proceedings of the 8th International Congress on Catalysis*, Dechema, Berlin, 1984, Vol. 2, p. 151
62. S-M Fang, J M White, T J Campione, J G Ekerrdt *J. Catal.*, 1985, **96**(2) 491
63. M A Vannice, S-Y Wang, S H Moon *J. Catal.*, 1981, **71**(1) 152
64. S D Jackson, R B Moyes, P B Wells *J. Chem. Soc., Faraday Trans.*, 1987, **83**(3) 905
65. C Dall'Agnol *J. Catal.*, 1985, **96**(1) 106
66. M A Vannice *J. Catal.*, 1982, **74**(1) 199
67. J A Horsley *J. Am. Chem. Soc.*, 1979, **101**(11) 2870
68. D R Short, A N Mansour, J W Cook, et al. *J. Catal.*, 1983, **82**(2) 299
69. M Koudelka, A Monnier, J Sanchez, J Augustynsky *J. Mol. Catal.*, 1984, **25**(1–3) 295
70. S J Tauster *Acc. Chem. Res.*, 1987, **20**(11) 389
71. G I Golodets, I T Chashechnikova, L G Svintsova, et al. *React. Kinet. Catal. Lett.*, 1987, **34**(2) 267
72. E V Prokhorenko, N V Pavlenko, G I Golodets *Kinet. Katal.*, 1988, **29**(4) 820
73. N I Il'chenko, Yu I Shmyrko, L N Raevskaya, G I Golodets *Teor. Eksp. Khim.*, 1988, **24**(5) 612
74. R F Hicks, Yen Qi-Jie, A T Bell *J. Catal.*, 1984, **89**(2) 498
75. T Huizinga, H F J Van't Blik, J C Vis, R Prins *Surf. Sci.*, 1983, **135**(1–3) 580
76. C-C Kao, S-C Tsai, Y-W Chung *J. Catal.*, 1982, **73**(1) 136
77. B A Sexton, A E Hughes, K Foger *J. Catal.*, 1982, **77**(1) 85
78. S-H Chien, B N Shelimov, D E Resasco, et al. *J. Catal.*, 1982, **77**(1) 301
79. E S Shpiro, B B Dyusenbina, G V Antoshin, et al. *Kinet. Katal.*, 1984, **25**(6) 1505
80. E S Shpiro, B B Dysenbina, O P Tkachenko, et al. *J. Catal.*, 1988, **110**(2) 262
81. H R Sadeghi, V E Henrich *J. Catal.*, 1988, **109**(1) 1
82. C Ocal, S Ferrer *J. Chem. Phys.*, 1986, **84**(11) 6474
83. C C Kao, S C Tsai, M K Bahl, Y W Chung *Surf. Sci.*, 1980, **95**(1) 1
84. Y-W Chung, W B Weissbard *Phys. Rev., B*, 1979, (8) 3456
85. Z Bastl, P Mikusik *Czech. J. Phys.*, 1984, **B34**(9) 989
86. D C Koningsberger, J H A Martens, R Prins, et al. *J. Phys. Chem.*, 1986, **90**(4) 3047
87. S Sakellson, M McMillan, G L Haller *J. Phys. Chem.*, 1986, **90**(9) 1733
88. D E Resasco, R S Weber, S Sakellson, et al. *J. Phys. Chem.*, 1988, **92**(1) 189
89. R T K Baker, E B Prestridge, R L Garten *J. Catal.*, 1979, **56**(3) 390
90. T Huizinga, R Prins *J. Phys. Chem.*, 1981, **85**(15) 2156
91. R T K Baker, E B Prestridge, R L Garten *J. Catal.*, 1979, **59**(2) 293
92. K A Gingerich, I Shim, S K Gupta, J E Kingcade *Surf. Sci.*, 1985, **156**(1) 495
93. D J C Yates, L L Murrell, E B Prestridge *J. Catal.*, 1979, **57**(1) 41
94. D G Mustard, C H Bartholomew *J. Catal.*, 1981, **67**(1) 186
95. R T K Baker, J J Chludzinski, J A Dumesic *J. Catal.*, 1985, **93**(2) 312
96. E Ruckenstein, S H Lee *J. Catal.*, 1987, **104**(2) 259
97. J A Dumesic, S A Stevenson, R D Sherwood, R T K Baker *J. Catal.*, 1986, **99**(1) 79
98. R T K Baker, E B Prestridge, G B McVicker *J. Catal.*, 1984, **89**(2) 422
99. R Szymanski, H Charcosset *Platinum Metals Rev.*, 1986, **30**(1) 23
100. R Szymanski, H Charcosset *J. Mol. Catal.*, 1984, **25**(1–3) 337
101. Chen Yi-Xuan, Chen Yan-Xin *J. Catal. (Chinese)*, 1987, **8**(3) 310
102. L Wang, G W Quao, H Q Ye, et al. *J. Electron Microsc. Techn.*, 1988, **10**(1) 7
103. A J Simoens, R T K Baker, D J Dwuyer, et al. *J. Catal.*, 1984, **86**(2) 359

104. D Tomanek, R Hauert, P Oelhafen, et al. *Surf. Sci.*, 1985, **160**(2) L493
105. U Bardi, D Dahlgren, P N Ross *J. Catal.*, 1986, **100**(1) 196
106. U Bardi, G A Samorjai, P N Ross *J. Catal.*, 1984, **85**(1) 272
107. V V Lunin, O V Kryukov, S O Kozhinskii, et al. *Neftekhimiya*, 1984, **24**(2) 233
108. E V Perikhanova, L A Erivanskaya, V V Lunin *Neftekhimiya*, 1986, **26**(5) 594
109. L A Rudnitskii, T N Sobolev, I I Bondartsova, et al. *Dokl. Akad. Nauk SSSR*, 1987, **295**(3) 650
110. A Dauscher, W Müller, G Maire *Catal. Lett.*, 1989, **2**(3) 139
111. A Baiker, D Gasser *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**(4) 999
112. Tang Ren-Yuan, Wu Rong-An, Lin Li-Wu Appl. Catal., 1984, **10**(2) 163
113. K Kunimori, Y Ikeda, M Soma, T Uchijima *J. Catal.*, 1983, **79**(1) 185
114. P A Chernyavskii, V V Kiselev, P Ya Yakunina, V V Lunin *Kinet. Katal.*, 1987, **29**(4) 921
115. X E Verykios, F P Stein, R W Coughlin *J. Catal.*, 1980, **66**(1) 147
116. E C Akubuiro, X E Verykios, T Ioannides *Appl. Catal.*, 1989, **46**(2) 297
117. B-H Chen, J M White *J. Phys. Chem.*, 1982, **86**(18) 3534
118. J-M Herrmann, P Pichat *J. Catal.*, 1982, **78**(2) 425
119. J-M Herrmann, J Disdier, P Pichat *Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, 1982, Vol. 11, p. 27
120. V A Poluboyarov, G A Dergaleva, V F Anufrienko, et al. *Kinet. Katal.*, 1989, **30**(3) 700
121. H-C Longe, A M Stacy *J. Am. Chem. Soc.*, 1985, **107**(15) 4567
122. T Huizinga, R Prins *Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, 1982, Vol. 11, p. 11
123. M A Vannice, B Sen *J. Catal.*, 1989, **115**(1) 65
124. S Taniguchi, Y Mori, T Hattori, et al. *J. Catal.*, 1989, **116**(1) 108
125. K Tamaru, U Bardi, Y Nihei *Surf. Sci.*, 1988, **197**(3) L281
126. K-H Stadler, H Schneider, K Kochloefl *Proceedings of the 8th International Congress on Catalysis*, Dechema, Berlin, 1984, Vol. 45, p. 229
127. E C Akubuiro, X E Verykios *J. Catal.*, 1987, **103**(2) 320
128. T Hayasaka, Y Ohbayashi, S Uchiyama, N Kawata *Catalysis by New Materials: The 8th Japan—Soviet Catalysis Seminar*, Tokyo, 1986, p. 55
129. S P Mehandru, A B Andersin, P N Poss *J. Catal.*, 1986, **100**(1) 210
130. R W Rice, G L Haller *J. Catal.*, 1975, **40**(2) 249
131. M Ichikawa, T Fukushima *J. Phys. Chem.*, 1985, **89** 1564
132. E Guglielminotti *J. Catal.*, 1989, **120**(1) 287
133. C W Garland, R C Lord, P F Troiano *J. Phys. Chem.*, 1965, **69** 1195
134. N J Nelson, N E Kime, D F Shriver *J. Am. Chem. Soc.*, 1969, **91** 5173
135. W M H Sachtler, D F Shriver, W B Hollenberg, A F Lang *J. Catal.*, 1985, **92**(2) 429
136. M N Bredikhin, Yu A Lokhov, B L Kuznetsov *Kinet. Katal.*, 1987, **28**(3) 671
137. M N Bredikhin, Yu A Lokhov *Kinet. Katal.*, 1987, **28**(3) 678
138. M N Bredikhin, Yu A Lokhov, K I Zamaraev *Dokl. Akad. Nauk SSSR*, 1988, **301**(5) 1124
139. M N Bredikhin, Yu A Lokhov *J. Mol. Catal.*, 1989, **55**(1—3) 55
140. D E Resasco, G L Haller *J. Catal.*, 1983, **82**(2) 279
141. L Bonneviot, G L Haller *J. Catal.*, 1988, **113**(1) 96
142. J S Rieck, A T Bell *J. Catal.*, 1986, **99**(2) 262
143. J A Cairns, J E E Baglin, G J Clark, J F Ziegler *J. Catal.*, 1983, **83**(2) 301
144. Y-M Sun, D N Belton, J M White *J. Phys. Chem.*, 1986, **90**(21) 5178
145. G B Hoflund, A L Grogan, J D A Asbury, *J. Catal.*, 1988, **109**(1) 226
146. S Takantani, Y W Chung *Appl. Surf. Sci.*, 1984, **19**(1—4) 341
147. A A Slinkin, A A Dulov, E S Shpiro, et al. *Kinet. Katal.*, 1988, **29**(3) 694
148. D N Belton, Y-M Sun, J M White *J. Catal.*, 1986, **102**(2) 338
149. Y-W Chung, G Xuong, C-C Kao *J. Catal.*, 1984, **85**(1) 237
150. D N Belton, Y-M Sun, J M White *J. Phys. Chem.*, 1984, **88**(22) 5172
151. S Takatani, Y-W Chun *J. Catal.*, 1984, **90**(1) 75
152. G B Raupp, J A Dumesic *J. Catal.*, 1985, **95**(2) 587
153. J S Reick, A T Bell *J. Catal.*, 1986, **99**(2) 262
154. M E Levin, K J Williams, M Salmeron, et al. *Surf. Sci.*, 1988, **195**(1—2) 341
155. G B Hoflund, A L Grogan Jr, D A Asbury *J. Catal.*, 1988, **109**(1) 226
156. M E Levin, M Salmeron, A T Bell, G A Somorjai *Surf. Sci.*, 1988, **195**(3) 429
157. K J Williams, M Salmeron, A T Bell, G A Somorjai *Surf. Sci.*, 1988, **204**(3) 745
158. U Bardi, K Tamaru, Y Nihei *Catal. Lett.*, 1989, **3**(2) 117
159. L Kraus, M I Zaki, H Knözinger, B Tesche *J. Mol. Catal.*, 1989, **55**(1—3) 6
160. H Yoshitake, K Asakura, Y Iwasawa *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**(12) 4337
161. X Guoxing, T Sheng, W Hongli *Proceedings of the China—Japan Symposium on the Noble Metals in Catalysis*, Dalina, 1987, p. 56
162. S Tang, G-X Xiong, H-L Cai, H-L Wang *J. Catal. (Chinese)*, 1987, **8**(3) 225
163. C S Ko, R J Gorte *J. Catal.*, 1984, **90**(1) 59
164. R J Gorte, E Altman *Surf. Sci.*, 1987, **188**(3) 327
165. P K DeBokx, R L C Bonne, J M Geus *Appl. Catal.*, 1987, **30**(1) 33
166. T H Fleisch, R F Hicks, A T Bell *J. Catal.*, 1984, **87**(2) 398
167. M S Spencer *J. Phys. Chem.*, 1984, **88**(5) 1046
168. M S Spencer *J. Catal.*, 1985, **93**(2) 216
169. R A Demmin, R J Gorte *J. Phys. Chem.*, 1985, **89**(7) 1151
170. M E Levin, M Salmeron, A T Bell, G A Samorjai *J. Catal.*, 1987, **106**(2) 401
171. Y-W Chung, G Xiong, C-C Kao *J. Catal.*, 1984, **85**(1) 237
172. Y-B Zhao, Y-W Chung *J. Catal.*, 1987, **106**(2) 369
173. Yu I Yermakov, Yu A Ryndin, O S Alekseev, et al. *Kinet. Katal.*, 1984, **25**(4) 1017
174. Yu I Yermakov, Yu A Ryndin, O S Alekseev, et al. *J. Chem. Soc., Chem. Commun.*, 1984, 1480
175. Yu I Yermakov, O S Alekseev, V A Shmachkov, et al. *Kinet. Katal.*, 1985, **26**(5) 1270
176. Yu I Yermakov, Yu A Ryndin, O S Alekseev, et al. *Appl. Catal.*, 1986, **26** 313
177. Yu A Ryndin, O S Alekseev, M N Vasileva, et al. *Kinet. Katal.*, 1987, **28**(4) 900
178. O S Alekseev, V A Shmachkov, Yu A Ryndin, Yu I Yermakov *Kinet. Katal.*, 1987, **28**(4) 908

179. O S Alekseev , Candidate's Thesis in Chemical Sciences, Institute of Catalysis, Siberian Branch of the USSR Academy of Sciences, Novosibirsk, 1989, p. 245
180. Yu I Yermakov, Yu A Ryndin, O S Alekseev, et al. *J. Mol. Catal.*, 1989, **49** 121
181. O S Alekseev, V A Poluboyarov, Yu A Ryndin, V F Anufrienko *React. Kinet. Catal. Lett.*, 1989, **38**(2) 319
182. A M Volodin, O S Alekseev, V A Bol'shov, Yu A Ryndin *Kinet. Katal.*, 1990, **31**(1) 179
183. O S Alekseev, V I Zaikovskii, Yu A Ryndin *Appl. Catal.*, 1990, **63** 37
184. Yu A Ryndin, O S Alekseev, E A Paukshtis, et al. *Appl. Catal.*, 1990, **63** 51
185. A Kiennemann, J P Hindermann, A Chakor-Alami *Bull. Soc. Chim. Fr.*, 1985, (3) 399
186. M Levin, M Salmeron, A T Bell, G A Somorjai *Surf. Sci.*, 1986, **169**(2) 123
187. Y Li, R Chen, G Xiong, H Wang *J. Mol. Catal.*, 1987, **42**(3) 337

Translated from *Uspekhi Khimii* **61** 792–814 (1992)

Inhibition–initiation in the pyrolysis of hydrocarbon mixtures

L V Shevel'kova, L E Gusel'nikov, G Bach, G Zimmermann
A V Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow
Central Institute of Organic Chemistry, Leipzig, Germany

ABSTRACT. **The results of investigations on the mutual influence of hydrocarbons of various classes on the rate and route of decomposition under copyrolysis conditions are correlated and discussed. A general concept has been formulated as to the mechanism of the inhibition–initiation phenomenon based on competing chain propagation reactions according to which a hydrocarbon may act both as an inhibitor and as an initiator of decomposition. The course of this action is determined by the character of partner behaviour and by the concentration of reactive radicals.**

The bibliography contains 90 references.

Contents

I.	Introduction	433
II.	Pyrolysis of mixtures of alkanes and alkenes	433
III.	Pyrolysis of mixtures of alkanes and dienes	434
IV.	Pyrolysis of mixtures of alkanes	435
V.	Pyrolysis of mixtures of alkanes and cycloalkanes	437
VI.	Effect of aromatic hydrocarbons	437
VII.	Mechanism of inhibition–initiation in the pyrolysis of hydrocarbon mixtures	437
VIII.	Conclusion	444

I. Introduction

The pyrolysis of hydrocarbons lies at the basis of the manufacture of fundamental products such as monomers and starting materials for fine organic synthesis in the chemical and petrochemical industries. The traditional raw material for pyrolysis is gas condensate and directly distilled solvent naphtha consisting mainly of alkanes, naphthenic hydrocarbons and a small quantity of aromatics. The involvement of gas oil and residual fractions after oil refining, of coal liquefaction products, carrying out the process under conditions of recirculation of short chain fractions separated from the products and also the preliminary treatment of a raw material by hydrogenation or hydrocatalytic treatment, complicates the composition of the raw material even more and demands consideration of the mutual influence of the components of the reaction mixture on the pattern of their thermal decomposition. This is also important because in addition to the initial hydrocarbons the products of their pyrolysis (hydrogen, methane, alkenes, aromatic hydrocarbons) are always present in the reaction zone.

The first investigations of the effect of added unsaturated hydrocarbons on the thermal decomposition of alkanes appeared in the thirties. With the development of industrial processes interest in the mutual effect grew further. This was particularly so in connection with the development of kinetic models of pyrolysis for which information is needed on the detailed mechanism of the decomposition of individual hydrocarbons and mixtures of them. Up to the present many experimental data have been accumulated on the behaviour of mixtures of hydrocarbons of different classes during pyrolysis. However the results and their interpretation by various authors are frequently in conflict.

The aim of the proposed review is to discuss the results of investigations of the thermal decomposition of mixtures of hydrocarbons and to formulate a general concept for the overall mechanism of their mutual effect as a system of competing reactions of radicals (intermediates) of various types propagating the chain. The pyrolysis considered is mainly of model binary mixtures of hydrocarbons present in the raw material or formed under the conditions of an industrial process.

II. Pyrolysis of mixtures of alkanes and alkenes

The pyrolysis of mixtures of alkanes with propene and 2-methylpropene, which are classic inhibitors of the process, has been investigated most. In the earlier work the overall kinetics of the process were generally studied by the change in pressure in the system. In this way no attention was paid to the conversion of the actual inhibitor,[1–4] assuming for example that it polymerised.[4] Attempts to assess the influence of ethane on the rate of decomposition of propene[5] and the development of these investigations[6–9,11] enabled exhaustive results to be obtained on the effect of an alkane on the decomposition of propene and 2-methylbutene at 700–900 °C. The investigations were carried out using propene labelled with radioactive carbon ^{14}C which enabled the course and rate of disappearance of even very small additions of propene to be followed. It was established as a result that ethane and propane show an initiating action on the decomposition of propene in its inhibition of alkane pyrolysis.

The rate constant for the decomposition of propene ($k_{C_3H_6}$) initiated by ethane is sharply reduced when the content of ethane in the initial mixture is reduced. Thus in a mixture with 99.9 vol.% ethane the rate constant for the decomposition of propene was approximately two orders of magnitude greater than the rate constant for the decomposition of pure propene. At the same time the rate constants for the decomposition of pure propene and for its equimolar mixture with ethane were practically equal.[7]

A smoother dependence of the rate constant for the decomposition of propene on propane concentration in the initial mixture was observed in the case of mixtures of propane with propene. Even in a mixture containing about 32 vol.% propane at a

temperature of 850 °C the rate constant for the decomposition of propene was approximately 5 times greater.[9] A further increase in the propane concentration in the mixture is accompanied by a proportionate increase in the rate constant for propene decomposition. The mutual effect of propane and propene on pyrolysis of their mixtures was first noticed in a study[12] in which it was shown that at 900 °C and atmospheric pressure the rate constant for propane decomposition ($k_{C_3H_8}$) fell sharply when the propene content in the initial mixture was increased and $k_{C_3H_6}$ increased with increase in propane concentration.

The yield of the main products from the pyrolysis of ethane and propane mixed with C_3H_6 differed from that calculated using the additivity hypothesis for their formation.[6–10,13] Thus a six-fold increase in the yield of 1-butene was recorded in the pyrolysis of a mixture of propane with propene.[13]

From the character of the change in overall rate constants for the decomposition of hydrocarbons[10,11] it was established that 2-methylpropene also shows an inhibitory action on the decomposition of C_2-C_4 alkanes. The rate of decomposition of 2-methylpropene in the mixtures increases with an increase in alkane content. However the inhibitory action of propene on the decomposition of ethane and propane is stronger than that of 2-methylpropene. The rate constants for the decomposition of propane in the presence of 20 vol.% propene and 2-methylpropene at 850 °C are 25 and 33 s^{-1} respectively.[10]

In the case of n-butane both C_3H_6 and iso-C_4H_8 show a less strong and approximately identical inhibitory action. At 850 °C the rate constants for the decomposition of n-butane in the presence of 20 vol.% propene and 2-methylpropene are about 90 and 95 s^{-1} respectively.[11]

In its turn n-butane shows the strongest initiating action on the decomposition of an inhibitor among the alkanes considered above. Thus at 800 °C the rate constants for the decomposition of iso-C_4H_8 in equimolar binary mixtures with ethane, propane and n-butane are about 2, 8 and 17 s^{-1} respectively.[10]

The yield of pyrolysis products of mixtures of alkanes with 2-methylpropene also differed from additivity and the greatest deviation from that calculated was observed on pyrolysis of mixtures of ethane with 2-methylpropane and of propane with propene.

An inhibitory action of propene and 2-methylpropene on the overall decomposition process of the higher n-alkanes ($>C_5$) has been recorded. At relatively low temperatures (450–540 °C) propene and 2-methylpropene inhibit the decomposition of pentanes,[14–16] and 2-methylpropene is a stronger inhibitor than propene. The accelerating action of the pentanes and of n-hexane on the decomposition of the inhibitors has also been established.[17]

According to other data[18,19] propene and 2-methylpropene act both as inhibitors and as initiators of the thermal decomposition of n-hexane. At 545 °C small additions (up to 4 vol.%) of propene inhibit the decomposition of n-hexane. Limitation of the decomposition rate for n-hexane was observed with an increase in the propene concentration. At higher temperatures (570 and 595 °C) on the other hand addition of propene shows an initiating action on n-hexane decomposition. The inhibitory action of 2-methylpropene on the decomposition of n-hexane weakens even at a concentration of about 2 vol.% and is transformed into an initiating action on increasing it further.[19] The dual action of additions of propene on the decomposition of propane was established in more recent work by the same authors.[20] A transition from an inhibitory to an initiating action was detected above 580 °C. An increase in the yield of methane and ethylene was recorded during this.

The conclusions are far more ambiguous concerning the action of additions of other alkenes (ethylene, 1-butene, 2-butene and larger) to the decomposition of alkanes. The inhibitory action of these alkenes on the decomposition of various alkanes is recorded in several studies. For example ethylene and 2-butene inhibit the decomposition of propane at 445–575 °C.[21] Ethylene, propene, *trans*-2-butene and 2-methyl-2-butene are inhibitors of the decomposition of isobutane at 470–510 °C.[22] Propene, 2-methylpropene and 2-methyl-2-butene show an inhibitory action on the decomposition of 2,2-dimethylbutane at 450 °C.[22]

Inhibition of the decomposition of n-nonane by 2-pentene at 725 °C has been reported.[23] The rate constant for the decomposition of n-nonane on pyrolysis was reduced by approximately 34% on admixture with 2-pentene. The rate constant for the decomposition of 2-pentene was practically unchanged by this but the activation energy of the process was increased.

According to other data[1] ethylene, n-butene and 2,2,4-trimethylpentene do not show a marked inhibitory action on the decomposition of iso-octane (2,2,4-trimethylpentane) at 550 °C. No mutual effect on the rate and course of the decomposition was detected in the copyrolysis of ethane with ethylene in the temperature range 800–900 °C.[24] The same result was obtained when investigating the pyrolysis of mixtures of ethane with ethylene at a lower temperature (770 °C).[25] The addition of butenes (1-butene and 2-butene) also did not change the rate of decomposition of propane and n-butane at 590–635 °C, however they inhibited the decomposition of ethane.[26] The inhibition in the case of ethane is explained by the formation of propene from the butenes. Propene is one of the main decomposition products of propane and butane and consequently some increase in its yield at the expense of the butenes does not have an appreciable effect on the overall rate of the process.

However when investigating the pyrolysis of ethane with small additions of 1-butene labelled with radioactive carbon ^{14}C, no effect of the alkene on the decomposition of ethane was detected at higher temperatures (750–930 °C).[27] In this case a weak initiating action of ethane on the decomposition of 1-butene appeared; this was traced particularly clearly in mixtures with a small addition of 1-butene (0.2 vol.%). The weak initiating action of the C_5-C_7 n-alkanes on the decomposition of 1-alkenes with 6–8 carbon atoms at 600–800 °C was also recorded.[28] In this study, the overall rate constants for the decomposition of the n-alkanes were practically unchanged. The yield of hydrogen and methane was different from the additive value, but the yields of ethylene and propene were close to the calculated values. The initiating action of the thermally more stable ethylene on the decomposition of n-hexane on copyrolysis at 800 °C has been demonstrated.[29] In truth these authors also recorded that the conversion of n-hexane was also increased in the presence of ethylene. The decomposition of n-hexane initiated by 1-hexene has also been observed at 650–690 °C.[30]

III. Pyrolysis of mixtures of alkanes and dienes

1,3-Butadiene, 2-methyl-1,3-butadiene and 1,3-pentadiene display an inhibitory effect on the decomposition of alkanes[1,31–33] which was demonstrated by experiments with radioactive (^{14}C) ethane and 1,3-butadiene.[31] The extent of conversion of ethane falls with an increase in the concentration of 1,3-butadiene in the initial mixture reaching a minimum at an approximately equimolar mixture of ethane and 1,3-butadiene, which at 800 °C was 2.8 times lower than

the degree of conversion of pure ethane. In this, ethane shows an initiating action on the decomposition of 1,3-butadiene. At 800 °C the conversion of 1,3-butadiene in mixtures containing about 99 vol.% ethane was 1.8 times higher than in pure 1,3-butadiene. The content of the main pyrolysis products of mixtures of ethane with 1,3-butadiene (H_2, CH_4, C_2H_4) did not change linearly with the change in composition of the mixture, which indicates the non-additive nature of their formation.

1,3-Pentadiene inhibits the decomposition of propane but propane shows an initiating action on the conversion of 1,3-pentadiene at 730–880 °C.[32] At 780 °C the overall rate constant for the decomposition of 1,3-pentadiene in mixtures with propane (90 vol.% C_3H_8) was increased approximately five-fold. An appreciable increase in the yield of 1,3-butadiene and a fall in the yield of cyclopentadiene was observed during this. The decomposition of propane slowed with an increase in the 1,3-pentadiene added to the initial mixture.

1,3-Butadiene and 2-methyl-1,3-butadiene show a strong inhibitory action on the decomposition of octanes at 550 °C.[1,33]

On the other hand allene initiates the thermal decomposition of n-alkanes.[34–36] Small additions of allene (0.23 wt.%) strongly accelerate the decomposition of n-hexane in the temperature range 630–690 °C.[34] At 630 °C the extent of decomposition of 0.23 wt.% allene was 2.5 and 23.0% respectively. The composition of the products was unchanged. Small additions of allene (0.42 mol%) also accelerate the decomposition of ethane in the temperature range 800–860 °C.[36] However the initiating action of allene in the decomposition of ethane was far weaker than in the decomposition of n-hexane[34] and n-hexadecane.[35] At temperatures of 800, 835 and 860 °C the ratio of the rate constants for the decomposition of ethane mixed with allene and of pure ethane were 1.43, 1.40 and 1.25 respectively.

IV. Pyrolysis of mixtures of alkanes

The investigations of the pyrolysis of mixtures of alkanes refer mainly to mixtures of the gaseous C_2–C_4 hydrocarbons. The majority of the studies report weak, sometimes contradictory, mutual effects of alkanes on the rate and course of decomposition on pyrolysis of mixtures of them. The absence of a mutual effect is characteristic for mixtures of alkanes with similar thermal stabilities. No change in rate constant was detected for the decomposition by combined pyrolysis for ethane and propane.[37,38] On the other hand an increase in the rate constant for the decomposition of propane in the presence of ethane and a reduction in the rate constant for the decomposition of ethane was recorded,[39] although the conversion of ethane was increased and the conversion of propane was reduced at 760–925 °C and on dilution with nitrogen.[40–42] According to other data[43] the rate of decomposition of propane was higher at 750 °C but at 800 °C it was comparable with the rate of decomposition of pure propane. However at 750 °C no change was observed in the rate of decomposition of ethane in mixtures but at 800 °C it was less than in the case of pure ethane. In this case and in another study[39] the yield of ethylene may be calculated from the hypothesis of the additivity of its formation. In addition there are reports on higher[41,42,44,45] (than additive) and lower[46] yields of ethylene on pyrolysis of these mixtures.

The difference in the data on the selectivity of C_2H_4 formation must also be noted. In some cases a lower[44] and in others a higher[6,47] selectivity of C_2H_4 formation was indicated,

The results of investigations on the mutual effect of ethane and n- and isobutane are also ambiguous.[37–40,48–52] Both an initiating action of n- and isobutane on the decomposition of ethane[48,50,51] and a strong inhibition of C_2H_6 decomposition by n-butane[49] have been recorded. Small additions of the butanes initiate the decomposition of C_2H_6 without an appreciable change in the distribution of products but larger additions (> 25%) inhibit.[50]

The results of investigations on the pyrolysis of mixtures of C_2H_6 with larger alkanes are also inconsistent. At 800 °C, atmospheric pressure and carrying out the process in a fluidised bed of quartz sand, additions of n-heptane and n-octane initiate the pyrolysis of ethane.[51] The initiating action is strengthened with an increase in the n-alkane content in the mixture and n-octane is a stronger initiator. The initiating action of the n-alkanes on the decomposition of ethane increased in the series n-C_4H_{10} > n-C_7H_{16} > n-C_8H_{18}. A deviation in the yield of the main products from that calculated using the additivity hypothesis (particularly in the case of additions of n-octane) was noted which was expressed particularly in the increase in the yields of C_2H_4 and C_3H_6 and a reduction in the yield of hydrogen.

At the same time an inhibitory action of small additions of mixtures of C_{11}–C_{14} n-alkanes on the decomposition of ethane has been reported.[52] This seems even more unlikely since the same additions show an initiating action on the decomposition of propane. In both cases a change in the distribution of products was recorded which was manifestly greater in mixtures with propane.

On pyrolysis of binary mixtures of propane with isobutane and neopentane at 650–690 °C and a molar ratio of components of 0.5 and 1 an initiating action was established for isobutane on the decomposition of propane which was strengthened by an increase in the isobutane content of the mixture.[37] Propane inhibits the decomposition of isobutane to an insignificant extent. However this effect does not depend on the quantity of propane added. In the pyrolysis of binary mixtures of neopentane with propane and isobutane an initiating action was recorded for neopentane (which was stronger for mixtures with propane).

In the case of the thermal decomposition of mixtures of propane with isobutane of varied composition and also of equimolar mixtures of isobutane with neopentane at higher temperatures (700–850 °C) isobutane also initiates the decomposition of propane which like ethane (but to a lesser extent), shows an inhibitory action on the pyrolysis of isobutane.[48] The distribution of the products differed from that expected from additivity. In equimolar mixtures of isobutane with neopentane the mutual effect of the hydrocarbons on the rate and course of decomposition was almost not apparent.

The pyrolysis of mixtures of n- and isobutane was characterised by the insignificant initiating action of isobutane over a wide temperature range, viz. 650–690 °C,[37] 640–790 °C,[53] 575–850 °C.[40] n-Butane shows a weak inhibitory effect. The observed distribution of products differed from that calculated from the additivity hypothesis for their formation. Thus on pyrolysis of an equimolar mixture of n- and isobutane at 660 °C the rate of decomposition of isobutane was reduced and of n-butane increased 1.1 and 1.4 times respectively.[37] On increasing the temperature in the range 575–850 °C the mutual effect is strengthened.[40] At the same time it was recorded that in equimolar mixtures of n- and isobutane the mutual effect of the butanes on the rate and course of the decomposition was almost invisible at 700–850 °C.[48]

An insignificant mutual effect on the rate of decomposition was recorded in the pyrolysis (600–790 °C) of a mixture of n-heptane and iso-octane of composition close to equimolar. n-Heptane retards the decomposition of iso-octane to an insignificant extent and, in its turn, iso-octane accelerates insignificantly the pyrolysis of n-heptane. The distribution of the products follows the additivity principle in cases of low conversion but deviates somewhat from it on extended conversion.[54,55] In general, no changes were detected in the distribution of products and conversion on pyrolysis of mixtures of n-nonane and n-octane at 650–725 °C.[23]

On pyrolysis of mixtures of alkanes the mutual effect of the hydrocarbons on the rate and course of the decomposition is weak and the character of this effect is determined by the experimental conditions (temperature, pressure, mixture composition). The data considered above are summarised for clarity with the experimental conditions in Table 1.

Table 1. Mutual effects on the decomposition rate on pyrolysis of binary mixtures of C_2–C_9 alkanes.

Mixture	Content of second component in mixture, %	Temperature, °C	Total pressure, atm	Type of action of components	Ref.
$\frac{C_2H_6}{C_3H_8}$	25–75	850–875	1.4–2.0	Initiator Inhibitor	[40]
$\frac{C_2H_6}{C_3H_8}$	1–77	807–923	0.9–2.0	No effect	[38]
$\frac{C_2H_6}{C_3H_8}$	0–100	759–925	1.1–1.3	Inhibitor Initiator	[42]
$\frac{C_2H_6}{C_3H_8}$	15.5; 50; 70	750	1	Initiator No effect	[43]
$\frac{C_2H_6}{C_3H_8}$	12.5; 50; 70	800	1	No effect Inhibitor	[43]
$\frac{C_2H_6}{C_3H_8}$	50	690	1	No effect	[37]
$\frac{C_2H_6}{C_3H_8}$	25; 50; 75	650–870	1.2–2.3	Initiator Inhibitor	[39]
$\frac{C_2H_6}{n-C_4H_{10}}$	25–75	575–850	1.4–2.0	Strong initiator Strong inhibitor	[40]
$\frac{C_2H_6}{n-C_4H_{10}}$	<25	700–850	–	– Initiator	[50]
$\frac{C_2H_6}{n-C_4H_{10}}$	>25	700–850	–	– Inhibitor	[50]
$\frac{C_2H_6}{n-C_4H_{10}}$	–	700–900	0.9–2	No effect	[38]
$\frac{C_2H_6}{n-C_4H_{10}}$	12.7–82.2	800	1	– Initiator	[51]
$\frac{C_2H_6}{iso-C_4H_{10}}$	14.1; 29.5; 51.5	755–856	0.13	Inhibitor Initiator	[48]
$\frac{C_2H_6}{iso-C_4H_{10}}$	<25	700–850	–	– Initiator	[50]
$\frac{C_2H_6}{iso-C_4H_{10}}$	>25	700–850	–	– Inhibitor	[50]
$\frac{C_2H_6}{iso-C_4H_{10}}$		700–900	0.9–2.0	No effect	[38]
$\frac{C_2H_6}{n-C_7H_{16}}$	52.4–81.5	800	1	– Initiator	[51]
$\frac{C_2H_6}{n-C_8H_{18}}$	60.0–89.1	800	1	– Initator	[51]
$\frac{C_3H_8}{n-C_4H_{10}}$	25.5; 50; 75	575–850	1.4–2.0	Weak inhibitor Weak inhibitor	[40]
$\frac{C_3H_8}{iso-C_4H_{10}}$	33.3; 50	650–690	1	Weak effect Strong initiator	[37]
$\frac{C_3H_8}{iso-C_4H_{10}}$	50	651	1	Weak inhibitor Strong initiator	[37]
$\frac{C_3H_8}{iso-C_4H_{10}}$	50	686	1	Weak initiator Strong initiator	[37]
$\frac{C_3H_8}{iso-C_4H_{10}}$	50	660	1	Weak initiator Strong initiator	[37]
$\frac{C_3H_8}{iso-C_4H_{10}}$	33.3	660	1	No effect Strong initiator	[37]
$\frac{C_3H_8}{iso-C_4H_{10}}$	50.4; 86.2	749–855	0.13	Inhibitor Initiator	[48]
$\frac{C_3H_8}{iso-C_4H_{10}}$	~10	749–855	0.13	Weak inhibitor No effect	[48]
$\frac{C_3H_8}{\text{neopentane}}$	50	660	1	Weak initiator Very strong initiator	[37]
$\frac{n-C_4H_{10}}{iso-C_4H_{10}}$	50	660	1	Weak inhibitor Initiator	[37]
$\frac{n-C_4H_{10}}{iso-C_4H_{10}}$	25; 50; 75	575–850	1.4–2.0	Weak inhibitor Weak initiator	[40]
$\frac{n-C_4H_{10}}{iso-C_4H_{10}}$	50	735–845	0.13	Practically no effect	[48]
$\frac{n-C_4H_{10}}{iso-C_4H_{10}}$	–	807–927	1–1.7	No effect	[38]
$\frac{iso-C_4H_{10}}{\text{neopentane}}$	50	721–860	0.13	Practically no effect	[48]
$\frac{iso-C_4H_{10}}{\text{neopentane}}$	50	660	1	No effect Initiator	[37]
$\frac{n-\text{heptane}}{iso-\text{octane}}$	~50	660–790	1	Weak inhibitor Weak initiator	[54, 55]
$\frac{n-\text{octane}}{n-\text{nonane}}$	25; 48; 75	650–725	1	No effect	[23]

V. Pyrolysis of alkanes and cycloalkanes

The few investigations on the pyrolysis of alkanes in mixtures with cycloalkanes indicate unambiguously the initiating action of alkanes on the decomposition of cycloalkanes.

Ethane and n-pentane initiate the decomposition of cyclopentane at 800–870 °C, n-pentane showing the stronger initiating action.[56]

On pyrolysis of cyclohexane in the presence of ethane, propane[57,58] and n-hexane[59] (725–900 °C) the initiating action of the alkanes was manifest most strongly in mixtures with a small cyclohexane content (10–15%). The conversion of alkanes falls sharply on increasing the cyclohexane content of the mixture. The extent of conversion of ethane was reduced to a minimum value in mixtures containing 10–15 vol.% cyclohexane.

Propane and n-hexane show approximately the same initiating action on the decomposition of cyclohexane. Ethane is a less strong initiator. An appreciable deviation is observed in all cases in the yield of the main products from that calculated from the additivity hypothesis. This was particularly strongly shown for hydrogen, methane, ethylene, and propene.

n-Heptane and iso-octane also show an initiating action on the decomposition of cyclohexane over a wide temperature range (600–850 °C).[54,55] n-Heptane is a strong initiator of the pyrolysis of cyclohexane compared with iso-octane, the accelerating action of which on cyclohexane decomposition is insignificant at 600–790 °C.[54] An appreciable deviation from additivity of the yields of main products from the pyrolysis of the mixtures was recorded in cases of extended conversion.[55] For low conversion the yields of pyrolysis products from mixtures of n-heptane with cyclohexane and of iso-octane with cyclohexane may be calculated by the additivity hypothesis.

Similarly, n-heptane inhibits the decomposition of methylcyclohexane (680 °C) but the latter shows an insignificant inhibitory action on the breakdown of n-heptane.[60]

An inhibition–initiation effect was also recorded in an investigation of the pyrolysis of mixtures of decalin with n-decane at 685–760 °C [61] and with n-dodecane at 480–525 °C.[62] The initiation effect appeared more clearly in mixures of decalin with n-decane while the inhibitory action of decalin is more marked on copyrolysis of decalin with n-dodecane. A deviation of the product distribution from that calculated from additivity of the thermal decomposition of the hydrocarbons in the mixtures was noted.[62]

VI. Effect of aromatic hydrocarbons

There are practically no literature data on the effect of aromatic hydrocarbons on the decomposition of hydrocarbons of other classes.† Only the inhibitory action of the polycyclic hydrocarbons naphthalene and phenanthrene on the decomposition of n-hexadecane and decalin on combined pyrolysis of binary mixtures of cycloalkanes and aromatic hydrocarbons in the temperature range 800–900 °C have been recorded.[63] It was shown that the inhibitory action of the aromatic hydrocarbons was more strongly developed in the pyrolysis of decalin than of n-hexadecane.

† The toluene and xylene procedures for investigating thermal decomposition under conditions of inhibiting the radical process are not considered in the present review.

The lighter alkanes (methane, ethane, propane, butane) initiate the decomposition of toluene at 800–1200 °C.[64] In the presence of CH_4, C_3H_8 and butanes, which generate methyl radicals, the yield of ethylbenzene and styrene are increased. Ethane affects the yield of ethylbenzene to a lesser extent but it enables an increase in the yield of n-propylbenzene to be achieved.

The initiating action of 1-hexene on the decomposition of toluene takes place at 630–720 °C.[30] Initiation of the decomposition of benzene by toluene was also noted.

VII. Mechanism of inhibition–initiation in the pyrolysis of hydrocarbon mixtures

The theory of the radical–chain decomposition of n-alkanes, developed initially in the thirties by Rice[65,66] and refined by him with Kossiakoff,[67] has been applied successfully to the description of thermal conversions of hydrocarbons of other classes, particularly alkenes,[68] cycloalkanes[57,69] and aromatic hydrocarbons.[70]

The radical–chain mechanism comprises three stages. The first is chain formation by fission of the weakest bond in the hydrocarbon molecule, then chain propagation and a termination stage by recombination and disproportionation of the radicals propagating the chain. The chain propagation (or development) stage comprises the reaction of the radicals propagating the chain (β-radicals) with a molecule of the initial hydrocarbon (abstraction of a H atom or addition at a double bond), and also β-decomposition and isomerisation of the resulting heavy radicals (μ-radicals).

This concept is the basis of the formal kinetics of the pyrolysis process.[71] A particularly important role is played here by reactions leading to the formation and disappearance of β-radicals which are responsible for the yield of the main products. On carrying out the process in the presence of other compounds the latter are also involved in reaction with the β-radicals. In addition the β-radicals react with the pyrolysis products and this becomes important at greater convesions. The rate of carrying out these processes and the probability of regenerating β-radicals is reflected both in the distribution of products and in the rate of the overall process.

1. Early ideas on the mechanism of inhibition

a) Addition of β-radicals to a double bond

The retardation of the thermal decomposition of n-alkanes by the products formed and also by addition of alkenes was first established by Dintses and Frost.[72] During the pyrolysis of a n-alkane the β-radicals add to the double bond of an alkene with the formation of unreactive radicals,[73] such as

$$R + C_3H_6 \longrightarrow CH_3-\underset{\displaystyle R}{\underset{|}{CH}}-\dot{C}H_2,$$

$$R + C_3H_6 \longrightarrow CH_3-\dot{C}H-CH_2-R,$$

which leads to chain termination and a reduction in the decomposition rate of the alkane. These ideas were used to explain the effect of some unsaturated hydrocarbons (propene, 2-methyl-1,3-butadiene, 2-methylpropene, 1,3-butadiene, butene, 2,2,4-trimethylpentene) on the decomposition of iso-octane.[1] The unsaturated hydrocarbons investigated may be arranged in the following series according to their efficiency of inhibitory action.

$$C_4H_6 > C_3H_6 > \text{2-methyl-1,3-butadiene} > \text{2-methylpropene}$$

Butene and 2,2,4-trimethylpentene do not inhibit the decomposition of iso-octane since they do not form inactive radicals on reaction with β-radicals. The addition of methyl radicals to 2-methyl-1,3-butadiene does not lead to the formation of stable unreactive radicals, consequently its inhibitory action is weaker than the action of propene and 1,3-butadiene. 2-Methylpropene, having only one double bond in the molecule, is a weaker inhibitor than 2-methyl-1,3-butadiene. As a rule, addition of the ethyl radical at the double bond of an inhibitor does not lead to the formation of a stable unreactive radical consequently reactions involving the ethyl radical are not considered in the mechanism of inhibition (addition reactions of H atoms are not taken into account).

b) The formation of low reactivity allyl radicals in reactions of H atom extraction

A mechanism for the inhibition of alkane decomposition by certain alkenes (C_3H_6, iso-C_4H_8) was considered in studies by Stepukhovich and collaborators,[3,74] Leidler and collaborators,[4] in the early work, of Niclause and collaborators[16] and by several other authors.[4,75–77] This is based on the occurrence of a reaction involving abstraction of hydrogen atoms from the inhibitor by the reactive radicals propagating the chain with the formation of radicals of an allylic type which do not participate in chain propagation reactions, such as

$$R(\dot{H},\ \dot{C}H_3) + C_3H_6 \longrightarrow C_3H_5 + RH. \qquad (1)$$

In fact, in recent studies by Stepukhovich a kinetic scheme is proposed for alkane decomposition retarded by additions of inhibitors (C_3H_6) which includes a chain propagation reaction involving an allyl radical.[19]

$$M \longrightarrow 2R + 2M^1,$$

$$R + M \longrightarrow RH + mM^1 + R,$$

$$R + I \longrightarrow RH + R^1,$$

$$R^1 + M \longrightarrow R^1H + mM^1 + R,$$

$$R + \text{walls} \rightarrow \text{products},$$

$$R^1 + \text{walls} \rightarrow \text{products},$$

where M and M_1 are molecules of alkane and alkene, R and R^1 are alkyl and allyl radicals respectively, and I is the inhibitor molecule.

Inhibition is effected by the reduction in the rate of the chain propagation reaction by the participation of the less reactive allyl radicals.

2. Mechanism of inhibition–initiation on pyrolysis of mixtures of hydrocarbons

a) Inhibition–initiation on joint pyrolysis of alkanes with low molecular alkenes

A drawback of the schemes give above is the lack of data characterising the kinetics of decomposition of the inhibitor itself under conditions of joint pyrolysis.

This is linked with the fact that, as a rule, the inhibitor or its decomposition products are no different from the decomposition products of the alkanes themselves. Consequently only the use of special methods of investigation enables the decomposition of the inhibitor on pyrolysis of mixtures to be followed. The method of introducing a labelled inhibitor is the most suitable for this.

Detailed investigations on the pyrolysis of ethane and propane with added propene labelled with radioactive carbon (^{14}C) have enabled the course of the conversion of propene on pyrolysis in mixtures to be traced and the effect of the alkane on the rate and course of its decomposition to be assessed.[6,9,78] It was established that the alkane shows an initiating action on the conversion of propene which is stronger for increased alkane concentration in the mixture (Fig. 1). It is therefore possible to speak of the phenomenon of a simultaneous inhibition–initiation in the pyrolysis of alkanes with propene. A mechanism is proposed to describe this phenomenon, which includes the replacement (with the participation of propene) of the hydrogen atoms most reactive in the chain propagation reaction by less reactive methyl radicals. This is effected through successive stages in the addition of H atoms to propene with the formation of an excited propyl radical and its subsequent breakdown:

$$\dot{H} + C_3H_6 \rightleftharpoons [(CH_2CH_2CH_3)^{\cdot}]^* \longrightarrow \dot{C}H_3 + C_2H_4. \qquad (2)$$

This leads, on the one hand, to inhibition by propene of the decomposition of the alkanes and, on the other, to initiation of the conversion of propene by hydrogen atoms generated on decomposition of the alkane.

It was established from the data on the distribution of radioactivity in the pyrolysis products, when investigating the pyrolysis of ethane with added propene labelled with ^{14}C at the centre carbon atom ($H_2C=^{14}CH-CH_3$), that up to 95% propene was consumed in the formation of ethylene[6] and only 5% went to the formation of other products.

$$R + C_3H_6 \longrightarrow RH + \dot{C}_3H_5,$$

$$\dot{C}_3H_5 \longrightarrow C_3H_4 + \dot{H}, \qquad (3a)$$

$$\dot{C}_3H_5 \longrightarrow C_2H_2 + \dot{C}H_3, \qquad (3b)$$

$$R = \dot{H}, \dot{C}H_3.$$

In the pyrolysis of propane mixed with radioactive propene the selectivity of forming C_2H_4 is lower and is reduced on increasing the propene concentration in the initial mixture but the selectivity of forming the remaining products was increased. At 850 °C and an extent of conversion of radioactive propene of about 40%, the selectivity of forming radioactive ethylene was 70, 65, 52 and 22.5% at propene contents in the initial mixture of 1.77, 6.41, 30.78 and 68.18 vol.% respectively.[9] It follows from this that reaction (2) is not the sole route for the conversion of propene in this case. In fact on pyrolysis of mixtures of ethane with propene the overall decomposition rate of radioactive propene coincides with the rate of accumulation of radioactive ethylene and on pyrolysis of mixtures of propane with propene the overall decomposition rate of radioactive propene is appreciably higher than the rate of formation of radioactive ethylene (see Fig. 1).

Consequently when describing the decomposition of ethane in the presence of small additions of propene (up to 10 vol.%) it is possible to consider just one route for the conversion of propene by reaction (2).

$$C_2H_6 \rightleftharpoons 2CH_3^{\cdot}, \quad (4)$$

$$CH_3^{\cdot} + C_2H_6 \longrightarrow CH_4 + C_2H_5^{\cdot},$$

$$C_2H_5^{\cdot} \longrightarrow C_2H_4 + H^{\cdot},$$

$$H^{\cdot} + C_2H_6 \longrightarrow H_2 + C_2H_5^{\cdot}, \quad (5)$$

$$H^{\cdot} + C_3H_6 \longrightarrow CH_3^{\cdot} + C_2H_4, \quad (2)$$

$$CH_3^{\cdot} + C_2H_5^{\cdot} \longrightarrow C_3H_8,$$

$$2C_2H_5^{\cdot} \longrightarrow C_4H_{10}.$$

In the pyrolysis of propane with even small additions of propene it is necessary to consider routes in addition to reaction (2) for the decomposition of C_3H_6. The main route at high temperatures (> 800 °C) is that leading to the formation of acetylene and C_3H_4 hydrocarbons [reactions (1) and (3)]:

$$C_3H_8 \rightleftharpoons CH_3^{\cdot} + C_2H_5^{\cdot},$$

$$C_2H_5^{\cdot} \longrightarrow C_2H_4 + H^{\cdot},$$

$$R(\dot{H}, \dot{C}H_3) + C_3H_8 \rightarrow RH + pr\text{-}C_3H_7^{\cdot},$$

$$R(\dot{H}, \dot{C}H_3) + C_3H_8 \rightarrow RH + sec\text{-}C_3H_7^{\cdot},$$

$$pr\text{-}C_3H_7^{\cdot} \rightarrow C_2H_4 + CH_3^{\cdot},$$

$$sec\text{-}C_3H_7^{\cdot} \rightarrow C_3H_6 + H^{\cdot},$$

$$H + C_3H_6 \longrightarrow C_2H_4 + CH_3^{\cdot}, \quad (2)$$

$$H + C_3H_6 \longrightarrow C_3H_5^{\cdot} + H_2, \quad (1a)$$

$$CH_3^{\cdot} + C_3H_6 \longrightarrow C_3H_5^{\cdot} + CH_4, \quad (1b)$$

$$C_3H_5^{\cdot} \longrightarrow C_3H_4 + H, \quad (3a)$$

$$C_3H_5^{\cdot} \longrightarrow C_2H_2 + CH_3^{\cdot}, \quad (3b)$$

$$CH_3^{\cdot} + C_3H_5^{\cdot} \longrightarrow C_4H_8,$$

$$2C_2H_5^{\cdot} \longrightarrow C_4H_{10}.$$

The fairly marked contribution of reaction (1) on pyrolysis of mixtures of propane with propene causes a higher running concentration of CH_3 radicals, the addition of which to propene at high temperatures does not occur in practice.[79] On pyrolysis of ethane the concentration of methyl radicals which are formed only at the initiation stage is low and correspondingly the contribution of reaction (1*b*) is not appreciable.

According to this scheme the rate constant for the overall decomposition of propene is described by the equation

$$k_{C_3H_6} = k_2[H] + k_{1a}[H] + k_{1b}[CH_3]. \quad (I)$$

Since $k_2 \gg k_{1a}$ it may be taken that

$$k_{C_3H_6} = k_2[H] + k_{1b}[CH_3]. \quad (II)$$

The first term of equation (II) is the specific rate of formation of ethylene from propene which is calculated from the data on the distribution of radioactivity in ethylene and propene. For the pyrolysis of propane with added 1.77 vol.% C_3H_6 the ratio $k_2[H]/k_{1b}[CH_3]$ is 1.5 at 850 °C.[9] Thus in mixtures with a small propene content its rate of reaction with H atoms is at least 1.5 times greater than with methyl radicals. This ratio is reduced with an increase in the propene concentration (Table 2). The ratio of the concentrations of H atoms and methyl radicals therefore changes with the change in the composition of the initial mixture. The concentration of methyl radicals increases with an increase in propene concentration and the contribution of reaction (1*b*) becomes more noticeable.

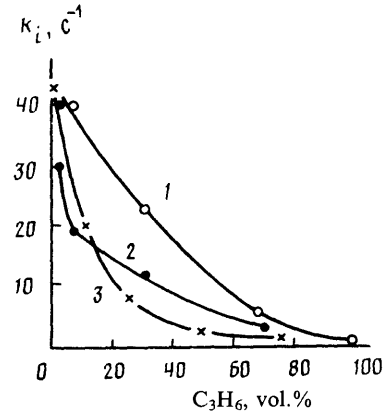


Figure 1. Change in rate constant for (*1*, *3*) the decomposition of propene and (*2*, *3*) the formation of ethylene with the change in composition of the initial mixture at 850 °C; *1*, *2*, mixture of propane and propene;[9] *3*, mixture of ethane and propene.[6]

Table 2. Ratio of hydrogen and methane and also rates of disappearance of propene with the partcipation of H atoms (k_2) and methyl radicals (k_{1b}) on pyrolysis of mixtures of propane and propene (850 °C).

C_3H_6 content in initial mixture, %	$[H_2]/[CH_4]$	$k_2[H]/k_{1b}[CH_3]$
1.77	1.0	1.5
6.41	1.0	1.0
30.78	0.8	1.0
68.18	0.5	0.8

The relative increase in the concentration of CH_3 radicals also shows in the ratio of hydrogen and methane in the pyrolysis products (Table 2).

The efficiency of the inhibitory action of propene is also dependent on reaction (2), since $k_2 \gg k_1$. In addition, in contrast to reaction (1) the conversion of C_3H_6 by reaction (2) leads to replacement of H by the less reactive methyl radical.

The concentration of H atoms is reduced as the concentration of propene in the initial mixture with propane is increased (Fig. 2).[9] In this way the rate of the overall decomposition of propane is also reduced practically in proportion (Fig. 3).

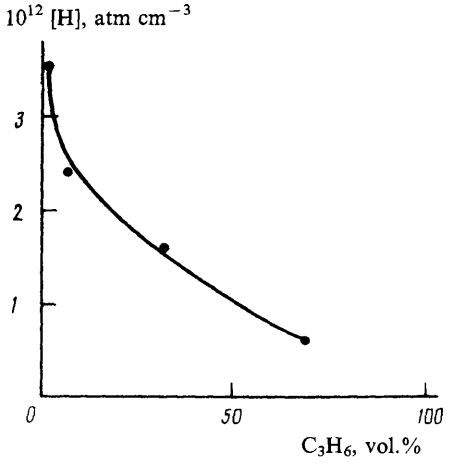


Figure 2. Change in concentration of hydrogen atoms in the pyrolysis zone of mixtures of propane and propene with the change in composition of the initial mixture at 850 °C.

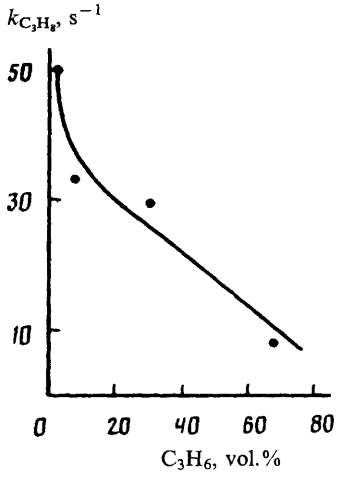


Figure 3. Reduction in the rate constant for propane decomposition with increasing content of propene in the initial mixture at 850 °C.

Propene is also converted according to reactions (1) and (2) on pyrolysis when mixed with n-butane. In this case too the inhibitory action of propene was dependent mainly on reaction (2). As a result the concentration of radicals propagating the chain was reduced and consequently chain propagation involving n-butane itself proceeds at a lower rate.

The inhibitory action of propene on the decomposition of alkanes was reduced on going from ethane to propane and n-butane (Fig. 4). This is linked with the increase in the contribution of the reactions of methyl radicals which are formed on pyrolysis of propane and n-butane both at the initiation and at the chain propagation stage.

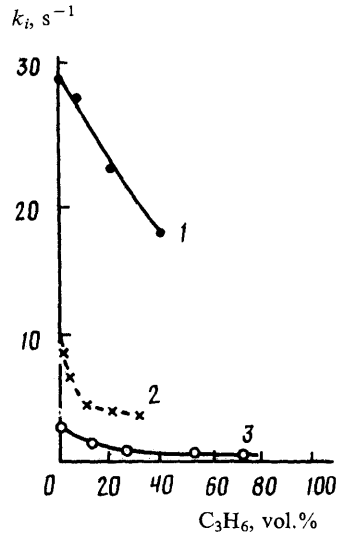


Figure 4. Dependence of the rate constant (k_i) for the decomposition of alkanes on C_3H_6 concentration in the mixture: *1*, $k_{n\text{-}C_4H_{10}}$; *2*, $k_{C_3H_8}$; *3*, $k_{C_2H_6}$, temperature 800 °C.

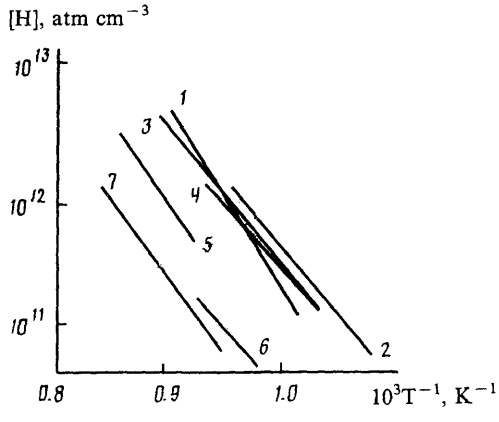


Figure 5. Temperature dependence of the hydrogen atom concentration in the pyrolysis zone of *1*, ethane; *2*, n-hexane; *3*, propane; *4*, n-butane; *5*, 1,3-butadiene, *6*, 1,3-pentadiene and *7*, propene at an overall pressure of 100 mmHg.

On pyrolysis of ethane, propene and butane the concentration of hydrogen atoms is approximately the same (Fig. 5).[80] It is possible to estimate the concentration of methyl radicals from the rate of accumulation of methane. Thus on pyrolysis of ethane the rate of hydrogen formation is more than an order of magnitude greater than the rate of methane formation.[31] On pyrolysis of propane these rates are approximately the same,[9] and on pyrolysis of n-butane methane is formed approximately 1.5 times more rapidly than

hydrogen.[11] Consequently in the pyrolysis of propane and n-butane the contribution of chain propagation reactions involving methyl radicals becomes more marked.

In addition it must be noted that according to the proposed mechanism the extent of the inhibitory action of an additive is determined by the ratio of the reaction rates of H atoms with the alkane and with the inhibitor. The rate constant for the reaction of H atoms with alkanes investigated increases on going from ethane to n-butane.[81] This leads to an increase in the contribution of reactions involving alkane in the series C_2H_6 < C_3H_8 < n-C_4H_{10} and consequently to a reduction in the inhibitory action of propene on this series of alkanes.

The stronger inhibitory action of propane compared with ethane in the decomposition of propene is explained by the higher overall concentration of the radicals propagating the chains (see Fig. 1). Regrettably due to the lack of data on the pyrolysis of mixtures of n-butane with radioactive propene it is as yet impossible to judge the extent of the inhibitory action of the former on the breakdown of the latter.

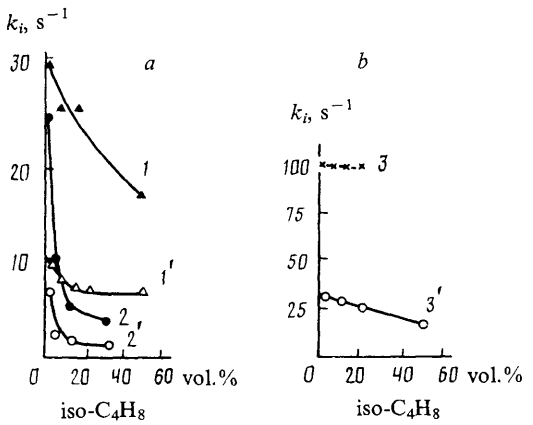


Figure 6. Dependence of the overall rate constant (k_i) for alkane decomposition on the 2-methylpropene concentration in the initial mixture with *a*: *1*, *1'*, propane; *2*, *2'*, ethane and *b*: *3*, 3', n-butane at 850 and 800 °C respectively.

On pyrolysis of mixtures of ethane, propane and n-butane with 2-methylpropene the mutual effect of hydrocarbons on their decomposition is also linked with the competing reactions:

$$R(\dot{H}, \dot{C}H_3) + \text{alkane} \rightarrow RH + R^1,$$

$$H + \text{iso-}C_4H_8 \rightarrow \text{iso-}\dot{C}_4H_9 \rightarrow \dot{C}H_3 + C_3H_6,$$

$$R(\dot{H}, \dot{C}H_3) + \text{iso-}C_4H_8 \rightarrow \text{iso-}\dot{C}_4H_7 + RH.$$

Like propene, 2-methylpropene shows a stronger inhibitory action on the decomposition of ethane (Fig. 6) but n-butane is the strongest initiator of the decomposition of 2-methylpropene (Fig. 7). However propene is a stronger inhibitor of the decomposition of the C_2-C_4 alkanes than 2-methylpropene (Figs. 4 and 6). This is seemingly caused by the higher value of the rate constant for the addition of H atoms to propene.

In principle Niclause and collaborators[22] arrived at the same mechanism of initiation–inhibition, based on literature data and on the results of their own kinetic investigations on the pyrolysis of ethane, isobutane and 2,2-dimethylbutane in the presence of alkenes (ethylene, propene, 2-methylpropene, *trans*-2-butene and two isopentenes, including 2-methyl-3-butene). However these authors considered that the addition of H atoms to the double bond of the inhibitor is responsible for the distribution of the products and the inhibitory action is caused by the removal of H atoms from the alkene.

$$\text{iso-}C_4H_{10} \rightarrow \text{radical formation},$$

$$R(\dot{H}, \dot{C}H_3) + \text{iso-}C_4H_{10} \rightarrow RH + \text{iso-}\dot{C}_4H_9, \qquad (6a)$$

$$R(\dot{H}, \dot{C}H_3) + \text{iso-}C_4H_{10} \rightarrow RH + \text{t-}\dot{C}_4H_9, \qquad (6b)$$

$$\text{iso-}\dot{C}_4H_9 \rightarrow \dot{C}H_3 + C_3H_6,$$

$$\text{t-}\dot{C}_4H_9 \rightarrow \dot{H} + \text{iso-}C_4H_8,$$

$$\dot{H} + C_3H_6 \leftrightarrows \text{sec-}\dot{C}_3H_7,$$

$$\text{sec-}\dot{C}_3H_7 + \text{iso-}C_4H_{10} \rightarrow C_3H_8 + \text{iso-}\dot{C}_4H_9,$$

$$\text{sec-}\dot{C}_3H_7 + \text{iso-}C_4H_{10} \rightarrow C_3H_8 + \text{t-}\dot{C}_4H_9,$$

$$\dot{H} + C_3H_6 \rightarrow \text{pr-}C_3H_7,$$

$$\text{pr-}\dot{C}_3H_7 \rightarrow \dot{C}H_3 + C_2H_4,$$

$$\text{t-}\dot{C}_4H_9 + \text{iso-}C_4H_{10} \rightleftarrows \text{iso-}\dot{C}_4H_9 + \text{iso-}C_4H_{10},$$

$$\dot{H} + C_3H_6 \rightarrow H_2 + \dot{C}_3H_5. \qquad (1a)$$

Chain termination occurs by recombination of CH_3, C_3H_5 and sec-C_3H_7 radicals.

The contributions of the following empirical reactions in the formation of the main products at 470 °C have been estimated for mixtures of propene and isobutane (at $[C_3H_6]/[\text{iso-}C_4H_{10}] = 0.10$).

$$\text{iso-}C_4H_{10} = CH_4 + C_3H_6, \quad 25.4\%$$

$$\text{iso-}C_4H_{10} = H_2 + \text{iso-}C_4H_8, \quad 51.2\%$$

$$\text{iso-}C_4H_{10} + C_3H_6 = C_3H_8 + \text{iso-}C_4H_8, \quad 13.7\% \qquad (7)$$

$$\text{iso-}C_4H_{10} + C_3H_6 = CH_4 + C_2H_4 + \text{iso-}C_4H_8, \quad 9.2\%$$

This mechanism differs from that given above in that the main route for the conversion of alkyl radicals formed by the addition of H atoms to the double bond of the inhibitor is the removal of a H atom from a molecule of the initial alkane. As a result the inhibitor is converted into the corresponding alkane [empirical reaction (7)]. However using radioactive additives it was shown convincingly that in mixtures with alkanes propene did not give rise to propane in practice. Such a difference is seemingly caused by the different pyrolysis temperatures 450–550 and 750–900 °C respectively.

The mechanism of the high temperature pyrolysis differs from that at lower temperatures by the fact that in practice only methyl radicals and H atoms participate in the chain propagation reactions. Other alkyl radicals are mainly decomposed. At temperatures below 600 °C for C_2-C_4 alkyl radicals not only is decomposition characteristic but also removal of H atoms from the initial alkene occurs.

b. Specific features of the inhibitory action of higher alkenes in the thermal decomposition of alkanes

In the thermal decomposition of mixtures of the higher n-alkanes with alkenes in contrast to mixtures of C_2-C_4 alkanes with propene the alkene is thermally less stable, due to the presence in the molecule of a weak C–C bond in the β-position to the double bond. It was established by low temperature IR spectroscopy in a nitrogen matrix[82,83] that the initiation stage of the decomposition of C_5-C_7 1-alkenes occurs by a radical mechanism under pyrolysis conditions with the formation of an allyl and the corresponding alkyl radical which initiates a radical chain process. It is assumed that in the pyrolysis of mixtures the alkene must initiate the decomposition of the alkane.[84] At the same time it was shown[23,27,28] that the alkene has an inhibitory action on alkane decomposition and the alkane initiates breakdown of the alkene. However the mutual effect is weakly expressed. This is linked with the fact that the alkene on the one hand acts as an initiator of the radical chain decomposition of the n-alkane and on the other as an inhibitor of the chain propagation stage since on pyrolysis the concentration of radicals propagating the chain is lower. Thus at 700–800 °C the concentration of hydrogen atoms in the decomposition of n-hexane is double that in the case of 1-hexene at a comparable concentration of methyl radicals.[85] On pyrolysis of mixtures of n-hexane and 1-hexene the ratio $[H_2]/[CH_4]$ is reduced on increasing the 1-hexene concentration (Fig. 8),[28] which indicates the fall in the relative concentration of H atoms in the reaction mixture. It follows from this that the initiating action of the alkanes is caused mainly by the increased rate of addition of H atoms, generated on decomposition of the n-alkane, to the alkene double bond and also by an increase in the rate of removal of H atoms, shown for the case of 1-hexene:

$$\dot{H} + C{=}C{-}C{-}C{-}C{-}C \longrightarrow \begin{cases} \dot{C}{-}C{-}C{-}C{-}C{-}C, \\ C{-}\dot{C}{-}C{-}C{-}C{-}C, \\ H_2 + C{=}C{-}\dot{C}{-}C{-}C{-}C, \\ H_2 + C{=}C{-}C{-}\dot{C}{-}C{-}C, \\ H_2 + C{=}C{-}C{-}C{-}\dot{C}{-}C, \\ H_2 + C{=}C{-}C{-}C{-}C{-}\dot{C}. \end{cases}$$

As a result the rate of chain propagation for the corresponding alkane is reduced [reaction (8)]

$$H + C{-}C{-}C{-}C{-}C{-}C \longrightarrow \begin{cases} H_2 + \dot{C}{-}C{-}C{-}C{-}C{-}C, & (8a) \\ H_2 + C{-}\dot{C}{-}C{-}C{-}C{-}C, & (8b) \\ H_2 + C{-}C{-}\dot{C}{-}C{-}C{-}C. & (8c) \end{cases}$$

As is known, the rate constant for the chain initiation reaction involving the alkene ($k_{C_nH_{2n}}$) is greater than that for the alkane ($k_{C_nH_{2n+2}}$). However the difference between them is not significant. Consequently the initiation rate of radicals on pyrolysis is determined mainly by the concentration of hydrocarbons in the initial mixture. For mixtures with a high alkene content, knowing that $k_{C_nH_{2n}}[C_nH_{2n}] \gg k_{C_nH_{2n+2}}[C_nH_{2n+2}]$, the alkene is responsible for the initiation of radicals and the decomposition of the n-alkane may be expected to be hastened. But this does not occur due to the low n-alkane concentration and the higher values of the rate constant for chain propagation involving 1-alkene. At the same time the overall concentration of radicals propagating the chain, for which the n-alkane is responsible, is not increased on pyrolysis of such mixtures. Consequently the initiating action of the n-alkane is not apparent in the decomposition of the 1-alkene.

On pyrolysis of mixtures with a low 1-alkene content when the rate of radical formation involving the alkane is at least comparable with the rate of their formation from the 1-alkene, initiation of 1-alkene decomposition by the n-alkane takes place and this effect is more apparent at lower 1-alkene concentrations. For these mixtures a higher concentration of H atoms propagating the chain is more characteristic than for 1-alkene.

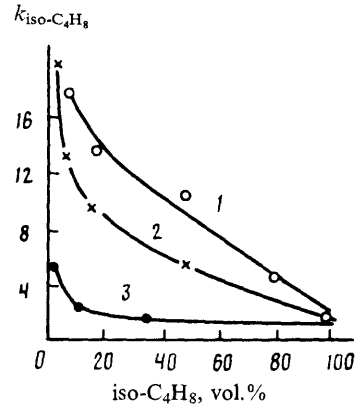


Figure 7. Rate constant for the decomposition of iso-C_4H_8 in mixtures with *1*, n-butane; *2*, propane; *3*, ethane at 800 °C.

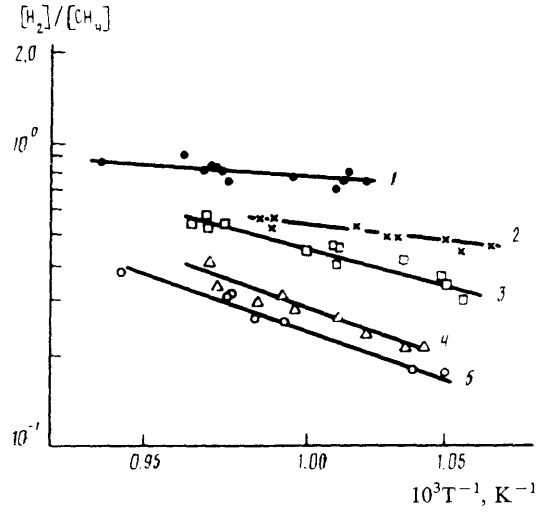


Figure 8. Temperature dependence of the ratio H_2/CH_4 in the pyrolysis products of *1*, hexane; *5*, 1-hexene and mixtures of hexane with *2*, 10% 1-hexene; *3*, 25% 1-hexene and *4*, 75% 1-hexene.

Consequently for the pyrolysis of mixtures of higher alkanes with 1-alkenes the mechanism of the mutual effect is also determined mainly by the competing chain propagation reaction involving

hydrogen atoms. But in contrast to mixtures with propene it is necessary to consider in the decomposition scheme the step of forming radicals involving the 1-alkene. Consequently the rate constants for radical formation in the decomposition of a n-alkane and 1-alkene, and also the concentration of H atoms are not appreciably different, the mutual effect of these hydrocarbons on the rate and route of the decomposition in mixtures is less clearly apparent and depends to a large extent on the composition of the mixture and the pyrolysis temperature.

c) Inhibition–initiation on pyrolysis of binary mixtures of hydrocarbons of other classes

The mutual effect on the rate and route of the decomposition of hydrocarbons on joint pyrolysis is readily explained by the difference in the concentration of the radicals propagating the chain as is the apparent inconsistency of the experimental data observed in the case of a weakly expressed inhibition–initiation effect.[86]

It was shown[80] that there is no significant difference in the concentration of hydrogen atoms formed in the pyrolysis of C_5-C_{15} n-alkanes. In fact at relatively low temperatures a small increase is recorded in the concentration of H atoms with chain length for C_3-C_6 alkanes (see Fig. 5). At the same time a very high concentration of hydrogen atoms exists in the pyrolysis at temperatures above 800 °C. Consequently at relatively low temperatures the n-alkanes show an initiating action on ethane decomposition which disappears at high temperatures.[49] The initiating action of ethane on the decomposition of n-alkanes at high temperatures may be apparent only in mixtures with a high ethane concentration, since only in this case can a higher concentration of H atoms be brought about in a mixture than on pyrolysis of an individual n-alkane. Thus a change in the composition of the initial alkane mixture and of the pyrolysis temperature leads to an inversion of the mutual effect.

Table 3. Concentration of radicals (mol litre^{-1}) on pyrolysis of hydrocarbons and their equimolar mixtures (660 °C).[37]

Starting material	$10^{11}[H]$	$10^{9}[CH_3]$	$10^{10}[C_2H_5]$
Propane	2.4	3.2	1.1
Isobutane	3.4	5.1	–
Neopentane	1.4	6.3	1.9
Propane + Neopentane	7.3	8.4	1.1
Isobutane + Neopentane	4.6	9.1	–

The thermal stability of the components of a mixture does not play a significant role. This is indicated by data on the pyrolysis of five binary equimolar mixtures based on ethane, propane, n- and isobutane and pentane at 650–690 °C.[37] It transpires that neopentane accelerates the decomposition of both the thermally less stable isobutane and of the thermally more stable propane. The decomposition rate of neopentane itself in the mixtures was practically unchanged. The authors of this study also arrived at the conclusion that the initiating action of a hydrocarbon on pyrolysis in a mixture is linked with the change in the concentration of the radicals propagating the chain at the expense of the partner (see Table 3).

As is seen from Table 3 $[R]_{C_3H_8} < [R]_{neo\text{-}C_5C_{12}}$ and $[R]_{iso\text{-}C_4H_{10}} < [R]_{neo\text{-}C_5H_{12}}$. However the concentration of the radicals driving the chain is greater in the case of the pyrolysis of mixtures of these hydrocarbons with neopentane. Consequently in the pyrolysis of mixtures chain propagation reactions proceed at a high rate due to the radicals generated on decomposition of neopentane. Since $[R]_{iso\text{-}C_4H_{10}} > [R]_{C_3H_8}$ and $[R]_{mix}/[R]_{iso\text{-}C_4H_{10}} < [R]_{mix}/[R]_{C_3H_8}$, the initiating actionof neopentane in the decomposition of propane is stronger than in the decomposition of isobutane.

Ethane, like propene, inhibits isobutane pyrolysis, but to a lesser exent.[48] In both cases the mechanism of the inhibition is described by competing reactions of chain propagation with the participation, mainly, of hydrogen atoms. In the case of mixtures of isobutane with C_2H_6 the reactions are:

$$\dot{H} + \text{iso-}C_4H_{10} \rightarrow H_2 + \text{iso-}\dot{C}_4H_9, \quad (6a)$$

$$\dot{H} + \text{iso-}C_4H_{10} \rightarrow H_2 + \text{t-}\dot{C}_4H_9, \quad (6b)$$

$$\dot{H} + C_2H_6 \rightarrow H_2 + \dot{C}_2H_5, \quad (5)$$

and in the case of isobutane with propene they are reactions (2) and (6*a*, *b*). The extent of the inhibitory action is determined by the ratio of the concentration of hydrogen atoms formed in the decomposition of ethane and propene. Since $[H]_{C_3H_6} \ll [H]_{iso\text{-}C_4H_{10}} > [H]_{C_2H_6}$, the rate of reaction (6) in the pyrolysis of mixtures is less than in the decomposition of pure isobutane.

The weaker inhibitory action of ethane compared with propene is linked with the fact that $[H]_{C_2H_6} \gg [H]_{C_3H_6}$ and consequently $[H]_{mix}/[H]_{C_2H_6} \ll [H]_{mix}/[H]_{C_3H_6}$.

In mixtures with other partners such as cyclohexane‡ ethane, like 1-hexene, displays an initiating action[57,87] which is caused by different ratios of the concentrations of H atoms, i.e. $[H]_{C_2H_6} \gg [H]_{cyclo\text{-}C_6H_{12}} < [H]_{C_6H_{12}}$.[80,85]

1,3-Butadiene acts both as an inhibitor and as an initiator of decomposition depending on the partner. On pyrolysis 1,3-butadiene shows an initiating action when mixed with propene.[88] At the same time 1,3-butadiene inhibits the decomposition of ethane.[31] The mechanism of inhibition–initiation on pyrolysis of these mixtures is determined in the first case by the competing reactions (2) and (9):

$$H + C_4H_6 \longrightarrow \dot{C}_4H_7 \longrightarrow \dot{C}_2H_3 + C_2H_4, \quad (9)$$

and in the second by reactions (5) and (9). But in the first case $[H]_{C_3H_6} < [H]_{C_4H_6}$, and in the second $[H]_{C_2H_6} > [H]_{C_4H_6}$. Consequently in mixtures with propene, reaction (9) proceeds more slowly and in mixtures with ethane more rapidly than in pyrolysis of 1,3-butadiene alone.

The mechanism of the initiating action of allene on the thermal decomposition of hydrocarbons of various classes is described[34–36] by the bimolecular reaction (10)

$$C_3H_4 + RH \longrightarrow \dot{C}_3H_5 + R, \quad (10)$$

‡ The radical chain character of cyclohexane pyrolysis with the formation of allyl and methyl radicals at the initiation stage was confirmed[83,88] by low temperature IR spectroscopy in a nitrogen matrix and also with radioactive additives.

providing the initiation stage is not unambiguous. The use of only small additions of allene (0.2–1.5%) and the lack of data on the effect of the partner on the rate and course of the decomposition of allene itself does not give a complete picture of the mutual effect of these hydrocarbons on pyrolysis in mixtures.

The allyl radical formed by reaction (10) being itself fairly reactive at relatively low temperatures in chain propagation reactions, [90] is mainly decomposed at relatively high temperatures under pyrolysis conditions generating H atom and the initial allene. It may therefore be suggested that allene does not simply initiate the radical formation stage but also acts as an additive which participates in the radical chain decomposition of the partner accompanied by an increase in the concentration of the radicals propagating the chains.

VIII. Conclusion

The vast majority of data considered above on the pyrolysis of mixtures of various classes of hydrocarbons is most adequately interpreted on the basis of ideas on the role of the components of the mixture in generating hydrogen atoms (and methyl radicals) the concentration of which controls the rate of chain propagation. This mechanism not only describes well the principles of the pyrolysis of mixtures of hydrocarbons of various classes but also enables the efficiency and course of action of one hydrocarbon on the decomposition of another to be explained as a function of its chemical structure and the reaction conditions. It also explains the non-additivity of product formation on pyrolysis of mixtures. The particularly significant deviation from additivity observed in the pyrolysis of alkanes with added propene and 2-methylpropene is caused by the rapid addition of hydrogen atoms to the alkene. The concentration of hydrogen atoms is greater than in the pyrolysis of the alkene alone. Under these conditions propene is decomposed mainly to methane and ethylene but the reaction associated with the formation of the hydrocarbons C_3H_4 and C_2H_2 is almost completely suppressed.

A deviation of the yield of products from additivity was observed even in the case of the pyrolysis of mixtures of the higher n-alkanes and 1-alkenes when the mutual effect of the hydrocarbons on the rate of decomposition is insignificant. This is linked with the high rate of reaction of 1-alkenes involving radicals generated in the decomposition of the alkane and mainly the addition of H atoms at the double bond. Since the selectivity of forming products is reduced on increasing the hydrocarbon chain length, it is difficult to separate the key course of decomposition of the 1-alkene and consequently to change significantly the selectivity of forming products in the mixture.

On pyrolysis of mixtures the mutual effect of one hydrocarbon on the thermal decomposition of another is therefore effected by a single mechanism based on competing chain propagation reactions involving the partner hydrocarbons, the rates of which are limited by the concentration of radicals progressing the chain. A single hydrogen may on copyrolysis act in some cases as an initiator and in others as an inhibitor of a process. The main characteristic of a hydrocarbon as an inhibitor is that the concentration of radicals propagating the chain and generated in the pyrolysis process is lower than that of its partner. The inhibition–initiation phenomenon of the radical chain process in the pyrolysis of mixtures is determined by a change in the concentration of radicals progressing the chain compared with that observed on pyrolysis of the individual hydrocarbons. In this way the thermal stability and the ability of a hydrocarbon to generate radicals unreactive in chain propagation reactions (for example radicals of the allyl type) are not determining and are important only as factors influencing the establishment of a definite level of radical concentration.

References

1. M P Eshevskaya *Zh. Obshch. Khim.*, 1939, **9** 2162
2. F J Stubbs, C Hinshelwood *Proc. R. Soc. London, A*, 1950, **220** 458
3. A D Stepukhovich, E S Shver *Zh. Fiz. Khim.*, 1953, **27** 1013
4. K Laidler, B Wojciechovski *Proc. R. Soc. London, A*, 1960, **259** 257
5. H G Davis, K D Williamson *V World Petroleum Congr.*, New York, 1959, Sec. IV, p. 37
6. R A Kalinenko, L V Shevel'kova, K P Lavrovskii, L M Vedeneeva *Dokl. Akad. Nauk SSSR*, 1967, **177** 1095
7. R A Kalinenko, K P Lavrovskii, L V Shevel'kova, et al. *Neftekhimiya*, 1969, **9** 542
8. S Nowak, G Bach, J Schroeder, et al. *Z. Phys. Chem.*, 1969, **241** 249
9. L V Shevel'kova, L M Vedeneeva, N S Nametkin *Neftekhimiya*, 1977, **17** 728
10. G Bach, S Nowak, R A Kalinenko, et al. *Z. Chem.*, 1975, **5** 165
11. G Bach, S Nowak, S I Korochuk, R A Kalinenko *Kinet. Katal.*, 1974, **15** 1103
12. T Haraguchi, F Nacashio, W Sakai *ACS Symp. Ser. N 32, Industr. and Laboratory Pyrolysis*, 1976, p. 99
13. K K Robinson, E Weger *Ind. Eng. Chem. Fundam.*, 1972, **10** 198
14. G I Zykova, A D Stepukhovich *Kinet. Katal.*, 1970, **11** 1371
15. G I Zykova, A D Stepukhovich, G I Pershina *Neftekhimiya*, 1971, **11** 381
16. F Baronnet, R Martin, M Niclause *C. R. Seances Acad. Sci.*, 1972, (20) 1744
17. G V Isagulyants, A A Greish, Yu M Zhorov, G V Kostina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, (7) 1556
18. A V Gorokhovskii, A D Stepukhovich *Izv. Vuz. Khim. Khim. Tekhnol.*, 1979, **22** 350
19. A V Gorokhovskii, A D Stepukhovich, E V Kostin *Zh. Fiz. Khim.*, 1981, **2**(2) 335 [English translation in *Russ. J. Phys. Chem.*, 1981(2)]
20. L I Karnaukova, A D Stepukhovich *Zh. Fiz. Khim.*, 1979, **53**(10) 2650 [English translation in *Russ. J. Phys. Chem.*, 1979(10)]
21. A Dombi, P Huhn *Magy. Kem. Foly.*, 1985, **91** 22, 27, 109, 113, 177
22. F Billaud, F Baronnet, M Niclause *Can. J. Chem.*, 1985, **63** 2869
23. J T Shah, S B Stuart, D Kunzru *Ind. Eng. Chem. Process. Des. Dev.*, 1973, **12** 344
24. K P Lavrovskii, R A Kalinenko, L V Shevel'kova *VIII Mirovoi Neftyanoi Kongress* (VIIIth World Petroleum Congress), Moscow, 1971, Proceedings L, Appl. Sci., 1971, 1972, Vol. 4, p. 357
25. K Kunugi, T Sakai, K Soma, Y Sasak *Ind. Eng. Chem. Fundam.*, 1969, **8** 374
26. A D Stepukhovich, I K Krol' *Zh. Fiz. Khim.*, 1956, **30** 1718
27. R A Kalinenko, L V Shevel'kova, K P Lavrovskii, L M Vedeneeva *Dokl. Akad. Nauk SSSR*, 1968, **179** 1102

28. L V Shevel'kova, L M Vedeneeva, N S Nametkin, et al. *Neftekhimiya*, 1984, **24** 362
29. G V Isagulyants, A A Greish, G V Kostina, Yu M Zhorov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, (6) 1340
30. N V Korzun, R Z Magaril *Zh. Fiz. Khim.*, 1974, **48**(4) 1059 [English translation in *Russ. J. Phys. Chem.*, 1974(4)]
31. L V Shevel'kova, L M Vedeneeva, R A Kalinenko, K P Lavrovskii *Kinet. Katal.*, 1973, **14** 834
32. L V Shevel'kova, I N Guseva, L M Vedeneeva, et al. *V Neftekhimicheskii Simpozium Sots. Stran.* (Vth Petrochemical Symposium of the Socialist States), Budapest, 1984, Review Vol., 62
33. M P Eshevskaya *Refiner*, 1940, **19** 264
34. R Z Magaril, L V Trushkova, N V Korzun, et al. *Izv. Vuzov. Neft' Gaz*, 1980, (8) 37
35. N V Korzun, L V Trushkova *Izv. Vuzov. Neft' Gaz*, 1985, (7) 36, 70
36. N V Korzun, L V Trushkova *Kinet. Katal.*, 1985, **26** 1236
37. M Murata, N Takeda, S Saito *J. Chem. Eng. Jpn.*, 1974, **7** 286
38. H G Davis, T J Farrell *Ind. Eng. Chem. Process. Des. Dev.*, 1973, **12** 171
39. G F Froment, B O Van de Steene, P S Van Damme, et al. *Ind. Eng. Chem. Process. Des. Dev.*, 1976, **15** 495
40. G F Froment, B O Van de Steene, P J Van de Berghe, A G Goossens *Am. Inst. Chem. J.*, 1977, **23** 93
41. R Zou, J Zou *Ind. Eng. Chem. Process. Des. Dev.*, 1986, **25** 828
42. R Zou, Q Lou, B Zhang, et al. *Ind. Eng. Chem. Process. Des. Dev.*, 1986, **25** 12
43. N L Barabanov, T N Mukhina *Neftekhimiya*, 1961, (3) 386
44. G F Froment, B O Van de Steene, O Sumedha *Oil Gas J.*, 1979, **77** 87
45. R G Minet, J D Hammond *Oil Gas J.*, 1975, **73** 80
46. L L Ross, W R Shu *Oil Gas J.*, 1977, **75** 58
47. A Mol *Hydrocarbon Proc.*, 1981, **60** 129
48. L V Shevel'kova, L M Vedeneeva, I N Shishkina, et al. *Neftekhimiya*, 1986, **26** 59
49. L V Shevel'kova, I N Guseva, N S Nametkin *Neftekhimiya*, 1984, **24** 214
50. L Popa, I Bolocan, F Cuiban *Rev. Chim. (Bucharest)*, 1985, **36** 101
51. M V Efremova, L A Kashevarov, T N Korneeva, R Z Magaril *Izv. Vuzov. Neft' Gaz.*, 1978, (1) 43
52. M Albu, R Dimitriu, F Cuiban *Rev. Chim. (Bucharest)*, 1984, **35**(7) 586
53. V Illes *Acta Chim. Acad. Sci. Hung.*, 1972, **72** 117
54. V Illes, I Plezkats *Acta Chim. Acad. Sci. Hung.*, 1974, **80** 247
55. V Illes, I Plezkats, L Szepesy *Acta Chim. Acad. Sci. Hung.*, 1974, **80** 267
56. R A Kalinenko, S G Shvedova, N S Nametkin *Neftekhimiya*, 1979, **19** 415
57. L V Shevel'kova, L M Vedeneeva *XI Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii* (XIth Mendeleev Convention on General and Applied Chemistry), Moscow, Nauka, 1975, No. 2, p. 262
58. R A Kalinenko, L V Shevel'kova, V B Titov, et al. *Neftekhimiya*, 1976, **16** 100
59. R A Kalinenko, E N Avdeeva, N C Nametkin *Neftekhimiya*, 1978, **18** 217
60. V V Chenets, O F Shepto'ko, Z B Avdeyuk *Neftekhimiya*, 1978, **18** 225
61. G Gunschel, M Scheller, C Schuhler, et al. *Z. Phys. Chem.*, 1983, **264** 113
62. G Pop, K Petre, G Ivenush, P Tomi *Neftekhimiya*, 1979, **19** 535
63. Yu M Zhorov, G S Volokhova *Khim. Tekhnol. Topl. Masel*, 1980, (8) 11
64. E J J Scott *Ind. Eng. Chem. Prod. Res. Dev.*, 1967, **6** 72
65. F O Rice *J. Am. Chem. Soc.*, 1931, **53** 1959
66. F O Rice *J. Am. Chem. Soc.*, 1933, **55**, 3035
67. F O Rice, A Kossiakoff *J. Am. Chem. Soc.*, 1943, **65** 590
68. V V Voevodskii *Voprosy Khimicheskoi Kinetiki, Kataliza i Reaktsionnoi Sposobnocti* (Problems in Chemical Kinetics, Catalysis and Reactivity, Izd. Akad.Nauk SSSR, Moscow, 1955, 150
69. S B Zdonik, E J Green, L P Hallee *Oil Gas J.*, 1967, (11) 98
70. M Szwarc *J. Chem. Phys.*, 1952, **20** 403, 407
71. G M Come *Chemical Kinetics, Vol. 24*, Elsevier, Amsterdam–Oxford–New York, 1983, p. 325
72. A I Dintses, A V Frost *Dokl. Akad. Nauk SSSR*, 1934, **3** 510
73. A V Frost *Usp. Khim.*, 1939, **8** 956
74. A D Stepukhovich, B I Birger *Zh. Fiz. Khim.*, 1959, **33**(1) 8 [English translation in *Russ. J. Phys. Chem.*, 1959(1)]
75. E W R Steacie *Atomic and Free Radical Reactions*, Reinhold, New York, 1954, Ch. IV.
76. N N Semenov *O Nekotorykh Problemakh Khimicheskoi Kinetiki i Reaktsionnoi Sposobnosti* (Some Problems of Chemical Kinetics and Reactivity), Izd. Akad. Nauk SSSR, Moscow, 1958, Chap. VII, Sect. 5, p. 365
77. J Purnell, C Quinn *Nature (London)*, 1961, **189** 656
78. R A Kalinenko, L V Shevel'kova, K P Lavrovskii, L M Vedeneeva *Neftekhimiya*, 1968, **8** 209
79. E J Scott *Ind. Eng. Chem. Prod. Res. Dev.*, 1967, **6** 67
80. L V Shevel'kova, L M Vedeneeva, N S Nametkin *Kinet. Katal.*, 1985, **26** 779
81. L V Shevel'kova, A N Rumyantsev, L M Vedeneeva, et al. *Dokl. Akad. Nauk SSSR*, 1981, **260** 393
82. L E Gusel'nikov, V V Volkova, U Zigler, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2152
83. L E Gusel'nikov, V V Volkova, L V Shevel'kova, et al. *Neftekhimiya*, 1986, **26** 216
84. R Z Magaril *Mekhanizm i Kinetika Gomogennykh Termicheskih Prevrashchenii Uglevodorov* (Mechanism and Kinetics of Homogeneous Thermal Conversions of Hydrocarbons), Khimiya, Moscow, 1970, p. 102
85. L V Shevelkova, N S Nametkin *Symposium uber Aktuel wissenschaftliche Probleme der Pyrolyse von Kohlenwasserstoffen, Leipzig*, 1979, p. 55
86. L V Shevelkova, L M Vedeneeva, L E Gusel'nikov, G Bach, W Zychlinski, G Zimmermann *J. Anal. Appl. Pyrolysis*, 1990, **17** 201
87. N V Korzun, R Z Magaril, G N Plyusnina, T M Semukhina *Zh. Fiz. Khim.*, 1979, **53**(5) 1113 [English translation in *Russ. J. Phys. Chem.*, 1979(5)]
88. L E Gusel'nikov, L V Shevel'kova, V V Volkova, et al. *V Neftekhimicheskii Simpozium Sotsialisticheskikh Stran.* (Vth Petrochemical Symposium of the Socialist States), Burgas, Bulgaria, 1986, p. 297
89. R A Kalinenko, L V Shevel'kova, K P Lavrovskii *Kinet. Katal.*, 1974, **15** 7
90. W Bryce, A Hardiman *Can. J. Chem.*, 1962, **40** 1031

Translated from *Uspekhi Khimii* **61** 815–863 (1992) U.D.C. 541.64

New bis(naphthalic anhydrides) and polyheteroarylenes based on them with improved processability

A L Rusanov
A N Nesmeyanov Institute of Heteroorganic Compounds, Russian Academy of Sciences, Moscow

ABSTRACT. New bis(naphthalic anhydrides) containing 'hinge' groups and/or bulky substituents are considered. It has been shown that the majority of these monomers may be synthesised from derivatives of naphthalic anhydride or acenaphthene with subsequent oxidation of the bisacenaphthyls obtained. Reaction of these compounds with aromatic diamines and bis(*o*-phenylenediamines) gives polynaphthalimides and polynaphthoylenebenzimidazoles combining solubility in organic solvents with high thermal and chemical stability.

The bibliography contains 154 references.

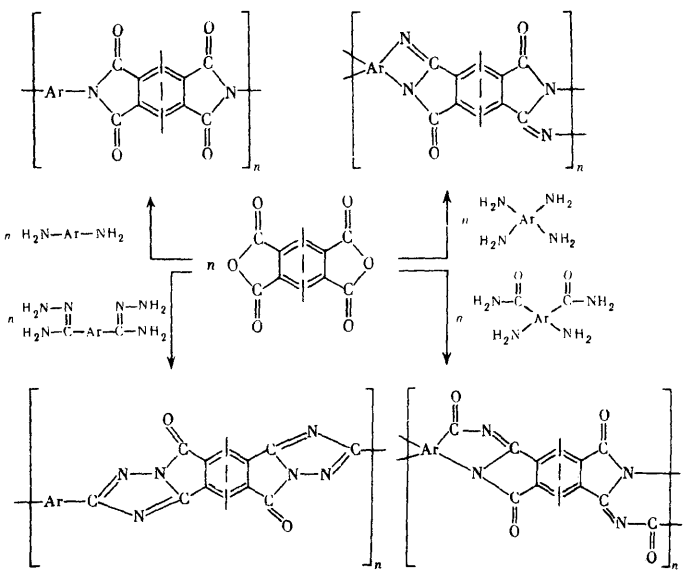
Contents

I. Introduction 446
II. Bis(naphthalic anhydrides) containing structural elements causing improved solubility for the heteroarylenes based on them 447
III. Polyheteroarylenes from bis(naphthalic anhydrides) 456

I. Introduction

The rapidly developing variety of modern techniques present ever-increasing requirements for the polymers used in them. Investigations on thermally and chemically stable polymers are fairly widespread[1–9] and in some of these the polyheteroarylenes, aromatic polymers containing heterocycles in the main chains of the macromolecule, have attracted particular interest. This interest is explained by the spectrum of valuable, occasionally unique, physicochemical and mechanical properties possessed by these polymers and the materials based on them.[1–21]

A significant portion of the studies on the synthesis of polyheteroarylenes is devoted to polymers based on bis(phthalic anhydrides). These monomers are widely used in the synthesis of polyimides[22–25] and of the completely and partially 'ladder' polyheteroarylenes,[26] the polybenzoylenebenzimidazoles, polybenzoylene-S-triazoles, polyisoindoloquinazolinediones,[27] etc., which are illustrated by the following scheme:

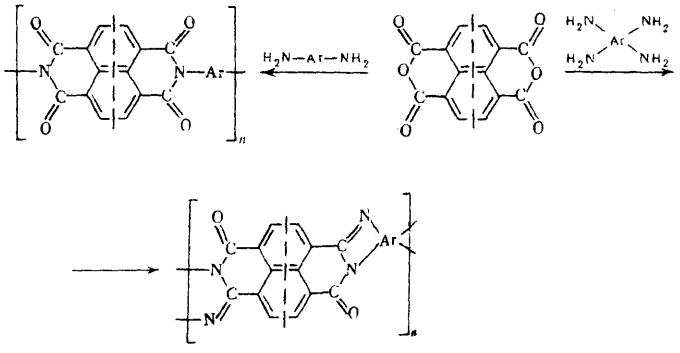


Practically all these polyheteroarylenes are obtained using stepwise processes with the possibility of stopping the reaction at the stages of formation, of prepolymers soluble in organic solvents, processing of the prepolymers into a product and subsequent cyclisation of them in the form of the finished products with the formation of the desired infusible and insoluble polyheteroarylenes as the already finished goods.

It must however be noted that both the polyimides and the ladder polyheteroarylenes based on bis(phthalic anhydrides) possess comparatively low thermal and chemical stability.[27] This is caused to a significant extent by the strain of the five-membered imide fragments of the resulting heterocycles and the high positive charges on the carbon atoms of the carbonyl groups of these systems.

The logical route leading to a potential increase in the thermal and chemical stability of the polyheteroarylenes is the replacement of the bis(phthalic anhydrides) in the above-mentioned reactions by bis(naphthalic anhydrides) the structure of which should be determined by the formation of systems containing six-membered imide rings, either on their own or condensed with other heterocyclic fragments.

Previous investigations[28–37] have shown that on using bis(naphthalic anhydrides) as monomers polynaphthalimides and polynapht'ioylenebenzimidazoles are obtained which possess high chemical and thermal stability and fire resistance compared with analogous systems based on the bis(phthalic anhydrides).[28–40]

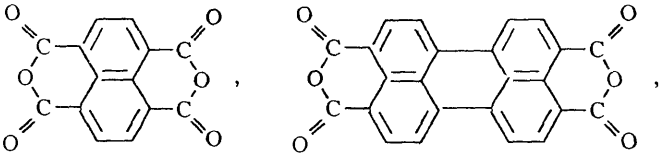


The polymers based on bis(naphthalic anhydrides) are therefore more promising than those based on bis(phthalic anhydrides) from the point of view of creating materials with improved properties.

It must however be noted that the polyheteroarylenes based on bis(naphthalic anhydrides) are generally systems with a low ability to be processed into articles. On the one hand the final polyheteroarylenes are infusible and are soluble in strong acids, such as sulphuric, methanesulphonic or polyphosphoric, and on the other the reactions using bis(naphthalic anhydrides) as stepwise processes are difficult due to the reduced electrophilic reactivity of bis(naphthalic anhydrides) and the ease of forming six-membered naphthalimide systems.

Hence it follows that the development of polyheteroarylenes based on bis(naphthalic anhydrides) characterised by a satisfactory processability into articles is an important and urgent problem in the chemistry of thermostable polymers. One of the most common routes of improving the processability of polyheteroarylenes is the conferring on them of solubility in organic solvents. The main ways to solve this problem are:

1. The synthesis of polyheteroarylenes based on the most common bis(naphthalic anhydrides), i.e. the anhydrides of naphthalene-1,4,5,8-tetracarboxylic and perylene-3,4,9,10-tetracarboxylic acids



and nucleophilic co-monomers differing in the structure which causes an improved processability of the desired polyheteroarylenes.

2. The development of bis(naphthalic anhydrides) containing structural elements causing improved processability of the polyheteroarylenes based on them and the use of the indicated bis(naphthalic anhydrides) in reactions with di- and tetra-functional nucleophilic comonomers.

Since the first of the above-mentioned approaches has been considered previously,[24,41,42] attempts will be undertaken in the present review to analyse the results obtained in the second direction.

The main approaches[43,44] to the conferment of solubility in organic solvents to the polyheteroarylenes by modifying the initial dianhydrides are:

a) the introduction of 'hinge' bonds into the molecules which facilitate to a maximal extent the rotation of the individual fragments of the macromolecule relative to one another and b) the introduction into the molecule of anhydrides with bulky substituents.

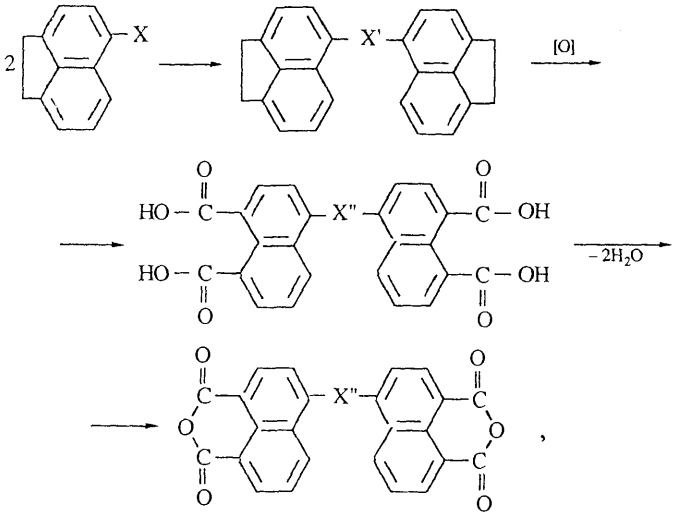
A combined approach is frequently used, i.e. both hinges and bulky substituents are introduced into the anhydride molecule.

These approaches and combinations of them were used in the development of new bis(naphthalic dianhydrides) intended for the preparation of polyheteroarylenes soluble in organic solvents.

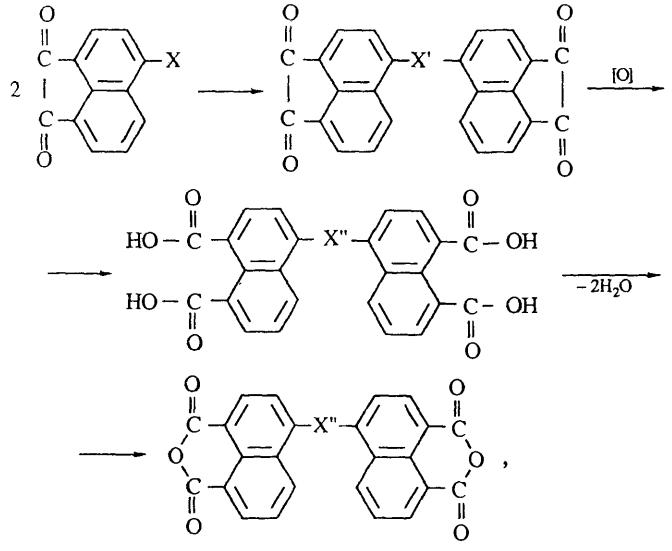
II. Bis(naphthalic anhydrides) containing structural elements causing improved solubility of the polyheteroarylenes based on them

The simplest modification of the most common bis(naphthalic anhydrides) directed towards improving the processability of the polyheteroarylenes derived from them is the introduction of a single bond or a hinge group between two naphthalic anhydride residues. Analogous bis(naphthalic anhydrides)[42] are most frequently obtained from acenaphthene[45] or its simplest derivatives using such approaches as:

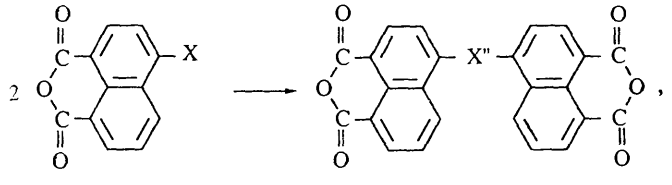
– the reaction of two molecules of acenaphthene or a derivative with the appropriate compounds leading to the formation of bis-acenaphthenes, subsequent oxidation[46] of them and dehydration of the resulting bis(naphthalic acids):



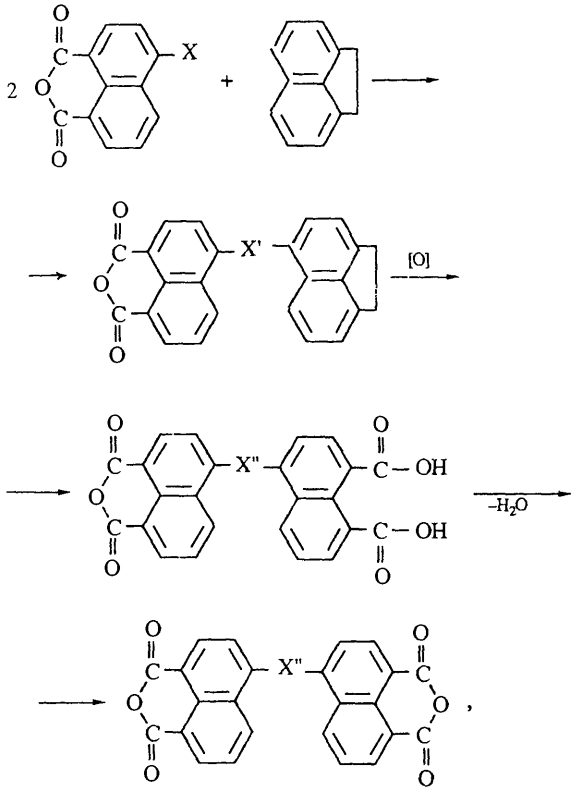
– the reaction of two molecules of acenaphthoquinone derivatives (product of partial oxidation of acenaphthene) with appropriate compounds and subsequent oxidation of the resulting bis-acenaphthoquinones to bis(naphthalic anhydrides):



– the reaction of two molecules of the naphthalic anhydride derivative (derived from acenaphthene[45]) with appropriate compounds leading to the formation of bis(naphthalic anhydrides):

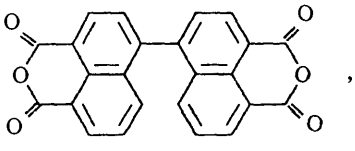


– the reaction of naphthalic anhydride derivatives with acenaphthene or a derivative of it leading to the formation of compounds containing both an acenaphthyl and an anhydride function with subsequent oxidation of the acenaphthyl group and dehydration of the resulting acid function:

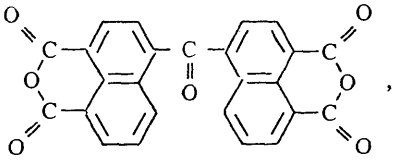


Certain monomers of this type containing separate naphthalic anhydride residues were obtained a fairly long time ago. Their simplest representatives are as follows:

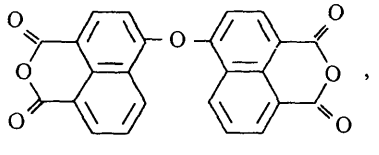
4,4′-Bis(naphthalic anhydride)[47,48]



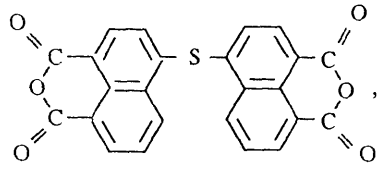
4,4′-Ketobis(naphthalic anhydride)[49,50]



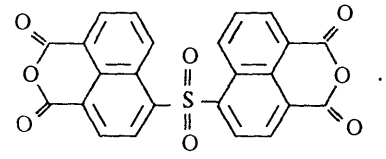
4,4′-Epoxybis(naphthalic anhydride)[51–54]



4,4′-Thiobis(naphthalic anhydride)[55,56]



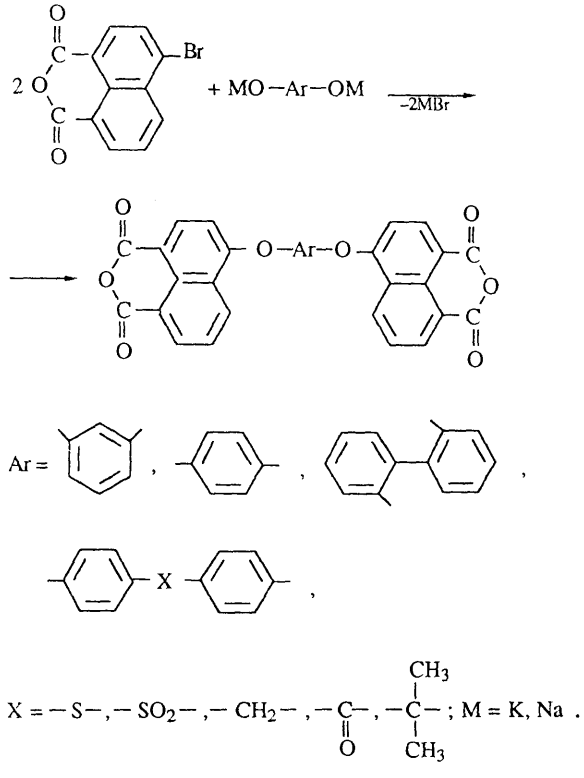
4,4′-Sulphonylbis(naphthalic anhydride)[56,57]



It must however be noted that polyheteroarylenes, primarily polynaphthoylenebenzimidazoles, obtained from bis(naphthalic dianhydrides) containing no more than one hinge group and the simplest bis(*o*-phenylenediamines), proved to be soluble only in strong acids and were practically insoluble in a single organic solvent.[55,57–61]

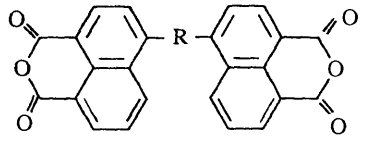
The simplest change in the structure of the bis(naphthalic dianhydrides) directed towards obtaining the desired polyheteroarylenes soluble in organic solvents is the introduction of additional hinge groups.

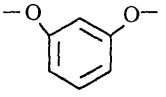
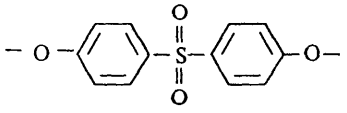
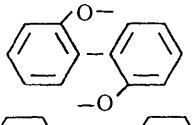
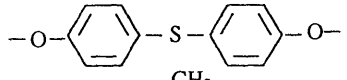
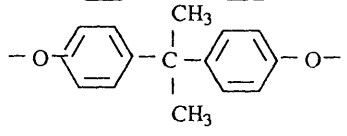
Significant attention has been paid to systems containing at least two ether bonds in several bis(naphthalic anhydrides) containing more than one hinge group. These monomers are obtained by the reaction of two moles of 4-bromonaphthalic anhydride with an alkali metal bisphenoxide in dipolar aprotic solvents[55,62–68] according to the following scheme:



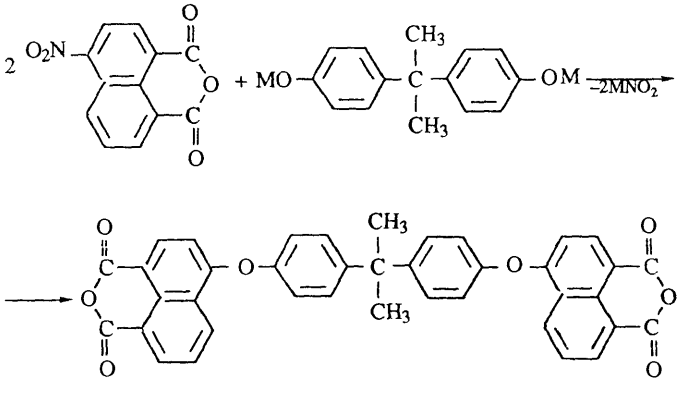
Some characteristics of individual bis(naphthalic anhydrides) containing ether groups are shown in Table 1.

Table 1. Bis(naphthalic anhydrides) of general formula

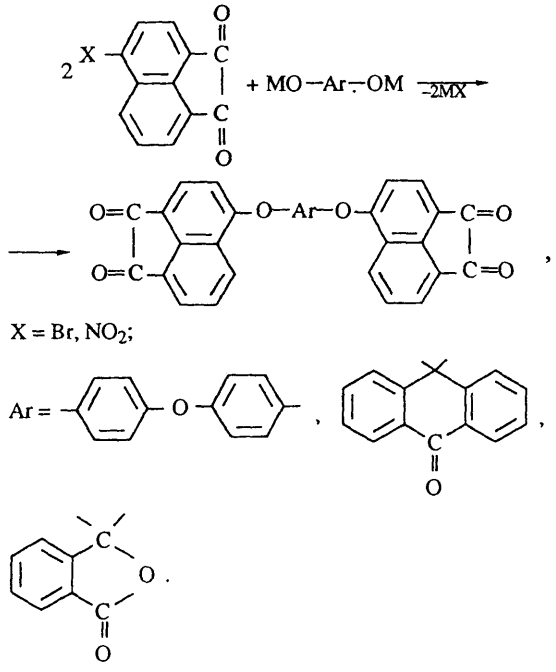


R	Mp, °C	Yield, %	Ref.
	271–272	81.6	[63]
	300	93.0	[63]
	287.5–287.6	95.0	[63]
	274.4–275.5	96.7	[63]
	294–295	70.0	[65]

An alternative method of synthesising similar bis(naphthalic anhydrides) is the use of 4-nitronaphthalic anhydride in place of 4-bromonaphthalic anhydride,[69] however this process has only been considered in an extremely fragmentary manner.



The 4-bromo and 4-nitro derivatives of acenaphthoquinone[66,70,72] also react with alkali metal bisphenoxides in the reactions considered above. In these cases bisacenaphthoquinones are formed in the first stage.



X = Br, NO_2;

Individual bisacenaphthoquinones were then oxidised further to bis(naphthalic acids) and then converted into bis(naphthalic anhydrides).[71,72]

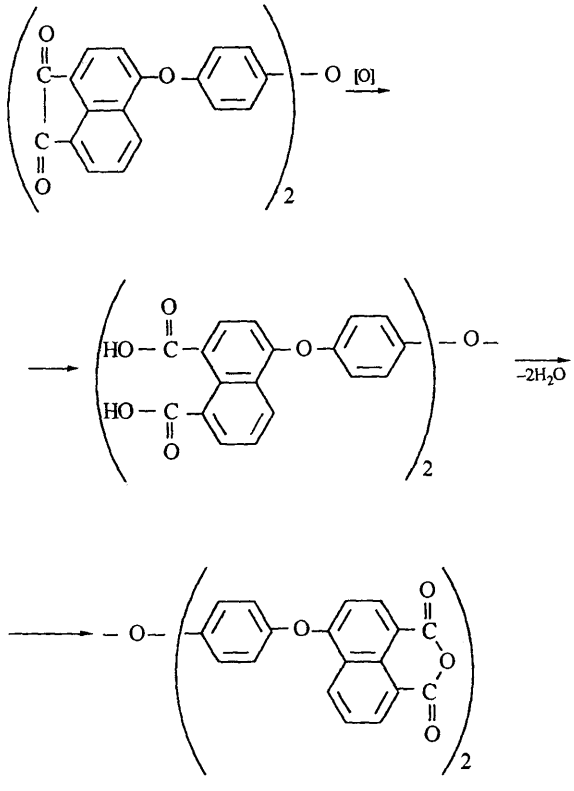
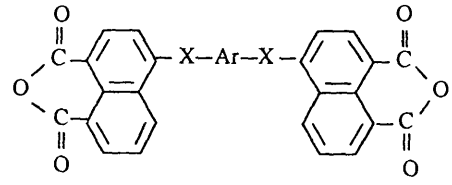
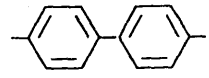
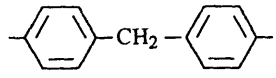
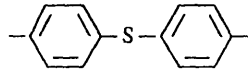
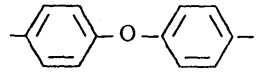
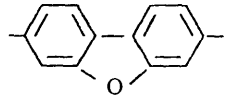
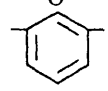
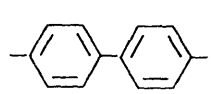
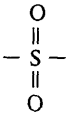
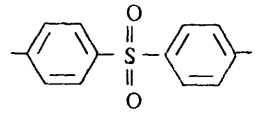
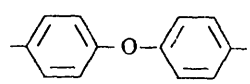
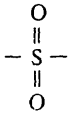
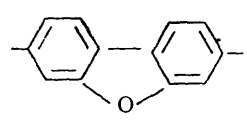
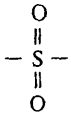
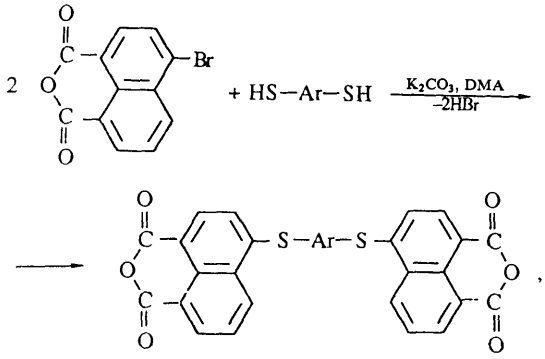


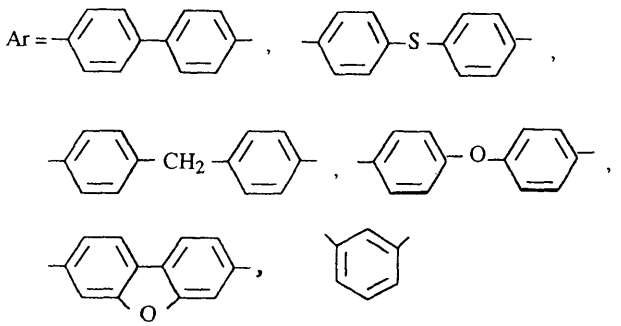
Table 2. Some characteristics of bis(naphthalic anhydrides) of general formula



Ar	X	Mp, °C	Yield, %	Ref.
	—S—	370–372	70	[73, 74]
	—S—	294–296	82	[73, 74]
	—S—	250–251	56	[55, 73, 74]
	—S—	289–291	80	[73, 74]
	—S—	372–374	73	[73, 74]
	—S—	222.5–223	75	[63]
		400–401	92	[73, 74]
		395–396	85	[73, 74]
		358–362	87	[73, 74]
		341–342	91	[73, 74]

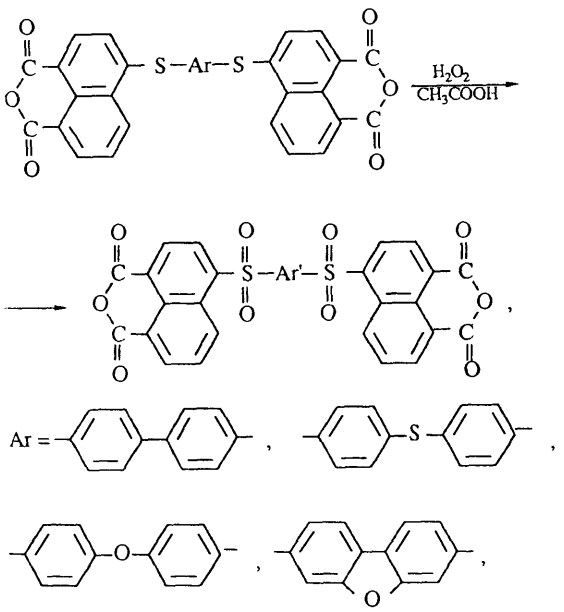
Practically all the reactions considered above for the synthesis of bis(naphthalic anhydrides) containing ether groups may be used for the preparation of bis(naphthalic anhydrides) containing thioether linkages.[55,63,73,74] In these reactions bis(thiophenoxides) are used as starting materials instead of alkali metal bisphenoxides.

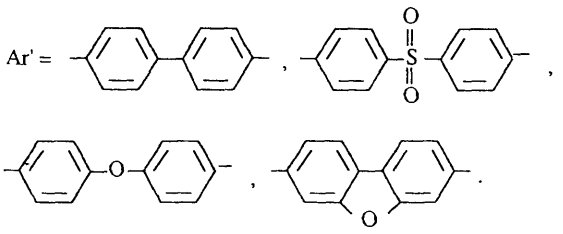




Some characteristics of bis(naphthalic anhydrides) containing thioether groups are given in Table 2.

The bis(naphthalic anhydrides) are characterised by a lower electrophilic reactivity than the bis(phthalic anhydrides). The introduction into them of ether and thioether groups, which are electron-donating substituents, causes a further reduction in their electrophilic reactivity. This led to a switch from electon-donating to electron-accepting hinge groups and in particular to the transition from dianhydrides containing thioether groups to dianhydrides with sulphone fragments. Synthesis was effected by the following scheme:[73,74]





Some characteristics of the bis(naphthalic anhydrides) containing sulphone groups are given in Table 2.

Another large group of bis(naphthalic anhydrides), the so-called bis(ketonaphthalic anhydrides), were obtained by the Friedel–Craft reaction of the diacid chlorides of aromatic dicarboxylic acids with two moles of acenaphthene with subsequent oxidation of the bis(acenaphthyls) to bis(ketonaphthalic acids) which undergo further dehydration to bis(ketonaphthalic anhydrides)[77–81] according to the following scheme:

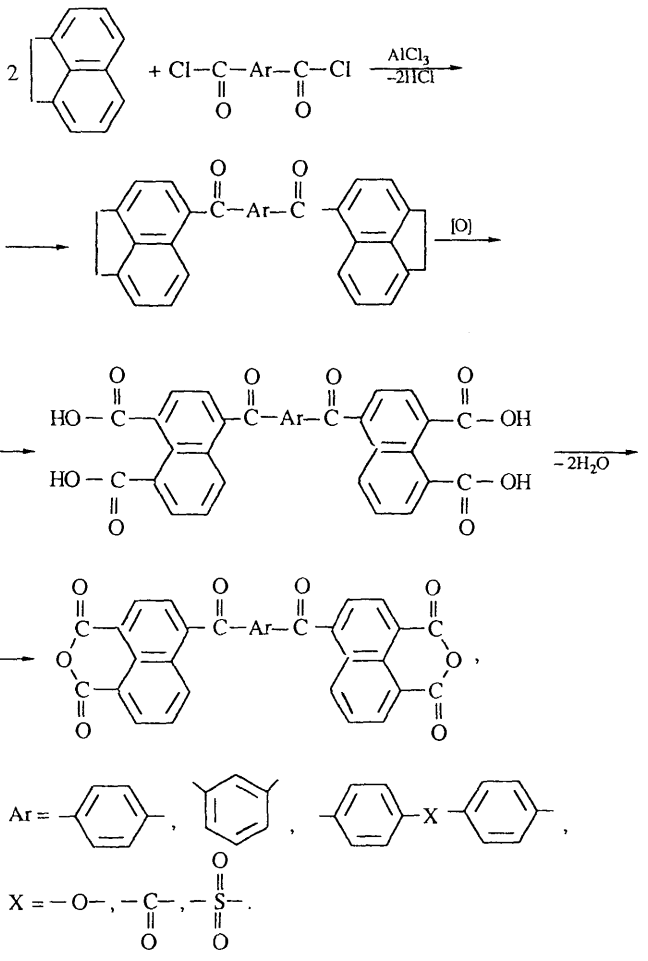
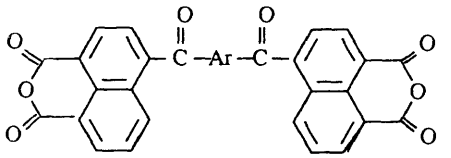
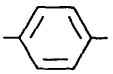
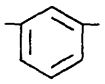
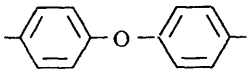
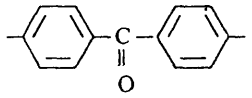
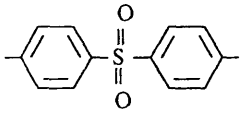
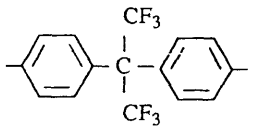
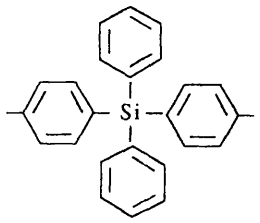


Table 3. Properties of aroylenebis(naphthalic anhydrides)



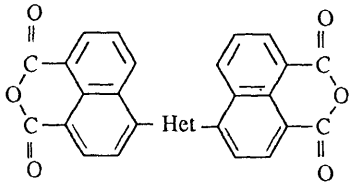
Ar	Mp, °C	Yield, %	Ref.
	> 450	70.8	[77, 78, 80]
	434–436	90.2	[77,80]
	309–311	93.0	[77,80]
	313–314	94.0	[77, 80]
	341–342.5	89.1	[77, 80]
	288–290	96	[77]
	308–309	57	[82, 84]
$-CB_{10}H_{10}C-$	278–280	35	[83, 84]

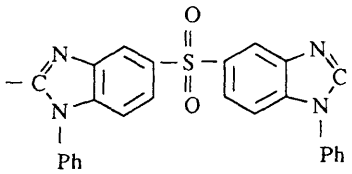
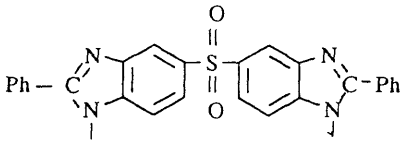
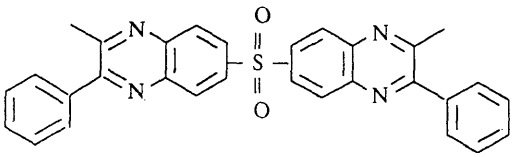
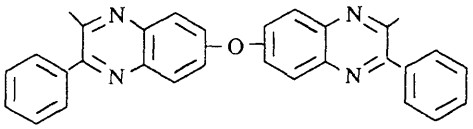
Some characteristics of the bis(ketonaphthalic anhydrides) synthesised are given in Table 3.

The same synthetic approach was used for obtaining bis(ketonaphthalic anhydrides) containing a heteroorganic central grouping, such as hexafluoroisopropylidene, diphenylsilyl and *m*-carboranylene (Table 3).[82–84]

An alternative method of synthesising the bis(ketonaphthalic anhydrides) considered above and systems isomeric with them is the Friedel–Craft reaction of a 4-chloroformylnaphthalic anhydride with aromatic hydrocarbons.[85]

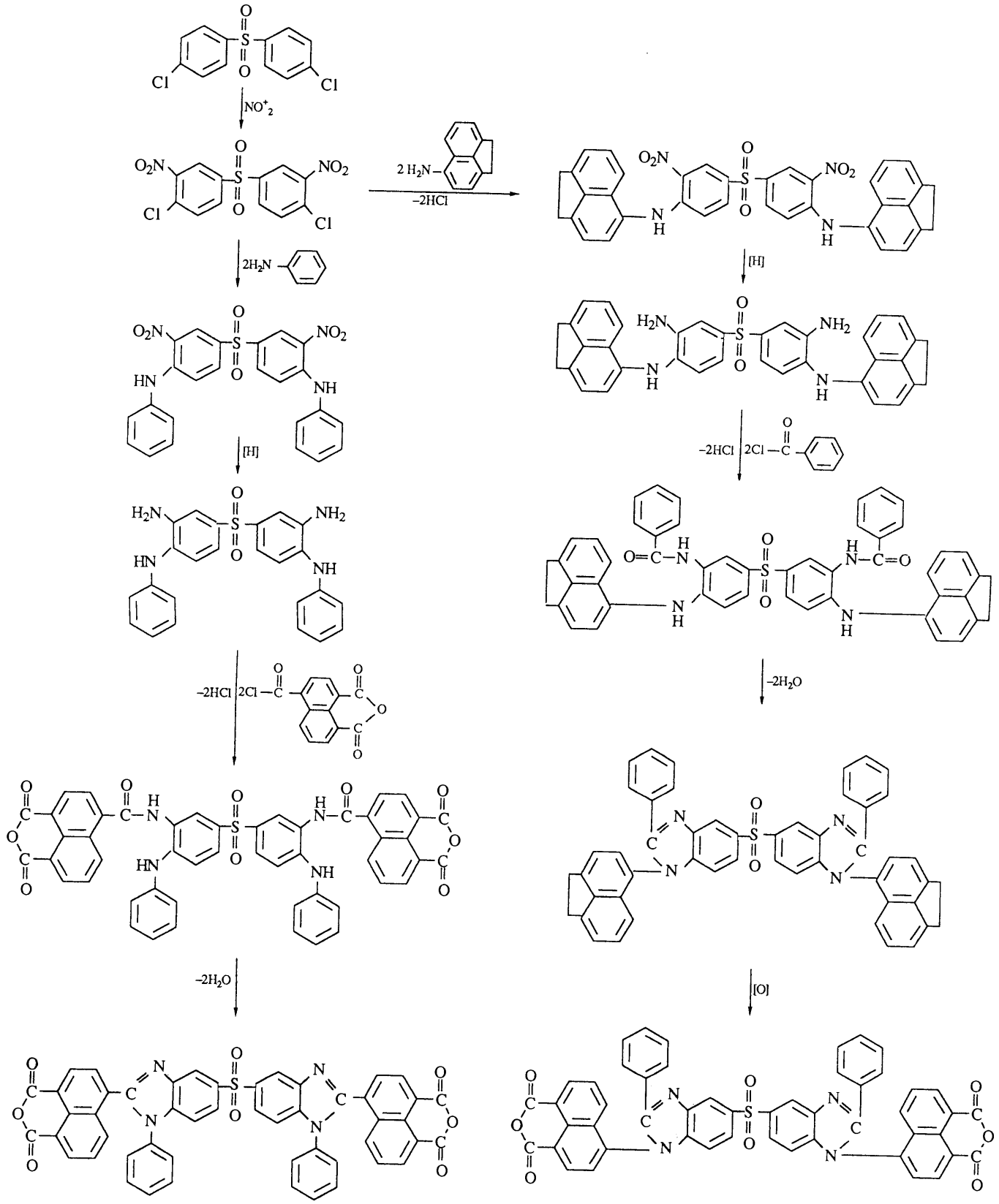
Table 4. Some characteristics of heteryl-containing bis(naphthalic anhydrides) of general formula



Het	Mp, °C	Yield, %	Ref.
	377–379	40	[86]
	355–356	42	[87]
	352–364	73	[89]
	315–335	68	[89]

4-Chloroformylnaphthalic anhydride was also used for obtaining bis(naphthalic anhydrides) containing phenyl substituted heterocycles. The dianhydride of bis[1-phenyl-2-(4,5-dicarboxynaphthyl)-benzimidazol-5-yl] sulphone was obtained by treating bis[(3-amino-4-phenylamino)phenyl] sulphone, a product from 4,4′-dichlorodiphenyl sulphone produced on an industrial scale, with two moles

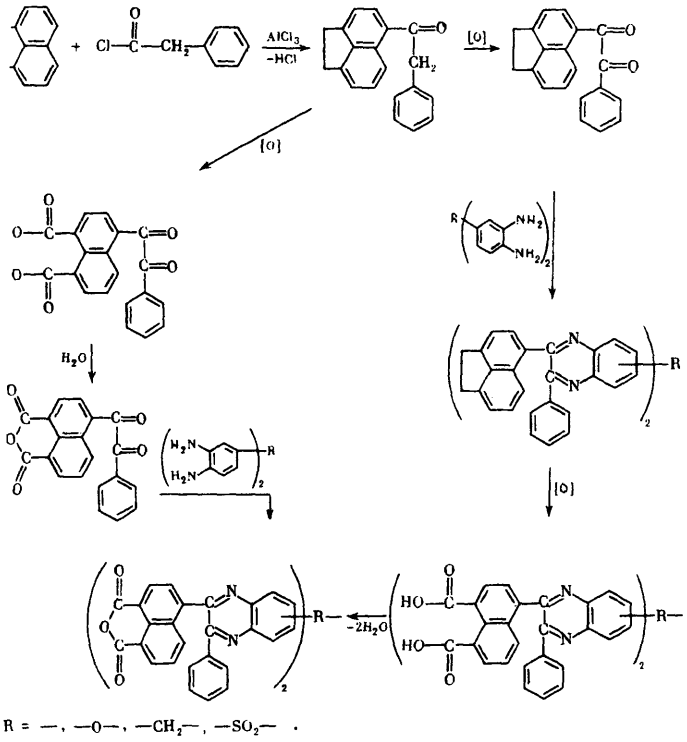
of 4-chloroformylnaphthalic anhydride and subsequent cyclodehydration of the compound obtained.[86,87]



The dianhydride of bis[2-phenyl-1-(4,5-dicarboxynaphthyl)benzimidazol-5-yl] sulphone, isomeric with this compound, was obtained by treating 4,4'-dichloro-3,3'-dinitrodiphenyl sulphone with 4-aminoacenaphthene, reduction of the nitro groups of the obtained 4,4'-di(aminoacenaphthyl)-3,3'-dinitrodiphenyl sulphone to primary amino groups, benzoylation of these amino groups, cyclodehydration of the 2-benzamido-imine fragments into 2-phenyl-1-acenaphthylbenzimidazole rings, oxidation of the acenaphthyl groups to peri carboxyl groups and anhydride formation of the latter.[87]

Individual characteristics of the synthesised bis(naphthalic anhydrides) containing various heterocycles are given in Table 4.

The derivatives of acenaphthene and naphthalic anhydride containing α-diketone groups in the 4 position have been used for obtaining bis(naphthalic anhydrides) containing phenylquinoxaline fragments.[88–91] The synthesis of these monomers was effected by the following scheme:

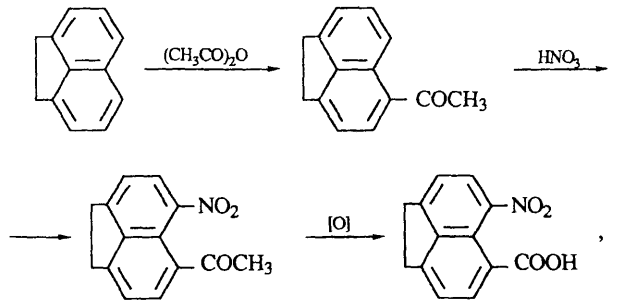


R = —, —O—, —CH_2—, —SO_2— .

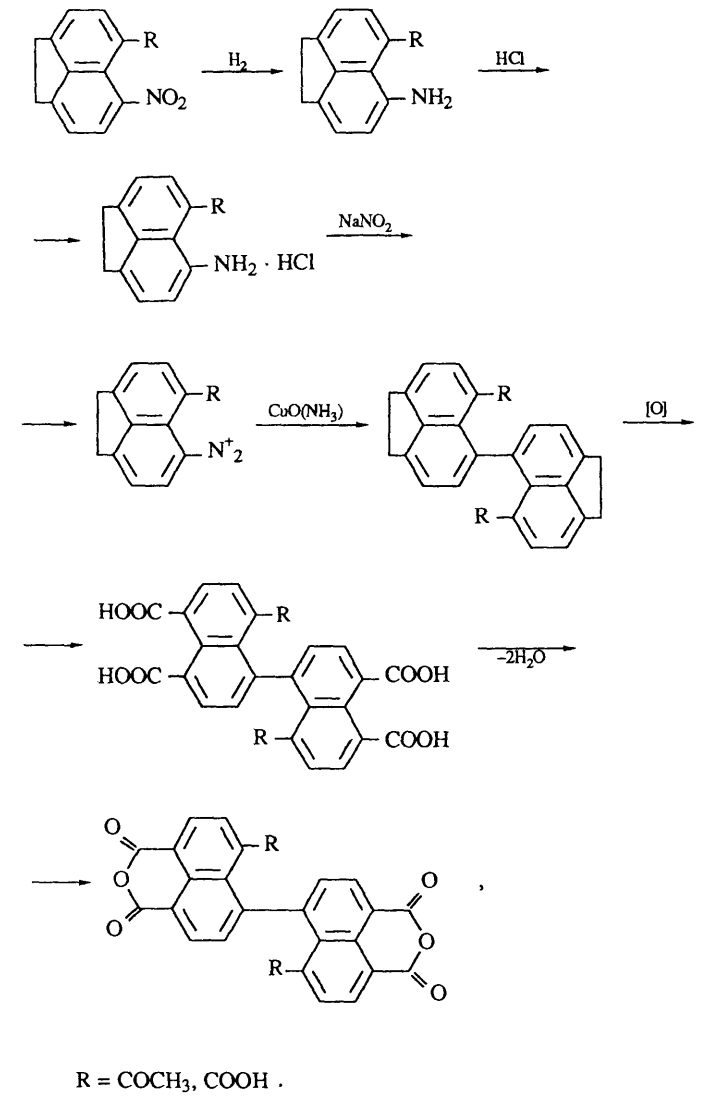
Some characteristics of the bis(phenylquinoxalinylnaphthalic anhydrides) are given in Table 4.

The diffuse melting points of the bis(phenylquinoxalinylnaphthalic anhydrides) are probably due to these products being mixtures of isomers, which is usual when forming bis and polyphenylquinoxaline systems.[92–94] In addition to phenyl, acetyl and carboxyl substituents, capable of increasing the solubility of the target polyheteroarylenes,[95] were also introduced into the bis(naphthalic anhydrides).

The diacetyl and dicarboxyl derivatives of bis(naphthalic anhydride) were obtained by the acetylation of acenaphthene, nitration of the 4-acetylacenaphthene obtained[96] and oxidation of the resulting acetylnitroacenaphthene[97]



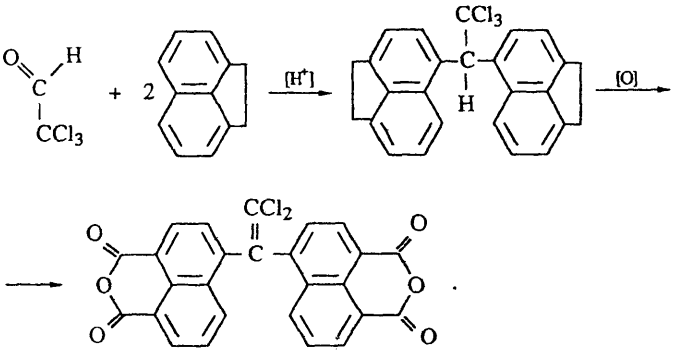
and subsequent formation and dimerisation of the diazo compounds.[98–100]



R = $COCH_3$, COOH .

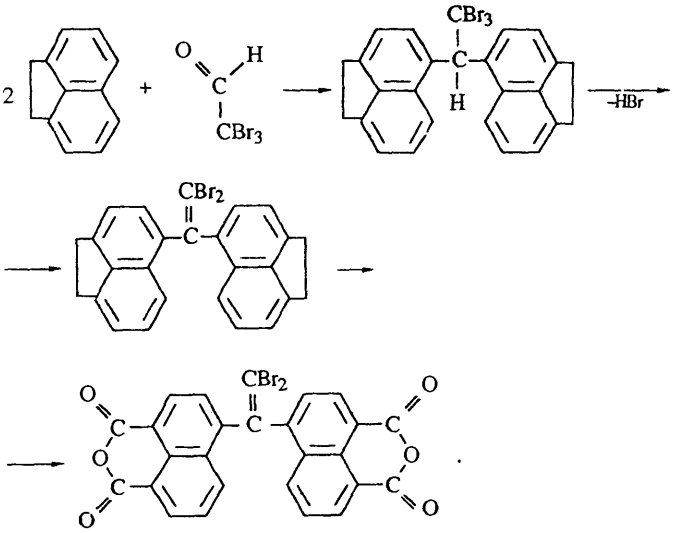
The dianhydride of 1,1′-bis(naphthyl)-4,4′,5,5′,8,8′-hexacarboxylic acid is manufactured in the USSR on a semi-industrial scale at the present time for the production of cubogens.[101,102]

Bis(naphthalic anhydrides) containing 1,1-dihaloethylene groups have been synthesised since it is known that the introduction of these fragments into macromolecules of various polyheteroarylenes are capable of improving the solubility of the latter.[102,108] Proceeding from the general chemistry of chloral derivatives,[103,114] it might be expected that the condensation of chloral with two molecules of acenaphthene must lead to di(acenaphth-4-yl)trichloroethane and this was found to be so. The oxidation of diacenaphthyltrichloroethane with potassium and sodium dichromate in glacial acetic acid at 90–110 °C was accompanied by dehydrochlorination of the central grouping and simultaneous anhydride formation of the peri dicarboxyl groups.[77,110,111]



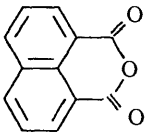
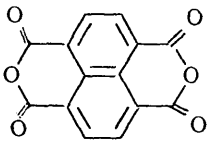
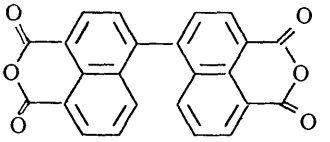
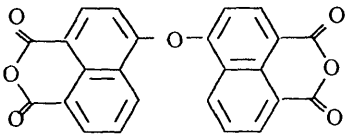
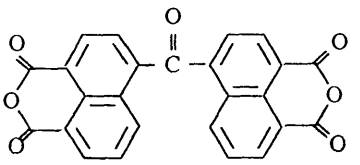
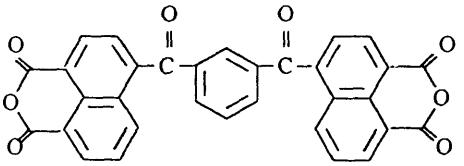
Neither dehydrochlorination of the 1,1,1-trichloroethane groups to 1,1-dichloroethylene nor oxidation of the 1,1-dichloroethylene group to carbonyl occurred when the usual conditions of carrying out these processes were applied to this system.

It is interesting to note that on replacing chloral by bromal the reactions considered occurred totally as expected[103,107,109,113] and led to the formation of the dianhydride of 1,1-bis(1,8-dicarboxynaphth-4-yl)-2,2-dibromoethylene.[80,112]



Since there are no literature data on the relative reactivities of bis(naphthalic anhydrides) a quantum chemical calculation of certain parameters was carried out by the PPP method,[113] particularly of the value of the electron affinity (A) which is a measure of the electrophilic reactivity of the dianhydrides in reactions with amines.[114] The results of the calculations of the values of A for various bis(naphthalic anhydrides) are given in Table 5.

Table 5. Electronic characteristics of bis(naphthalic anhydrides).

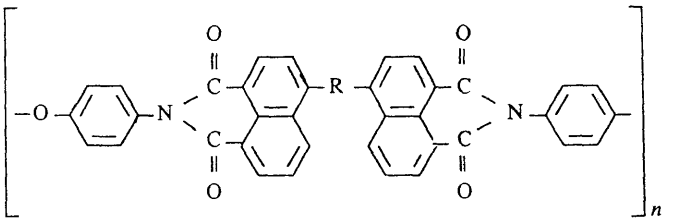
Compound	A, eV		q_1	q_2
	from Koopmans' theorem	from energy difference		
	3.1493	1.7426	0.2478	0.2478
	4.0102	2.6044	0.2477	0.2477
	3.7990	2.4770	0.2474	0.2469
	3.4488	2.0819	0.2097	0.2184
	3.8704	2.4896	0.2486	0.2475
	3.6475	2.1878	0.2490	0.2475

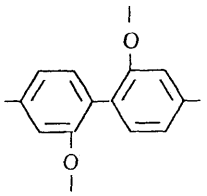
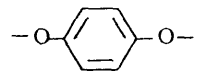
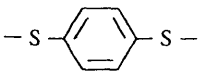
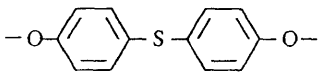
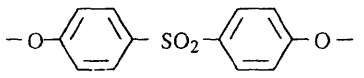
Note: q_1 is the positive charge on the 5 and 5′ carbon atoms, q_2 is the positive charge on the 4 and 4′ carbon atoms.

As in the case of the bis(phthalic anhydrides) the greatest value of A was found for the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid and the values of A for bis(naphthalic anhydrides)

containing electron-accepting hinge groups were greater than those for the bis(naphthalic anhydrides) with electron-donating groups. Comparison of the absolute values of A shows that the values of A for the bis(naphthalic anhydrides) were significantly greater than for the bis(phthalic anhydrides), which agrees with the literature[114] and is explained by the high aromaticity of the bis(naphthalic anhydrides). However the high values of A are not linked with the higher reactivity of the bis(naphthalic anhydrides) compared with the bis(phthalic anhydrides) since the reactivity depends on the strain in the anhydride ring.

Table 6. Some characteristics of polynaphthoylenebenzimidazoles of general formula[62,63]



R	η_{inh}(H_2SO_4, 30 °C)	T_g, °C
	0.15	260
	0.20	260
	0.26	253
	0.30	269
	0.29	317

Values have been calculated for the positive charges on the carbonyl carbon atoms to determine the reaction centre primarily subject to nucleophilic attack.[113] In the bis(naphthalic anhydrides) containing electron-donating hinge groups a high positive charge q is characteristic of the carbonyl carbon atoms at positions 5 and 5′. In bis(naphthalic anhydrides) with electron-accepting hinge groups the high positive charge is a characteristic of the carbonyl carbon atoms in the 4 and 4′ positions.

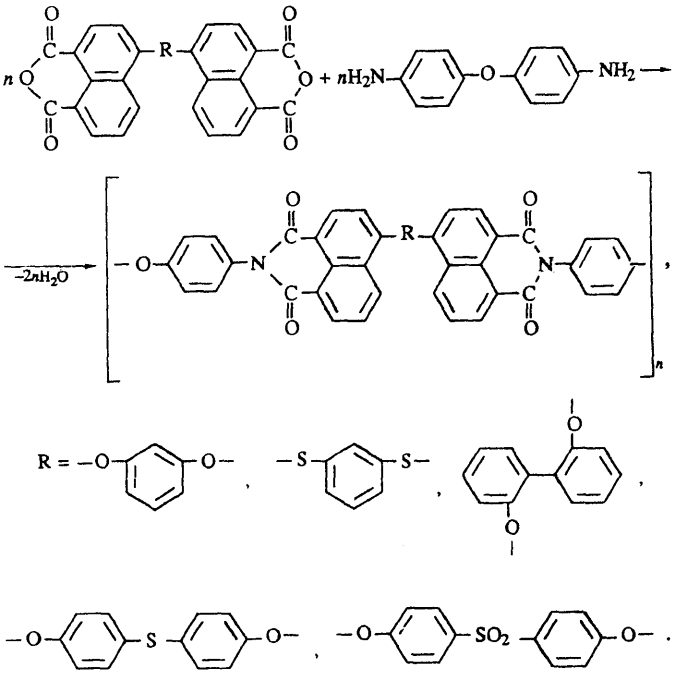
The fact that all the bis(naphthalic anhydrides) possess a lower reactivity than the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid points to the expediency of synthesising polyheteroarylenes from them using catalytic processes which are being used more in polycondensation and polycyclocondensation reactions.[115]

III. Polyheteroarylenes from bis(naphthalic anhydrides)

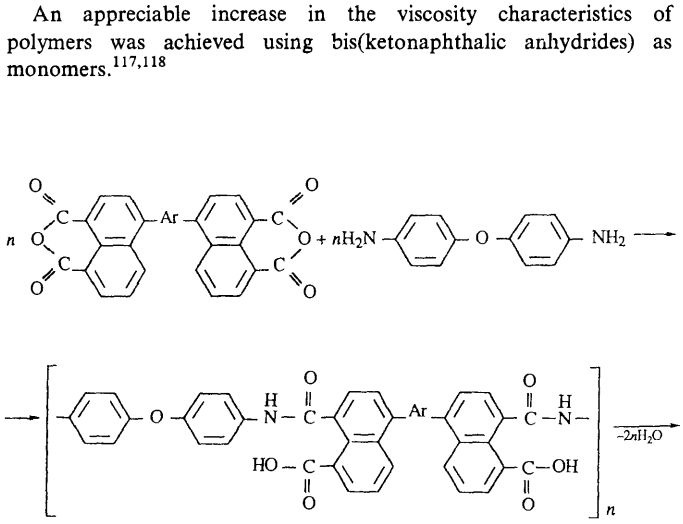
1. Polynaphthalimides

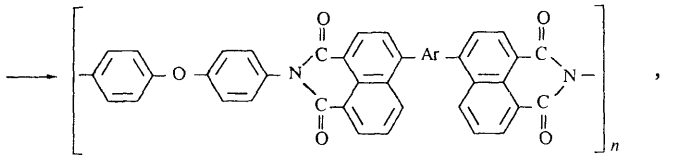
The majority of polynaphthalimides described in the literature are products of the reaction of naphthalene-1,4,5,8-tetracarboxylic acid with various diamines.[116] Several bis(naphthalic anhydrides) containing hinge groupings have been used for the synthesis of polynaphthalimides.

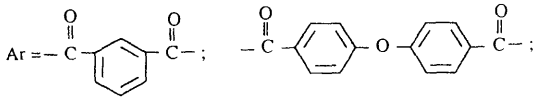
Polynaphthalimides containing ether and thioether groups, which are soluble in phenolic solvents, have been obtained by the reaction of ether- and thioether-containing bis(naphthalic anhydrides) with 4,4′-diaminodiphenyl oxide.[62,63] Reactions were carried out in *m*-cresol at 10% concentration (calculated on the final polymer) using quinoline or isoquinoline as catalyst. In contrast to the tougher polymer from the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid, which is precipitated from *m*-cresol at this concentration, the polyimides obtained were soluble in *m*-cresol up to 15% concentration though their molecular weights were fairly low (η_{inh} = 0.15–0.30 dlitre g^{-1}). The logarithmic viscosities and glass points of the polynaphthalimides synthesised are given in Table 6. Thermogravimetric analysis of the polymers showed the start of a mass loss at 450 °C in air and at 500 °C in a nitrogen atmosphere.

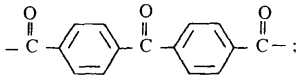


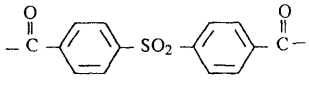
An appreciable increase in the viscosity characteristics of polymers was achieved using bis(ketonaphthalic anhydrides) as monomers.[117,118]





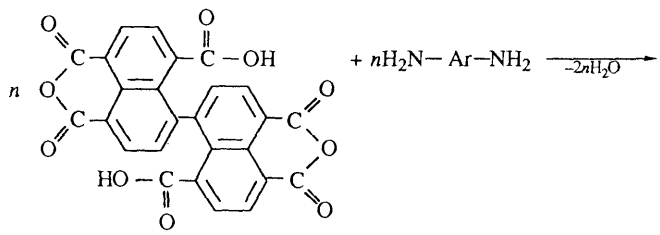


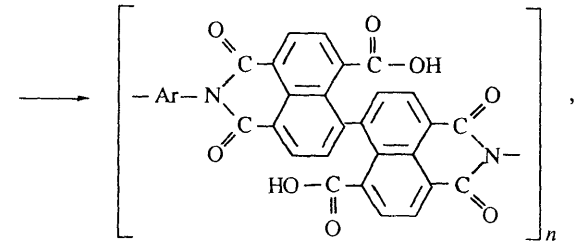


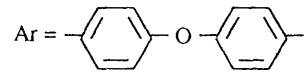


Synthesis of the polynaphthalimides was effected in *m*-cresol using benzoic acid as catalyst. The polynaphthalimides dissolved in H_2SO_4, phenolic solvents and mixtures of tetrachloroethane with phenol but polymers from dianhydrides containing ether bonds in the central group dissolved in tetrachloroethane as well. Some characteristics of the polynaphthalimides are given in Table 7.

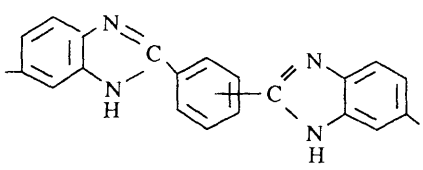
Polynaphthalimides containing free carboxyl groups were obtained by the reaction of the dianhydride of 1,1-dinaphthyl-4,4',5,5',8,8'-hexacarboxylic acid with 4,4'-diaminodiphenyl oxide and benzimidazole-containing aromatic diamines.[119–121]







$[\eta] = 1,4$

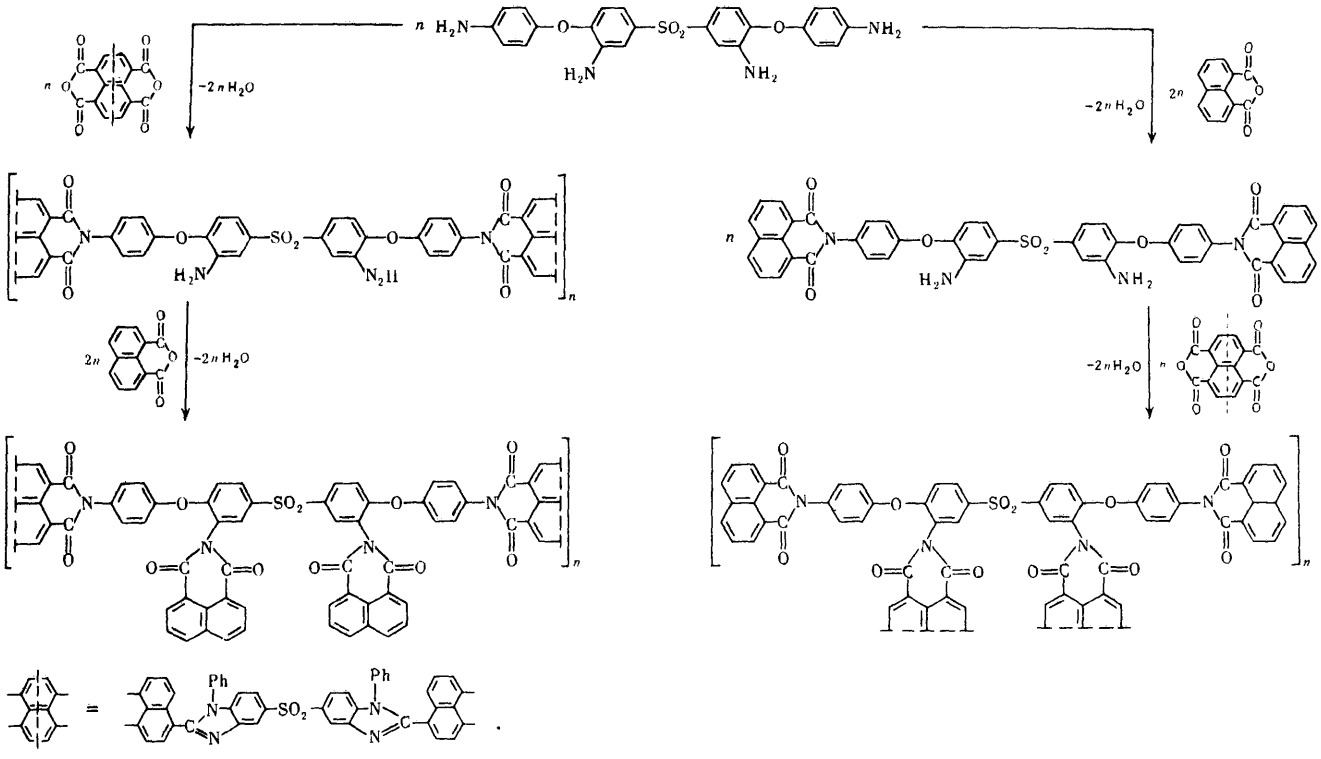


$[\eta] = 2,0$

High temperature (125–130 °C) polycyclocondensation was carried out in dipolar organic solvents with the addition of base. The polycondensation proceeds best of all in DMSO on adding sodium acetate in equimolar quantities. This is linked with the better solubility and stability of the monosodium salts formed at the strongly acidic carboxyl group of the dianhydride and the polynaphthalamide.[122] The remaining free carboxyl groups are probably catalysts of the polycyclocondensation process. The high molecular polynaphthalamides obtained dissolve readily in the presence of base in organic solvents (DMSO, DMAA) and in water. The polynaphthalimides do not soften until decomposition begins at 520–525 °C according to TGA (ΔT = 10 °C min^{-1}). When preparing polynaphthalimides in a chloride precipitating bath they form films and filaments with a strength up to 35 cN tex^{-1} and an elongation at break of up to 20%.

High solubility in organic solvents is also inherent of polynaphthalimides containing *N*-naphthylimide or *N*-(4-phenoxy)-naphthylimide substituents and which are synthesised as described[123]

by the following scheme:



Polynaphthalimides with *N*-naphthalimide *o*-substituents are obtained by the reaction of 3,3′-diamino-4,4′-di-(4-aminophenoxy)-diphenyl sulphone with an equimolar quantity of the bis(naphthalic anhydride) with subsequent treatment with two moles of the naphthalic anhydride under high temperature catalytic polycyclo-condensation conditions in *m*-cresol with benzoic acid. This polymer dissolves in phenolic solvents, in *N*-methyl-2-pyrrolidone (N-MP) and also in tetrachloroethane, it has a molecular weight of the order of 60000, softens at 340 °C and has a 10% weight loss temperature of 480 °C.

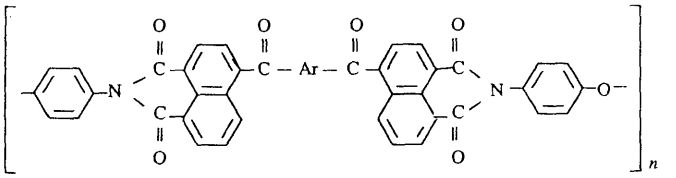
When the alternative sequence of adding mono- and dianhydride to the reaction is used a polynaphthalimide with even more bulky *N*-(4-phenoxy)naphthalimide *ortho* substituents is obtained which is soluble in a wide range of solvents, including those mentioned above and chloroform. The thermal characteristics of the polynaphthalimide synthesised were assessed from a thermomechanical curve and from dynamic TGA data and were comparable with the thermal characteristics of the polynaphthalimides with *N*-naphthalimide substituents (Table 8). The molecular weight of the synthesised polymer was of the order of 25000 but it was not possible to obtain films from it with satisfactory characteristics.

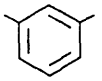
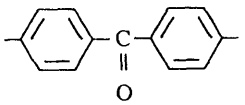
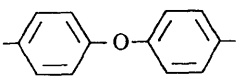
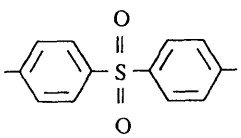
The high solubility of the systems obtained by both the first and second routes is seemingly determined by the lack of symmetry of the polymer molecules, by the presence of bulky side substituents, which aid its solubility by breaking up the polymer structure, and by the positive effect of the SO_2 group and the mild cyclisation conditions.

2. Polynaphthoylenebenzimidazoles

Significantly more attention has been paid to the polynaphthoylenebenzimidazoles based on the bis(naphthalic anhydrides) described above than to the polynaphthalimides. This is readily explainable even allowing for the fact that the bis(*o*-phenylenediamines), which are used to obtain the polynaphthoylenebenzimidazoles, are less accessible and more expensive than the aromatic diamines used in the synthesis of polynaphthalimides. The naphthoylenebenzimidazole ring is one of the most stable heterocycles (both thermally and hydrolytically),[124] and polynaphthoylenebenzimidazoles from naphthalene-1,4,5,8-tetracarboxylic acid dianhydride have been used successfully to obtain fibres with a unique set of properties.[125–135]

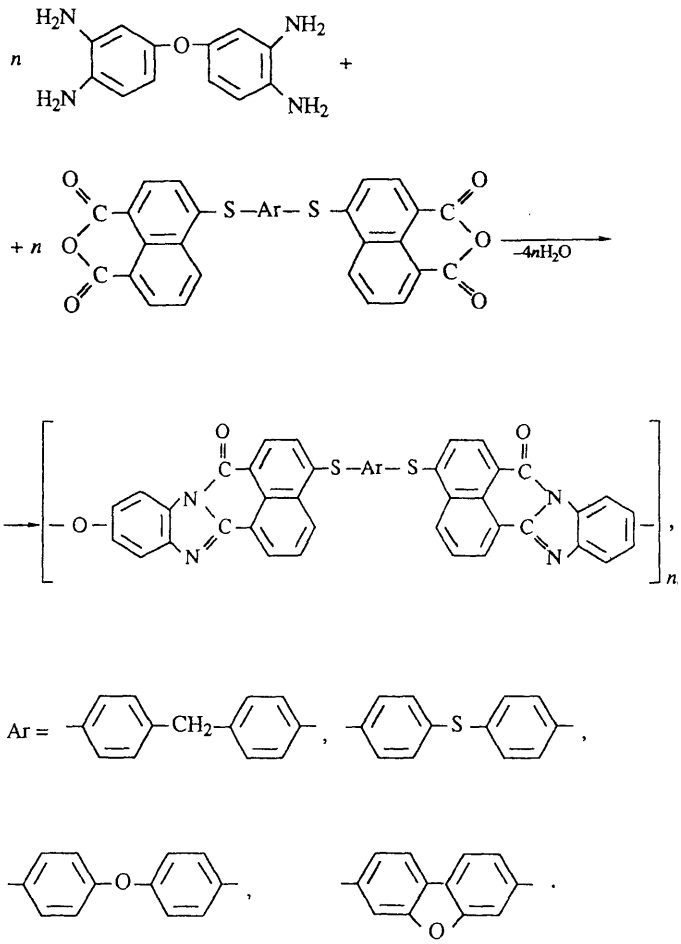
Table 7. Some characteristics of polynaphthalimides of general formula[117]



Ar	η_{red}*, dlitre g^{-1}	T_{soft}**, °C	$T_{10\%}$***, °C	Solvent**** H_2SO_4	*m*-cresol	TCE: phenol (3 : 1)	TCE
	0.72	310	500	+	+	+	+/−
	0.53	300	515	+	+	+	+/−
	0.78	275	490	+	+	+	+/−
	0.78	335	520	+	+	+	+/−

*Reduced viscosities of 0.5% solutions of polymers in H_2SO_4 at 25 °C.
**Softening points of polymers from thermomechanical analysis.
***10% Weight loss temperatures from dynamic TGA in air, ΔT = 5 °C min^{-1}.
****+ signifies soluble, − insoluble, +/− partially soluble.

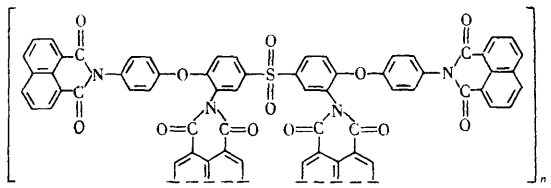
Sulphide-containing polymers were among the first to be synthesised among the polynaphthoylenebenzimidazoles from bis(naphthalic anhydrides) containing more than one hinge group.[55,73–76] These polymers were obtained by high temperature catalytic polycyclocondensation in *m*-cresol using benzoic acid as catalyst. The reaction proceeds as follows:

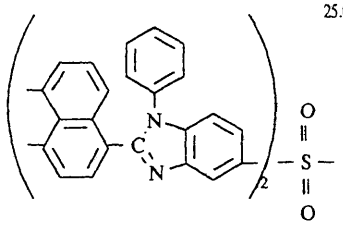
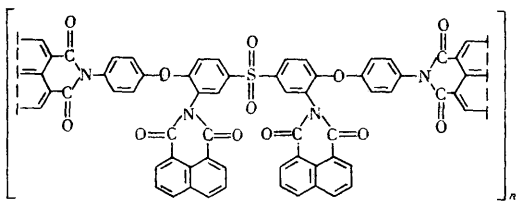


All the polycyclocondensations proceeded in solution (homogeneously) and led to the preparation of well cyclised polymers, the individual characteristics of which are given in Table 9.

The sulphide-containing polynaphthoylenebenzimidazoles synthesised were soluble in H_2SO_4 and in phenolic solvents (*m*-cresol, phenol : tetrachloroethane mixture) which in conjunction with high temperatures for softening (T_{soft} = 310−380 °C) and decomposition (T_{dec} = 450−470 °C) determine the well-known practical value of these systems. At the same time all the sulphide-containing polynaphthoylenebenzimidazoles have low viscosity characteristics (η_{red} = 0.4−0.9 dlitre g^{-1}) which do not permit materials with usable deformational strength characteristics to be obtained from them.

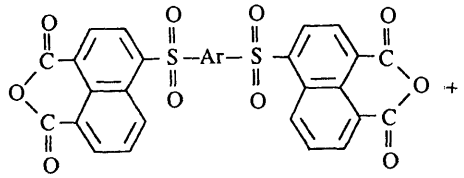
Table 8. Some characteristics of polynaphthalimides of general formula

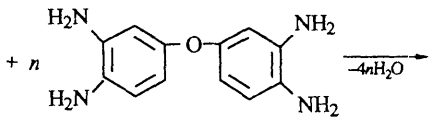


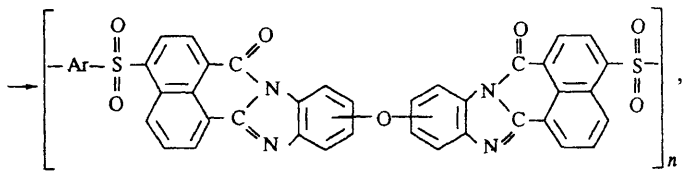
	$\bar{M}^*_w$	T_{soft}, °C	$T_{10\%}$, °C	Solvent			
				N-MP	*m*-cresol	TCE	$CHCl_3$
	25.000	340	480	+	+	+	+
	60.000	340	480	+	+	+	–

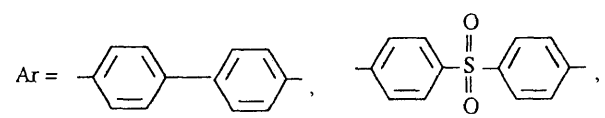
*Determined by sedimentation equilibrium.

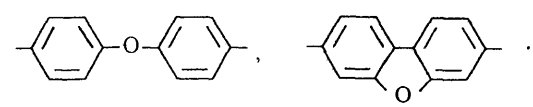
The low viscosity and corresponding molecular weight characteristics of the sulphide-containing polynaphthoylenebenzimidazoles may be due to the presence of the electron-donating sulphide groups in the initial bis(naphthalic anhydrides) which determines the reduced electrophilic reactivity of these monomers. With the aim of increasing the latter, attempts were undertaken to obtain polynaphthoylenebenzimidazoles using bis(naphthalic anhydrides) containing at least two sulphonyl groups in the molecule.[55,73–76]











These systems were synthesised by high temperature catalytic polycyclocondensation in *m*-cresol using benzoic acid as catalyst as in the preparation of the polynaphthoylenebenzimidazoles from sulphide-containing bis(naphthalic anhydrides).[55,73–76]

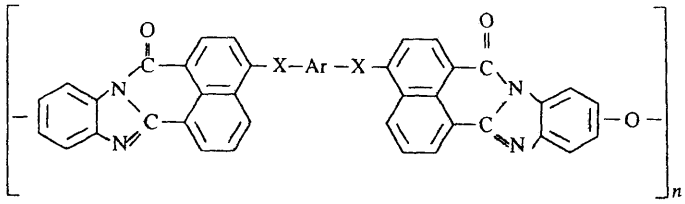
All the reactions for polyheteroarylene synthesis with the exception of processes using the dianhydride of 4,4′-bis(1,8-dicarboxynaphthalene-4-sulphonylphenyl) sulphone took place under homogeneous conditions and led to the preparation of the desired polyheteroarylenes in close to quantitative yield.

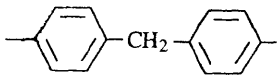
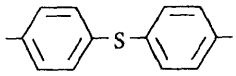
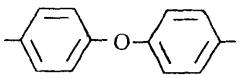
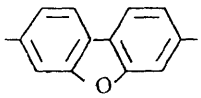
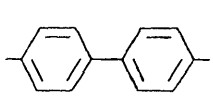
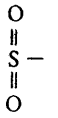
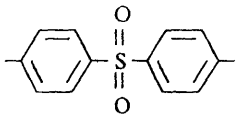
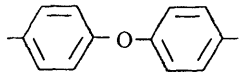
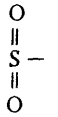
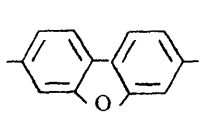
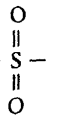
Some characteristics of the synthesised polynaphthoylenebenzimidazoles are given in Table 9.

The synthesised polynaphthoylenebenzimidazoles are more soluble than the polymers of this class obtained previously from 4,4′-sulphonylbis(naphthalic anhydride),[55] which indicates the positive effect of the introduction of a second sulphonyl group into the dianhydride and correspondingly into the main chain of the macromolecule. An exception is the polymer with three sulphonyl groups in the chain. The lack of solubility of this polynaphthoylenebenzimidazole in the solvents listed is explained by its crystallinity which was 20–30% according to X-ray data.

On the other hand the polynaphthoylenebenzimidazoles containing two or more sulphonyl groups were less soluble than the analogous systems containing sulphide groups.

Table 9. Some characteristics of polynaphthoylenebenzimidazoles of general formula[73–76]



Ar	X	η_{red}, dlitre g^{-1} (25 °C)		T_{soft}, °C	$T_{10\%}$, °C
		H_2SO_4	TCE, phenol		
	—S—	0.4	0.5	330	450
	—S—	0.5	0.5	310	470
	—S—	0.8	0.7	330	460
	—S—	-	0.4	380	460
		0.4	-	380	430
		0.4	-	-	400
		-	0.3	350	420
		0.4	-	370	410

The low viscosity characteristics of the polymers, which are somewhat unexpected for systems based on dianhydrides activated by sulphonyl groups, are probably explained by the occurrence of side reactions breaking the naphthoylenebenzimidazole rings by *o*-phenylenediamine fragments of the monomers or by the end groups of the growing chains of the macromolecule.

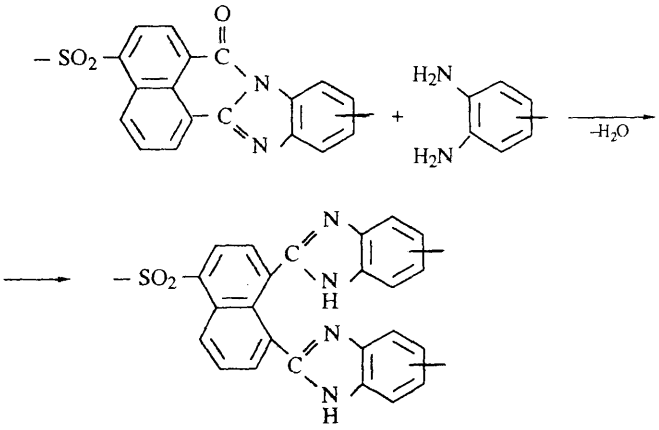
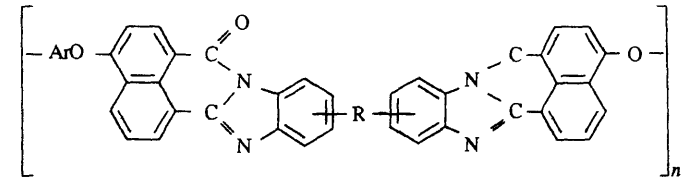


Table 10. Reduced viscosities of polynaphthoylenebenzimidazoles of formula



synthesised in mixtures of *m*-cresol with P_2O_5 (method *a*) and *m*-cresol with benzoic acid (method *b*), reaction time 30 h.[137]

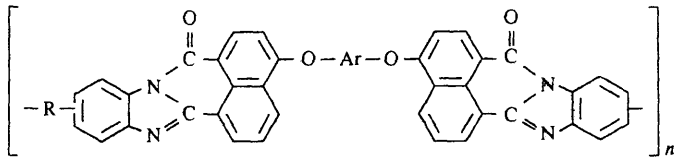
Ar	R	η^*_{red}, dlitre g^{-1}	
		method *a*	method *b*
p-C_6H_4–$C(CH_3)_2$–*p*-C_6H_4–	-	1.10	1.00
	-O-	0.94	0.75
m-C_6H_4–	-	3.95	1.10
	-O-	1.18	0.68
p-C_6H_4–SO_2–*p*-C_6H_4–	-	1.00	0.49
	-O-	0.97	0.30
p-C_6H_4–S–*p*-C_6H_4–	-	1.89	1.03
	-O-	1.03	0.62

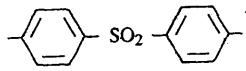
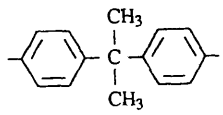
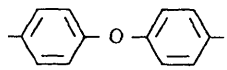
*η_{red} was measured in tetrachloroethane : phenol mixture at 25 °C.

This hypothesis is in complete agreement with the concept of a correlation between the electrophilic reactivity of the initial anhydrides and the sensitivity of the desired carbonyl-containing heterocycles towards hydrolysis and the action of nucleophilic reagents.[136] The same circumstance determines the low thermal stability of the synthesised polynaphthoylenebenzimidazoles during TGA in air. As is seen from Table 9 the 10% weight loss temperature was 400–430 °C under these conditions. The

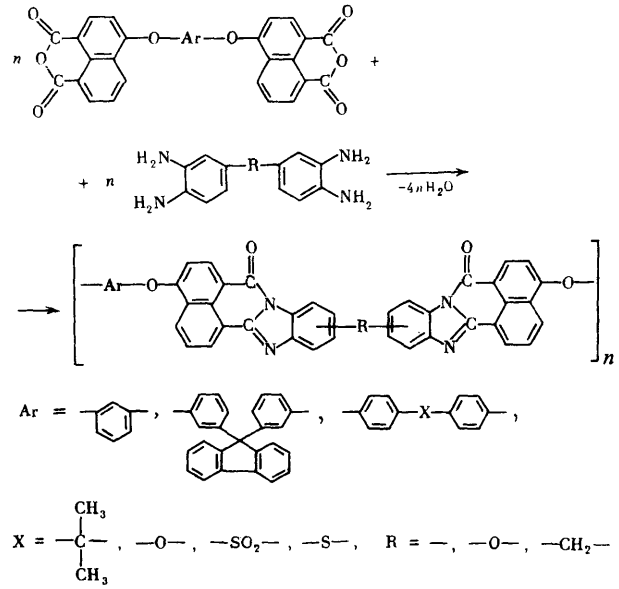
unsatisfactory properties of the synthesised polyheteroarylenes indicates the inexpediency of using bis(naphthalic anhydride) systems containing sulphonyl groupings bound directly to the anhydride rings.

Table 11. Some characteristics of polynaphthoylenebenzimidazoles of general formula



Ar	R	η_{red}, dlitre g^{-1}	T_g, °C	T_{dec}, °C		Solvent		
				argon	air	CF_3COOH	*m*-cresol	TCE: phenol (1 : 3)
	–	1.10	395	490	470	+	–	–
	-O-	0.68	368	490	490	+	+/–	+/–
	$-CH_2-$	0.29	–	460	440	+	+	+
	–	0.49	404	450	430	+	+	+
	-O-	0.30	360	460	430	+	+	+
	$-CH_2-$	0.20	380	450	340	+	+	+
	–	1.00	373	460	450	+	+	+
	-O-	0.75	312	460	450	+	+	+
	$-CH_2-$	0.37	355	460	440	+	+	+
	–	0.40	340	–	520	–	+	+
	-O-	0.50	320	–	500	–	+	+
	$-CH_2-$	0.70	320	–	380	–	+	+

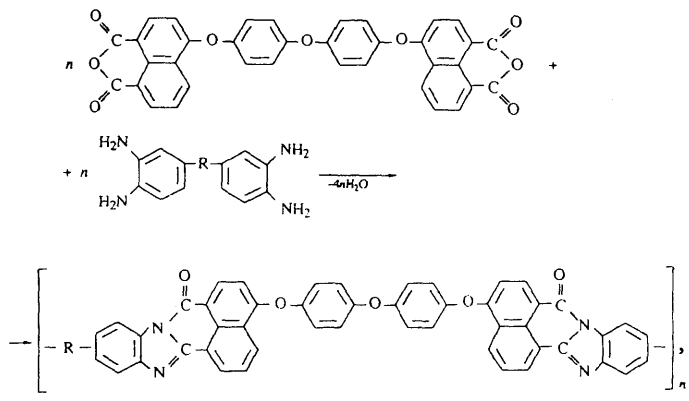
Significantly better results were obtained in the synthesis of polynaphthoylenebenzimidazoles from bis(naphthalic anhydrides) containing ether bonds.[65–68] These reactions were effected under conditions traditional for the synthesis of similar systems, viz. high temperature polycondensation in *m*-cresol using benzoic acid as catalyst,[65] and in other solvents[137] (mixtures of *m*-cresol with polyphosphoric acid, *m*-cresol with di-*m*-cresyl phosphate, *m*-cresol with P_2O_5, phenol with P_2O_5 and *p*-chlorophenol with P_2O_5).



The best of the systems studied proved to be *m*-cresol with P_2O_5 which is particularly obvious from the comparative data given in Table 10 on the viscosity characteristics of the polynaphthoylenebenzimidazoles obtained in mixtures of *m*-cresol with P_2O_5 and *m*-cresol with benzoic acid.[137] Nevertheless the polynaphthoylenebenzimidazoles synthesised in other solvents and particularly in a mixture of *m*-cresol and benzoic acid possessed viscosity characteristics (Table 11) and molecular weights which are sufficiently high for obtaining strong and elastic films (Table 12) possessing interesting electrical and physical properties.

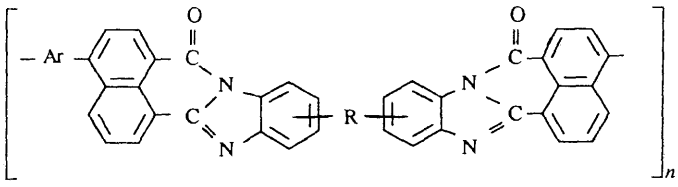
The thorough investigations on the thermal,[138] dynamic, mechanical[138] and relaxation[139,140] characteristics of the polynaphthoylenebenzimidazoles of this series showed that these systems are of significant practical interest.

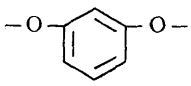
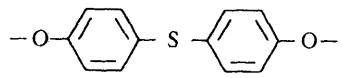
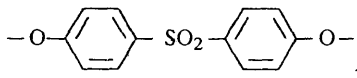
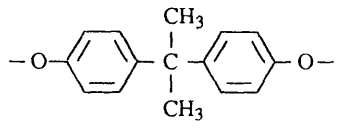
A logical evolution and continuation of the studies in this field is the development of polynaphthoylenebenzimidazoles from the dianhydride of 4,4′-epoxybis[(*p*-phenyloxy)dinaphthalene-1,1′,8,8′-tetracarboxylic acid].[71] Reaction of this with bis(*o*-phenylenediamine), 3,3′,4,4′-tetra-aminodiphenyl oxide, 3,3′,4,4′-tetra-aminodiphenylmethane and 3,3′-diaminobenzidine occurred according to the following scheme:



under conditions of high temperature catalytic polycyclisation in phenolic solvents. All the reactions in the synthesis of the polynaphthoylenebenzimidazoles proceeded from beginning to end under homogeneous conditions and led to the formation of polymers with moderate viscosity characteristics (Table 12).

Table 12. Properties of films based on polynaphthoylenebenzimidazoles of general formula



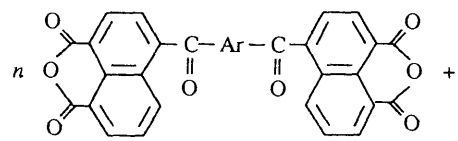
Ar	R	Mechanical properties, 25 °C		Electrical properties	
		σ, kg cm^{-2}	ε, %	$10^{-16}\rho^{*}$, Ω.cm	$10^{-3}\tan\delta^{**}$
	–	1120	85	2	1.7
	–O–	1080	85	7	1.4
	–	1350	70	3	1.2
	–O–	910	75	4	1.4
	–	920	60	1	1.5
	–O–	1110	80	3	1.4
	–	950	70	6	0.94
	–O–	980	113	1	1.6

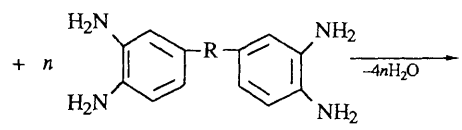
*ρ is the bulk resistance, **tan δ is the loss factor.

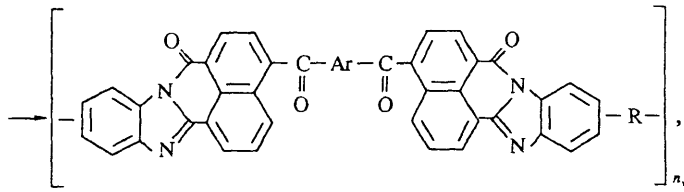
The introduction of an additional oxygen atom did not lead to an improvement in polymer solubility. The polymers were soluble in acidic and phenolic solvents but were insoluble in DMSO and N-MP.

Comparison of the softening temperatures and the region of marked thermal destruction indicated that these polymers may be successfully processed into objects by pressing.

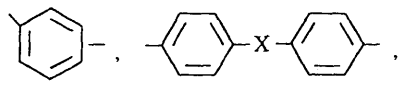
Polynaphthoylenebenzimidazoles based on aroylene-bis(naphthalic anhydrides) are of significant interest and are obtained according to the following scheme:[77,80,81]

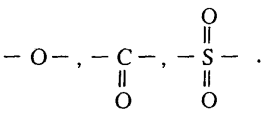






R = –, –O–, $-SO_2-$, $-C(CF_3)_2-$, $-CH_2-$;

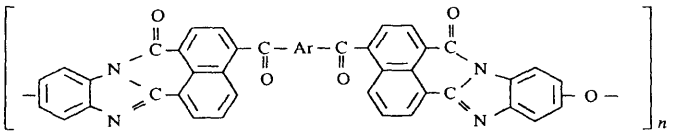
Ar = 

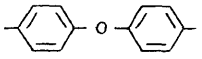
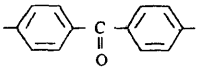
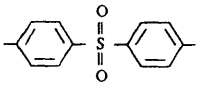
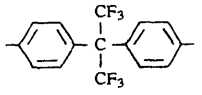
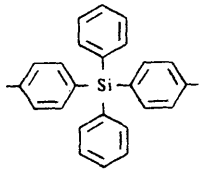
X = 

The synthesis of these polynaphthoylenebenzimidazoles was effected by high temperature polycondensation in *m*-cresol using benzoic acid as catalyst. All the reactions to synthesise polynaphthoylenebenzimidazoles occurred in a homogeneous manner and led to the preparation of fully cyclised high molecular polymers. Some characteristics of the polynaphthoylenebenzimidazoles based on aroylene-bis(naphthalic anhydrides) and 3,3',4,4'-tetra-aminodiphenyl oxide are given in Table 13.

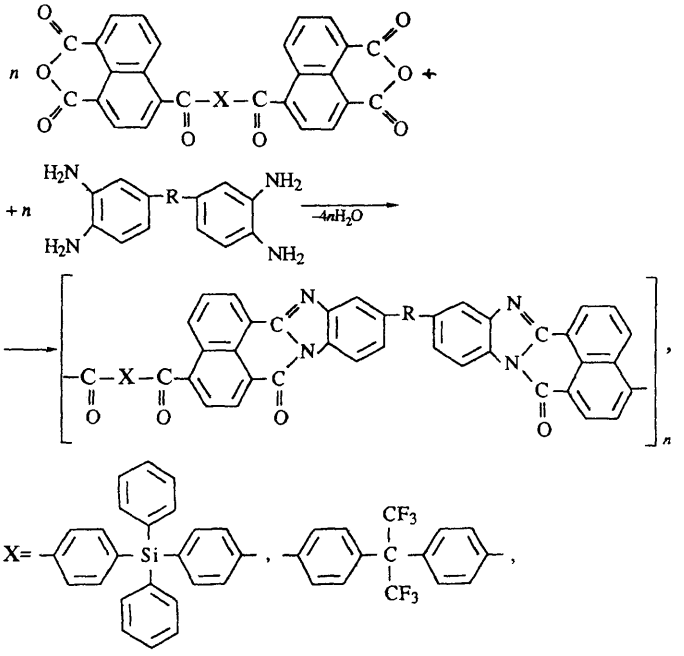
As is evident from the data of Table 13 the polynaphthoylenebenzimidazoles synthesised are soluble in H_2SO_4 and in phenolic solvents. The molecular weights of the polymers were sufficiently high to make stable films from them and the decomposition temperature (490–550 °C) was sufficiently large for these polymers to be processed into objects by pressing.

Table 13. Some characteristics of polynaphthoylenebenzimidazoles of general formula[77,80,82–84]



Ar	η_{red}, dl litre g^{-1} (H_2SO_4)	T_{soft}, °C	$T_{10\%}$, °C	Solvent				Film properties, 25 °C	
				m-cresol	TCE: phenol (3 : 1)	H_2SO_4	N-MP	σ, kg cm^{-2}	ε, %
	1.00	345	550	+	+	+	–	1260	15
	1.40	355	520	+	+	+	–	1100	13
	1.35	375	525	+	+	+	–	1000	11
	3.90	370	530	+	+	+	–	1040	11
	0.53	–	490	+/–	+	+	–	–	–
	1.80	360	545	+	+	+	–	1080	13
	1.57	375	550	+	+	+	–	920	10
$-CB_{10}H_{10}C-$	0.40	–	550	+	+	+	+	–	–

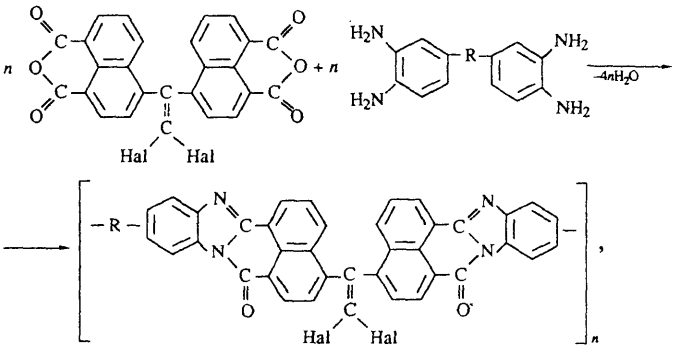
Even better solubility was a characteristic of the polynaphthoylenebenzimidazoles based on bis(naphthalic anhydrides) with a heteroorganic central group, such as hexafluoroisopropylidene,[82,84] diphenylsilyl[83,84] and *m*-carboranylene.[82,84] These polymers were synthesised by the following scheme:



$-CB_{10}H_{10}C-$, R = –, –O–.

The synthesis of these polymers was effected by high temperature catalytic polycyclocondensation in *m*-cresol using benzoic acid as catalyst. Some characteristics of the polynaphthoylenebenzimidazoles containing heteroorganic central groupings are given in Table 13. The introduction of diphenylsilyl and hexafluoroisopropylidene groups led only to a quantitative increase in the solubility of the polynaphthoylenebenzimidazoles in phenolic solvents[82–84] while the introduction of the *m*-carboranylene group into the macromolecule was accompanied by conferment of solubility in N-MP to the polymer.[83,84]

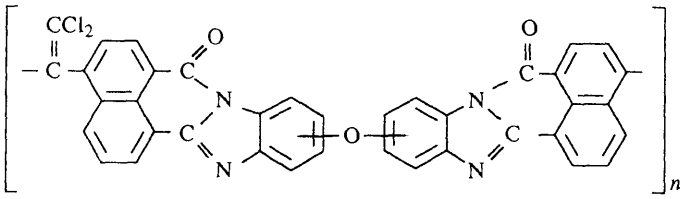
The introduction of the 1,1-dichloroethylene and 1,1-dibromoethylene groups into the macromolecule by the use of the appropriate bis(naphthalic anhydrides) has an extremely important effect on the properties of the polynaphthoylenebenzimidazoles.[111,112,141]



R = –, –O–, ; Hal = Cl, Br.

The synthesis of polynaphthoylenebenzimidazoles with 1,1-dichloroethylene and 1,1-dibromoethylene bridge groups[77,80,111,112,141] was effected in *m*-cresol with benzoic acid fulfilling the function of catalyst. In every case the synthesis of the polynaphthoylenebenzimidazoles took place homogeneously and led to the formation of fully cyclised and in some cases high molecular systems.

Table 14. Viscosity and molecular weight characteristics of polynaphthoylenebenzimidazoles of formula[141]

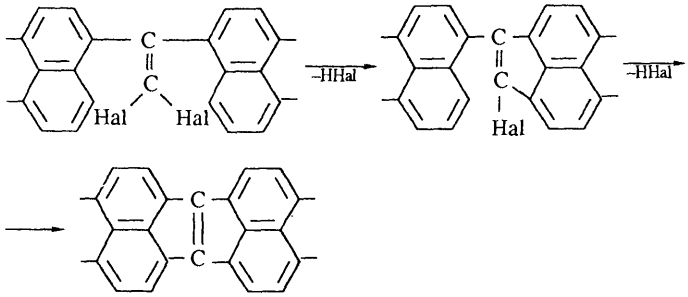


η_{sp}, H_2SO_4, 25 °C	10^{-3}M
0.39	33
0.73	80
0.98	108
1.14	117

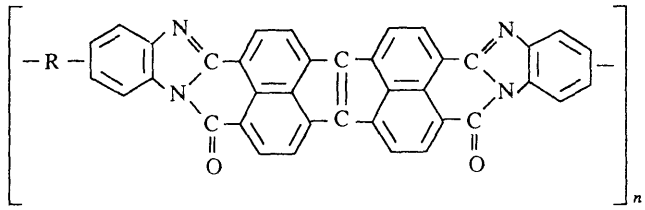
Comparison of the viscosity and molecular weight characteristics[142] of one of the similar polynaphthoylenebenzimidazoles is shown in Table 14.

Some characteristics of the synthesised polynaphthoylenebenzimidazoles containing 1,1-dihaloethylene groups are given in Table 15. It follows from an analysis of these data that all the polynaphthoylenebenzimidazoles synthesised are soluble in sulphuric acid and in phenolic solvents. High softening temperatures and high decomposition points under conditions of dynamic TGA are characteristic of the majority of these systems.

Under conditions of isothermal storage at temperatures exceeding 300 °C all the polymers considered underwent significant weight loss mainly with evolution of hydrogen halide. Among the alternative dehydrohalogenation reactions, monomolecular and intramolecular, the latter is more probable since in the heat treatment process the polymers do not lose their solubility in H_2SO_4. In view of the high lability of the peri protons[143] it might be suggested that the most probable course for the dehydrohalogenation is that expressed by the following scheme:

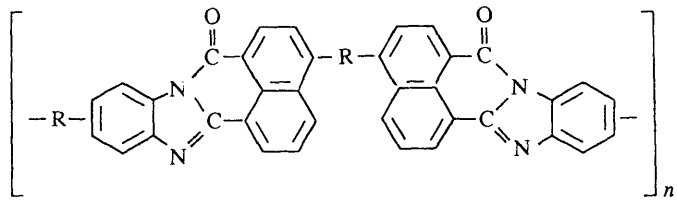


Similar 'naphtho-(9,10)-acenaphthyl' structures have been described in the literature.[144] When applied to the polymers their formation may lead to a new highly condensed system of general formula



which enables the results obtained to be considered as a new approach to the synthesis of ladder or double-chain polymers.[26,27]

Table 15. Some characteristics of polynaphthoylenebenzimidazoles of general formula

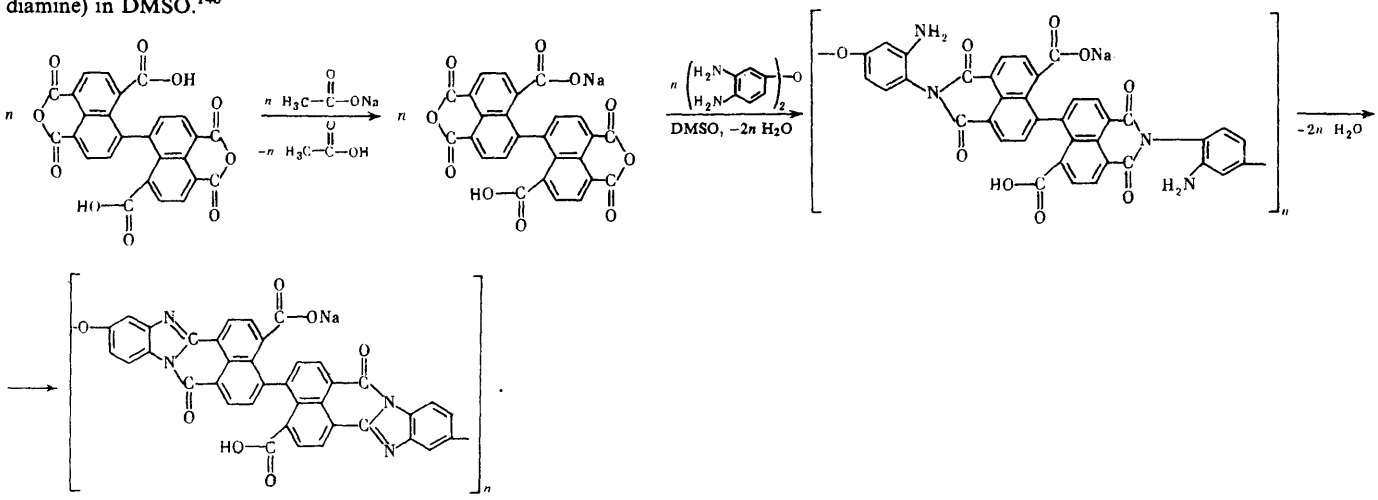


R	R'	η_{red}, dl/litre g^{-1}	T_{soft}, °C	$T_{10\%}$, °C	Solvent		
					m-cresol	TCE, phenol	H_2SO_4
–	$-C(=CCl_2)-$	0.80	450	500	+	+	+
-O-	$-C(=CCl_2)-$	2.00	380	500	+	+	+
$-SO_2-$	$-C(=CCl_2)-$	0.50	410	490	+	+	+
$-CH_2-$	$-C(=CCl_2)-$	0.70	370	490	+	+	+
$-C(CF_3)_2-$	$-C(=CCl_2)-$	0.80	380	500	+	+	+
-O-	$-C(=CBr_2)-$	0.30	380	490	+	+	+

In appearance the polymers based on 1,1'-bisnaphthyl-4,4',5,5',8,8'-hexacarboxylic acid[145–148] are systems extremely close to the polynaphthoylenebenzimidazoles containing 1,1-dihaloethylene groups.

The polynaphthoylenebenzimidazole based on 3,3',4,4'-tetraaminodiphenyl oxide and the dianhydride of 1,1'-binaphthyl-4,4',5,5',8,8'-hexacarboxylic acid has been studied in most detail. The optimum method of synthesising this polymer is the reaction of the

monosodium salt of the acid component with the bis(*o*-phenylenediamine) in DMSO.[146]



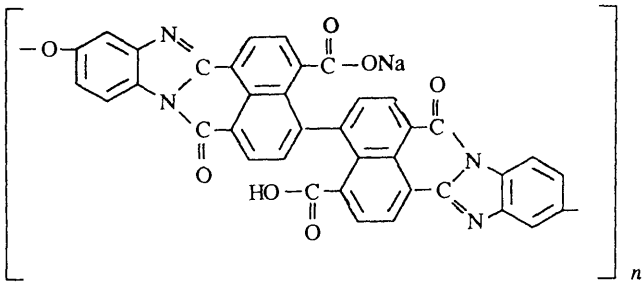
As a result of the increased basicity of the tetramine compared with the diamines[149] the reaction to prepare the polynaphthoylenebenzimidazole took 3–5 h at 115–120 °C, i.e. was more rapid than the synthesis of the polynaphthalimides, leading to the preparation of a polymer with $[\eta] \geqslant 1.3$ dlitre g^{-1}. Carrying out the synthesis of the polynaphthoylenebenzimidazole at higher temperatures led to gel formation and an increase in polymer viscosity.

This polynaphthoylenebenzimidazole dissolved in organic solvents only on addition of concentrated alkali solutions (10% KOH). After precipitation in an acid bath the polymer underwent 10–15% destruction.

Stable films were obtained by drying solutions of the monosodium salts of the polynaphthoylenebenzimidazole. The formation of fibres took place in a stable manner in baths of composition DMSO–water–conc. HCl.

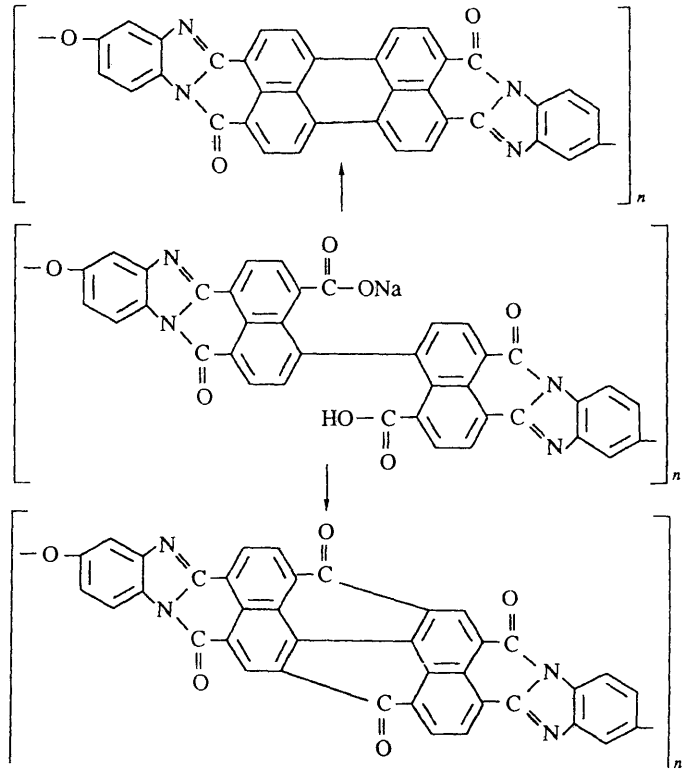
Significant attention has been paid to the product of converting polynaphthoylenebenzimidazole into perylene-[147] and anthanthrone-containing[148] systems.

Table 16. Characteristics of the threads and elementary fibres from the initial polynaphthoylenebenzimidazole



and of the products of its chemical and thermal cyclisation.

Characteristic	Initial polymer	Chemical cyclisation products		Thermal treatment product
		perylene-containing	anthanthrone-containing	
σ_{thr}, sR tex^{-1}	20–25	7	12	20–25
Elongation to break thread, %	20–25	13	15–27	15–30
Tensile strength *E*, GPa	5.7	–	–	6.9
T_{dec}, °C				
in air	530	540	550	550
in inert medium	600	610	620	610
Zero tensile strength temperature T_0, °C	580	–	–	630
OI, %	–	–	–	65



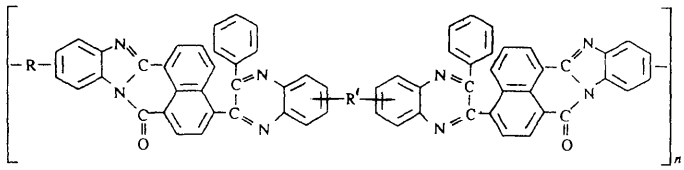
In order to convert the initial polynaphthoylenebenzimidazole into a perylene-containing structure it was decarboxylated in 10% KOH solution (attempts to prepare a 1% solution of the polymer in a less alkaline medium were unsuccessful). The conversion of the dicarboxydinaphthyl into perylene fragments produced 70% but [η] for the polymer solutions reached 0.8 dlitre g^{-1} which is significantly greater than the viscosity of the polynaphthoylenebenzimidazoles from the dianhydride of perylene-3,4,9,10-tetracarboxylic acid.[150,151]

A cyclisation reaction with H_2SO_4 was used to convert the initial polynaphthoylenebenzimidazole into an anthranthrone-containing structure. The process proceeded efficiently in 2% oleum at 40 °C giving 80% cyclisation after 2 h and the reduction of [η] of the polymer did not exceed 0.1 dlitre g^{-1}.

In addition to cyclisation by alkaline and acidic reagents the highly condensed systems may be obtained by thermal treatment of the initial polynaphthoylenebenzimidazoles in an inert medium. Not only was cyclodehydration observed but in addition cyclodecarboxylation processes occurred as a result of which the thermally treated systems contain both perylene and anthanthrone rings. Thermal treatment is the optimum method of cyclisation of polynaphthoylenebenzimidazole fibres which is confirmed by the data of Table 16.

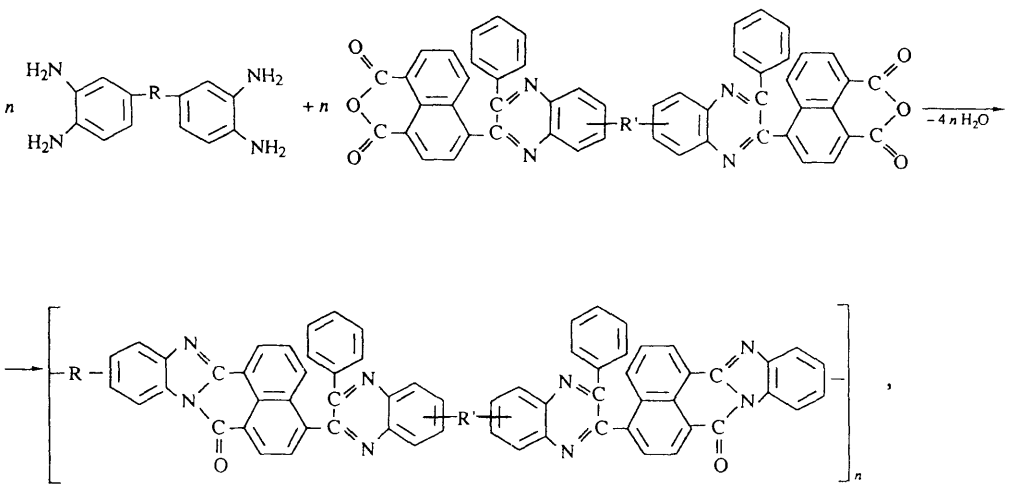
The products of thermal treatment of the initial polynaphthoylenebenzimidazole exceed the threads 'Arimid-PM' and 'LOLA' in the magnitude of the oxygen index (OI). In decomposition point they are superior to 'LOLA' however they are inferior to it in thermal stability assessed by heat treatment and are inferior to 'Arimid-PM' threads in strength. Polynaphthoylenebenzimidazoles soluble in organic solvents were obtained by the reaction of various bis(*o*-phenylenediamines) with bis(naphthalic anhydrides) containing phenylquinoxaline rings[88,90] according to the following scheme:

Table 17. Some characteristics of polynaphthoylenebenzimidazoles of general formula



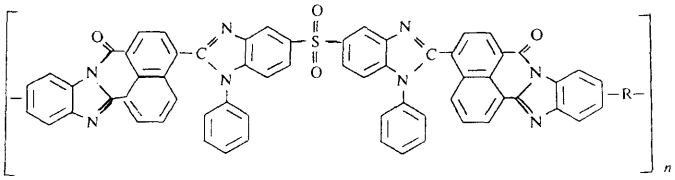
R	R'	η_{red}, dlitre g^{-1} (H_2SO_4, 25 °C)	T_{soft}, °C	$T_{10\%}$, °C	Solvent			Film properties, 25 °C	
					m-cresol	TCE: phenol	phenol	σ, kg cm^{-2}	ε, %
–	–O–	1.4	340	455	+	+	+/–	1020	18
–O–	–O–	2.1	320	470	+	+/–	+/–	950	24
$–CH_2–$	–O–	1.0	320	455	+	+	+/–	1080	20
$–SO_2–$	–O–	0.8	340	460	+	+	+/–	990	20
–	$–SO_2–$	1.6	360	480	+	+	+/–	1100	20
–O–	$–SO_2–$	2.3	340	470	+	+	+	1300	25
$–CH_2–$	$–SO_2–$	1.8	340	460	+	+	+/–	1050	23
$–SO_2–$	$–SO_2–$	0.4	350	490	+	+	+/–	980	23

The synthesis of these polynaphthoylenebenzimidazoles was effected in *m*-cresol using benzoic acid as catalyst. The polycondensation reaction occurred in a homogeneous manner and led to the formation of high molecular (Table 17) polymers with a high degree of cyclisation.



R = –, –O–, $–CH_2–$, $–SO_2–$; R' = –, –O–, $–CH_2–$, $–SO_2–$

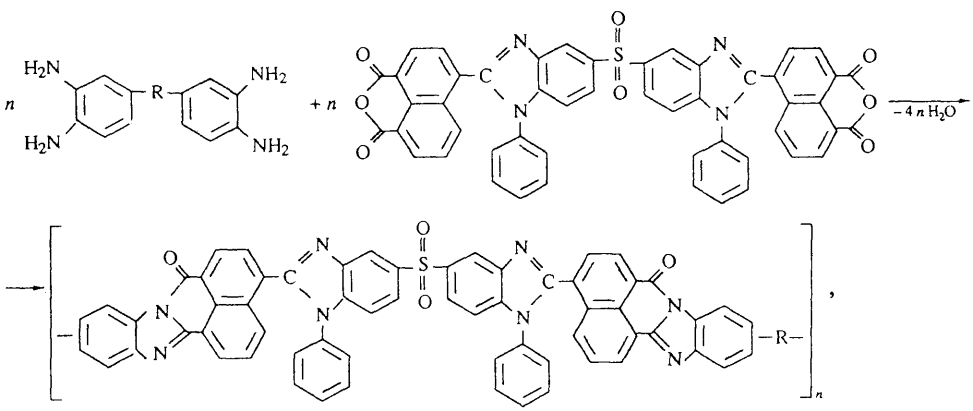
Table 18. Some characteristics of polynaphthoylenebenzimidazoles of general formula[152]



R'	η_{red}, dl litre g^{-1} (H_2SO_4, 25°C)	T_{soft}, °C	$T_{10\%}$, °C	Solvent				Film properties, 25 °C	
				m-cresol	TCE: phenol	N-MP	TCE	σ, kg cm^{-2}	ε, %
–	2.50	460	550	+	+	+/–	–	1000	7
–O–	1.20	420	500	+	+	+/–	–	1020	7
$-CH_2-$	0.90	430	500	+	+	+/–	–	1080	6.5
$-C(=O)-$	–	430	500	+	+	+/–	–	1000	7
$-C(CF_3)_2-$	0.60	420	520	+	+	+	+	–	–

Polynaphthoylenebenzimidazoles based on other bis(naphthalic anhydrides) containing phenylquinoxaline rings also possess characteristics closely similar to those given in Table 17.

These systems combine high (350 ± 20 °C) softening temperatures with high viscosity characteristics (sufficient for reliable film formation) and solubility in organic solvents. It must however be noted that these polymers are only soluble in phenolic solvents or mixtures of the latter with halogenated hydrocarbons. From this point of view there is considerable interest in polynaphthoylenebenzimidazoles obtained from bis(*o*-phenylenediamines) and bis[1-phenyl-2-(1,8-dicarboxynaphth-4-yl)benzimidazol-5-yl] sulphone[152] by the following scheme:



R = R = –, –O–, $-CH_2-$, –CO–, $-C(CF_3)_2-$.

The polynaphthoylenebenzimidazoles were synthesised in *m*-cresol using benzoic acid as catalyst at 160–190 °C. The polycondensation reactions were carried out under homogeneous conditions and led to the formation of the desired polymers possessing high viscosity characteristics (Table 18) and a high degree of cyclisation.

A distinctive feature of the polynaphthoylenebenzimidazoles considered is their solubility in N-MP which is a most acceptable solvent.

It is interesting to note that the polynaphthoylenebenzimidazoles are more soluble than the corresponding polynaphthalimides which is explained by the presence in their molecules of a 'pyridine' nitrogen atom[153,154] which is readily protonated (being the first stage of the solution of these polymers in protogenic solvents) and also by the amorphous nature of these systems caused by the presence in them of a broad set of isomeric structures.[153,154]

- - - o0o - - -

Analysis of the data given in this review indicates the emergence during the last two decades of many new accessible bis(naphthalic anhydrides) characterised by the presence in their structures of elements determining improved solubility (and general processability) of the polyheteroarylenes based on them. The bis(naphthalic anhydrides) containing ether groups may be used for preparing systems related to the polyesterimides but differing from them in a higher glass point. At the same time the majority of the new bis(naphthalic anhydrides) may be used for preparing new polynaphthoylenebenzimidazoles combining satisfactory processability with very high thermal, fire and chemical resistance.

References

1. C L Segal (Editor) *High Temperature Polymers*, Dekker, New York, 1967, p. 197
2. V V Korshak *Termostoikie Polymery* (Thermostable Polymers), Nauka, Moscow, 1969, 411 pp
3. V V Korshak *Khimicheskoe Stroenie i Temperaturnye Kharakteristiki Polimerov* (Chemical Structure and Temperature Characteristics of Polymers), Nauka, Moscow, 1970, 419 pp

4. A H Frazer *High Temperature Resistant Polymers (Polymer Reviews, Vol. 17)* (Translated into Russian), Khimiya, Moscow, 1971, 294 pp
5. H L Lee, D G Stoffey, K Neville *New Linear Polymers* (Translated into Russian), Khimiya, Moscow, 1972, 280 pp
6. R J Cotter, M Matzner *Ring-Forming Polymerisation, Pt. B-1*, Academic Press, New York, 1972, p. 568
7. R J Cotter, M Matzner *Ring-Forming Polymerisation, Pt. B-2*, Academic Press, New York, 1972, p. 395
8. K Buehler *Teplo- i Termostoikie Polimery* (Thermostable Polymers), Khimiya, Moscow, 1984, 1055 pp
9. A L Rusanov, D S Tugushi, V V Korshak *Uspekhi Khimii Poligeteroarilenov* (Progress in the Chemistry of Polyheteroarylenes), TGU Izd., Tbilisi, 1988, 180 pp
10. I E Kerdash, E N Teleshov *Itogi Nauki. Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii* (Progress in Science. Chemistry and Technology of High Molecular Compounds), VINITI Izd., 1971, Vol. 6, 168 pp
11. I I Jones *Macromol. Sci. Rev.*, 1968, **C2** 303
12. C S Marvel *Pure Appl. Chem.*, 1968, **16** 351
13. C S Marvel *Appl. Polymer Symp.*, 1973, (22) 47
14. C S Marvel *J. Macromol. Sci., Rev. Macromol. Chem.*, 1975, **13** 219
15. E S Krongauz *Usp. Khim.*, 1973, **42**(10) 1854 [English translation in *Russ. Chem. Rev.*, 1973(10)]
16. A A Izyneev, M M Teplyakov, V G Samsonova, A D Maksimov *Usp. Khim.*, 1967, **36**(12) 2090 [English translation in *Russ. Chem. Rev.*, 1967(12)]
17. V V Korshak, M M Teplyakov *Progress Polimernoi Khimii* (Progress in Polymer Chemistry), Nauka, Moscow, 1968, p. 198
18. V V Korshak, M M Tepliakov *J. Macromol. Sci., Rev. Macromol. Chem.*, 1971, **C5** 409
19. G Mandric *St. Cerc. Chim.*, 1972, **20** 1001
20. V V Korsak, A L Rusanov, L K Plieva *Faserforsch. und Textiltechn.*, 1977, **28** 371
21. E W Neuse *Advances in Polymer Science*, Springer Verlag, Berlin–Heidelberg–New York, 1982, Vol. 47, p. 1
22. N A Adrova, M I Bessonov, L A Laius, A P Rudakov *Poliimidy–Novyi Klass Termostoikikh Polimerov* (Polyimides, a New Class of Thermostable Polymers), Nauka, Leningrad, 1968, 211 pp
23. M M Bessanov, M M Koton, V V Kudryavtsev, L A Laius *Poliimidy–Klass Termostoikikh Polimerov* (Polyimides, a Class of Thermostable Polymers), Nauka, Leningrad, 1983, 328 pp
24. V V Korshak, A L Rusanov, I Batirov *Novoe v Oblasti Termostoikikh Poliimidov* (Progress in the Area of Thermostable Polyimides), DONISh, Dushanbe, 1986, 102 pp
25. C E Sroog *J. Polym. Sci., Macromol. Rev.*, 1976, **11** 161
26. M M Tessler *J. Polym. Sci., A1*, 1966, **4** 2521
27. A L Rusanov, S N Leont'eva, Ts G Iremashvili *Usp. Khim.*, 1975, **44**(1) 151 [English translation in *Russ. Chem. Rev.*, 1975(1)]
28. Z Yu Plonka, V M Al'brekht *Vysokomol. Soedin., Ser. A*, 1965, **7** 2117
29. R L Van Deusen, O K Goins, A J Sicree *ACS Polymer Preprint*, 1966, **7** 528
30. R L Van Deusen *J. Polym. Sci., B*, 1966, **4** 211
31. R L Van Deusen, O K Goins, A J Sicree *J. Polym. Sci., A*, 1968, **6** 1777
32. F E Arnold, R L Van Deusen *Macromolecules*, 1969, **2** 497
33. F E Arnold, R L Van Deusen *J. Appl. Polym. Sci.*, 1971, **15** 2035
34. A H Gerber *J. Polym. Sci., Polym. Chem. Ed., A*, 1973, **11** 1703
35. A A Berlin, B I Liogon'kii, V M Shamraev, G V Belova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, (5) 945
36. G M Shamraev, A A Dulov, B I Liogon'kii, A A Berlin *Vysokomol. Soedin., Ser. A*, 1970, **12** 401
37. V V Korshak, A L Rusanov, S A Pavlova, et al. *Dokl. Akad. Nauk SSSR*, 1975, **221** 1334
38. V K Belyakov, I V Belyakova, S S Medved', et al. *Vysokomol. Soedin., Ser. A*, 1971, **13** 1739
39. E P Krasnov, V A Aksenova, A A Belyaev, et al. *Vysokomol. Soedin., Ser. A*, 1973, **15** 1606
40. E P Krasnov, V A Aksenova, S N Khar'kov *Vysokomol. Soedin., Ser. A*, 1973, **15** 2093
41. S V Vinogradova, Ya S Vygodsky, V V Korsak, T N Spirina *Acta Polymerica*, 1979, **30** 3
42. V I Zapadinskii, B I Liogon'kii, A A Berlin *Usp. Khim.*, 1973, **42**(11) 2037 [English translation in *Russ. Chem. Rev.*, 1973(11)]
43. F W Harris, W A Feld, L N Lanier *ACS Polymer Preprint*, 1976, **17**(2) 353
44. F W Harris, L N Lanier *Structure-Solubility Relationships in Polymers*, Academic Press, New York–San Francisco–London, 1977, p. 183
45. M M Dashevskii *Atsenaften* (Acenaphthene), Khimiya, Moscow, 1966, 460 pp
46. B V Suvorov, D Kh Sembaev, G D Tkacheva, et al. *Khimiya i Fizika Vysokomolekulyarnykh Soedinenii* (Chemistry and Physics of High Molecular Compounds), Nauka, Alma-Ata, 1981, Pt. 14, Vol. 55, p. 3
47. L A Jones, R Watson *Can. J. Chem.*, 1972, **51** 1833
48. K Gurdeska, G Kabas, A Pugin, et al., US P. 3 898 234, 1975
49. K Dziewonski, W Kahl, W Koczorowska, A Wulfson *Roczn. Chem.*, 1933, (13) 154
50. J G Robinson, S A Brain, US P. 4 334 055, 1982
51. Z Jedlinski, U Gaik, Z Mzyk, et al. *ACS Polymer Preprint*, 1979, **20**(2) 559
52. Z Jedlinski, B Kowalski, G Fabjanska-Sweca, U Gaik *Chem, Stosow.*, 1985, **29** 73
53. German P. 545 212; Published in *Frdl.*, 1933, (18), 1510
54. G T Morgan, H A Harrison *J. Indian Chem. Soc.*, 1930, **49** 413
55. T V Kravchenko, T I Dvalishvili, T A Romanova, G D Tkacheva *Vysokomol. Soedin., Ser. B*, 1982, **24** 852
56. L I Rudaya, L A Smolenkova, I Ya Kvitko, et al., Author's Certificate No. 977 457, USSR; *Byull. Izobret.*, 1982, (44)
57. A L Rusanov, A M Berlin, S Kh Fidler, et al. *Vysokomol. Soedin., Ser. A*, 1981, **23** 1586
58. U Gaik, B Koval'ski, Z Edlinski, et al. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, 1981, (5) 19
59. Z Jedlinski, U Gaik, B Kowalski, et al. *Macromol. Chem.*, 1982, **183** 1615
60. U Gaik, B Koval'ski, A L Rusanov, et al. *Tez. Dokl. Mezhdunarodnogo Mikrosimpoziuma po Polikondensatsii* (Abstracts of Reports of the International Microsymposium on Polycondensation), Alma-Ata, 1981, p. 19
61. A L Rusanov, A M Berlin, S Kh Fidler, et al. *Vysokomol. Soedin., Ser. A*, 1981, **23** 1586
62. G A Loughran, F E Arnold, US P. 3 987 003, 1980
63. G A Loughran, F E Arnold *ACS Polymer Preprints*, 1977, **18**(1) 831

64. G A Loughran, F E Arnold *Org. Prep. Proced. Int.*, 1976, **8** 98
65. Z J Jedlinski, B Kowalski, U Gaik *Macromolecules*, 1983, **16** 522
66. Z J Jedlinski *Macromol. Chem. Suppl.*, 1984, **7** 17
67. Z J Jedlinski, U Gaik, B Kowalski, Polish P. 131 685, 1986; *Ref. Zh. Khim.*, 1987, 18S554P
68. Z J Jedlinski, B Kowalski, Polish P. 133 225, 1986; *Ref. Zh. Khim.*, 1987, 8S588P
69. F J Williams, US P. 3 850 964, 1974
70. Z J Jedlinski, Polish P. 234 517, 1981
71. V V Korshak, A L Rusanov, A M Berlin, et al. *Vysokomol. Soedin., Ser. A*, 1989, **31** 51
72. V A Ustinov, E P Perepechkina, V V Plakhtinskii, et al., Author's Certificate No. 653 249, USSR; *Byull. Izobret.*, 1979, (11)
73. V V Korshak, A L Rusanov, A M Berlin, et al. *Vysokomol. Soedin., Ser. B*, 1984, **26** 713
74. V V Korshak, A L Rusanov, A M Berlin, et al. *Chem. Stosow.*, 1986, **30** 171
75. V V Korshak, E G Bulycheva, A M Berlin, et al. *Tez. Dokl. XI Mezhdunarodnogo Mikrosimpoziuma po Polikondensatsii* (Abstracts of Reports of the XIth International Microsymposium on Polycondensation), Prague, 1987, p. A7
76. A L Rusanov, V V Korshak, M O Shalikiani, et al. *XXXI IUPAC Macromolecules Symposium. Merseburg*, 1987, p. 187
77. V V Korshak, A L Rusanov, A M Berlin, et al., USSR P. 784 258, 1980; Swiss P. 666 032, 1988; French P. 2 584 407, 1988; British P. 2 176 778, 1989; Indian P. 164 541, 1989; German P. 3 526 155, 1987
78. British P. 1 069 337, 1965
79. V V Korshak, A L Rusanov, A M Berlin, et al. *Dokl. Akad. Nauk Tadzh. SSR*, 1988, **3** 311
80. V V Korshak, E G Bulycheva, Z B Shifrina, et al. *Acta Polymerica*, 1988, **39** 460
81. V V Korshak, A L Rusanov, Z Jedlinski, et al. *Acta Polymerica*, 1991, **42**(2/3) 53
82. V V Korshak, A L Rusanov, A M Berlin, et al. *Dokl. Akad. Nauk SSSR*, 1988, **301** 115
83. V V Korshak, A L Rusanov, M P Prigozhina, et al. *Plastmassy*, 1990, (3) 5
84. E G Bulycheva, M P Prigozhina, I I Ponomarev, et al. *Acta Polymerica*, 1991, **42**(2/3) 63
85. J Sonnenberg, US P. 4 002 645, 1977; *Chem. Abs.*, 1977, **86** 140666x
86. V V Korshak, A L Rusanov, A M Berlin, et al. *Vysokomol. Soedin., Ser. A*, 1992, **34**
87. A L Rusanov, V V Korshak, I Batirov, et al. *Tez. Dokl. I Regional'no Soveshchaniya po Khimicheskim Reaktivam Respublik Srednei Azii i Kazakhstana* (Abstracts of Reports of the Ist Regional Conference on Chemical Reactions of the Republics of Central Asia and Kazakhstan), Dushanbe, 1986, p. 77
88. V V Korshak, A L Rusanov, T V Lekae, Author's Certificate No. 1 037 646, USSR, 1983; *Byull. Izobret.*†
89. V V Korshak, A L Rusanov, T V Lekae, Author's Certificate No. 1 100 871, USSR, 1984; *Byull. Izobret.*
90. V V Korshak, A L Rusanov, T V Lekae *Vysokomol. Soedin., Ser. B*, 1988, **30** 439
91. A L Rusanov, S S Bocharov, T V Lekae, et al. *Dokl. Akad. Nauk Tadzh. SSR*, 1989, **32** 463
92. P M Hergenrother *J. Macromol. Sci., Rev., C*, 1971, **6** 1
93. P M Hergenrother *Polym. Eng. Sci.*, 1976, **16** 303
94. E S Krongauz *Usp. Khim.*, 1977, **46**(1) 112 [English translation in *Russ. Chem. Rev.*, 1977(1)]
95. V V Korshak, A L Rusanov *Usp. Khim.*, 1983, **52**(5) 812 [English translation in *Russ. Chem. Rev.*, 1983(5)]
96. W Eskert, German P. 535 069, 1931
97. N S Dokunikhin, G N Vorozhtsov *Zh. Org. Khim.*, 1966, **2** 148
98. N S Dokunikhin, G N Vorozhtsov, F I Kichina *Zh. Org. Khim.*, 1968, **4** 2000
99. G N Vorozhtsov, N S Dokunikhin, N B Fel'dblyum *Zh. Org. Khim.*, 1975, **11** 1517
100. G N Vorozhtsov, N S Dokunikhin, N I Vorozhtsov *Zh. Org. Khim.*, 1976, **11** 1499
101. B I Stepanov *Vvedenie v Khimiyu i Tekhnologiyu Organicheskikh Krasitelei* (Introduction to the Chemistry and Technology of Organic Dyestuffs), Khimiya, Moscow, 1977, p. 432
102. N S Dokunikhin, G N Vorozhtsov, V I Alekseev *Khim. Promst. (Moscow)*, 1981, (10), 592
103. V V Korshak, A L Rusanov *Usp. Khim.*, 1989, **58**(6) 1006 [English translation in *Russ. Chem. Rev.*, 1989(6)]
104. A L Rusanov *Itogi Nauki i Tekhniki. Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii* (Progress in Science and Technology. Chemistry and Technology of High Molecular Compounds), Izd. VINITI, Moscow, 1990, Vol. 26, p. 3
105. V V Korshak, A L Rusanov, S Kh Fidler, et al. *Plastmassy*, 1984, (10), 28
106. E R Kekharsaeva, E B Shustov, A K Mikitaev, V T Dorofeev *Plastmassy*, 1985, (2) 9
107. T Lesiak, J Nowakowski *Polimery*, 1980, **25** 81
108. T Lesiak, J Nowakowski *Polimery*, 1981, **26** Q
109. F I Luknitskii *Chem. Rev.*, 1975, **75** 259
110. V V Korshak, A L Rusanov, A M Berlin, et al., Author's Certificate No. 866 999, USSR; *Byull. Izobret.*
111. V V Korshak, A L Rusanov, A M Berlin, et al. *Dokl. Akad. Nauk SSSR*, 1988, **299** 131
112. V V Korshak, A L Rusanov, A M Berlin, et al. *Soobshch, Akad. Nauk GSSR*, 1986, **121** 537
113. V V Korshak, V A Kosobutskii, A I Bolduzev, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1553
114. D V Pebalk, B V Kotov, O Ya Neiland, et al. *Dokl. Akad. Nauk SSSR*, 1974, **236** 1379
115. V V Korshak *Usp. Khim.*, 1982, **51**(12) 2096 [English translation in *Russ. Chem. Rev.*, 1982(12)]
116. V V Korshak, A L Rusanov, I Batirov *Plastmassy*, 1982, (8) 14
117. A L Rusanov, E G Bulycheva *Abstracts of Posters, STEPI, Montpellier, France, June 4–7*, 1991, pp. 1–12
118. D Sek, P Pijet, A Wanic *Abstracts of Posters, STEPI, Montpellier, France, June 4–7*, 1991, pp. 1–9
119. B O Kalashnikov, L S Efros, G N Vorozhtsov, et al. *Vysokomol. Soedin., Ser. B*, 1986, **28** 232
120. G B Kyznetsova, I G Silinskaya, O V Kallistov, et al. *Vysokomol. Soedin., Ser. A*, 1988, **30** 586
121. G B Kuznetsova, B O Kalashnikov, M A Lazareva, et al. *Vysokomol. Soedin., Ser. B*, 1989, **31** 763
122. G N Vorozhtsov, N S Dokunikhin, N I Vorozhtsova *Zh. Org. Khim.*, 1975, **11** 1499

† The year and page number in *Byull. Izobret.* are not given in the Russian original for references 88, 89, 110, 141 and 152 (Ed. of Translation).

123. V V Korshak, A L Rusanov, Z B Shifrina, et al. *Dokl. Akad. Nauk SSSR*, 1986, **289** 367
124. V V Korshak, S A Pavlova, P N Gribkova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, (6) 1381
125. US P. 3 539 677, 1970
126. US P. 3 562 380, 1971
127. *Chem. Eng. News*, Sept. 23, 1968, p. 40
128. W H Gloor *Fiber Spinning and Rawing* (Edited by E Coplan), Interscience Publications, New York, 1967, p. 151
129. *Chem. Week*, Sept. 19, 1966, p. 121
130. W H Gloor *ACS Polymer Preprint*, 1966, 7(2) 819
131. W H Gloor *ACS Polymer Preprint*, 1967, **6** 151
132. W H Gloor *ACS Polymer Preprint*, 1969, **9** 159
133. G I Kudryavtsev, A M Shchetinin *Khim. Volokna*, 1968, (6) 2
134. *Khim. Volokna*, 1975, (3) 68
135. G I Kudryavtsev, A A Askadskii, I F Zhudoshchev *Vysokomol. Soedin., Ser. A*, 1978, **20** 1879
136. V V Korshak, A L Rusanov *J. Macromol. Sci., Rev. Macromol. Chem., C*, 1982, **21** 275
137. Z Jedlinski, B Kowalski, U Gaik *Macromol. Chem.*, 1985, **186** 457
138. U Gaik, B Kowalski, Z Jedlinski, et al. *Thermochim. Acta*, 1985, **83** 309
139. S Smigasiewicz, B Kowalski *Mater. Sci. (PRL)*, 1984, **10** 491
140. S Smigasiewicz, B Kowalski *J. Polym. Sci., Polym. Phys. Ed.*, 1986, **24** 1961
141. V V Korshak, A L Rusanov, A M Berlin, et al., Author's Certificate No. 866 999, USSR, 1981; *Byull. Izobret.*
142. V N Tsvetkov, V B Novakovskii, I A Strelina, et al. *Vysokomol. Soedin., Ser. A*, 1989, **31** 40
143. B A Reinbardt, T T Tsai, F E Arnold *New Monomers and Polymers*, Plenum Press, New York–London, 1984, p. 41
144. R L Letsinger, G A Gilpin, W J Vulvo *J. Org. Chem.*, 1962, **27** 672
145. V V Korshak, A L Rusanov, A M Berlin, et al. *Vysokomol. Soedin., Ser. B*, 1981, **23** 42
146. B O Kalashnikov, L S Efros, B Kh Strelets, et al. *Vysokomol. Soedin., Ser. B*, 1986, **28** 671
147. B O Kalashnikov, L S Efros, B Kh Strelets, et al. *Vysokomol. Soedin., Ser. A*, 1987, **29** 2415
148. R A Sadekova, I K Pronichkina, E P Perepechkina, et al. *Khim. Volokna*, 1987, (1) 29
149. L N Balyatinskaya, Yu F Milyaev, V V Korshak, et al. *Dokl. Akad. Nauk SSSR*, 1978, **238** 862
150. A A Berlin, B I Liogon'kii, B I Zapadinskii, G M Shamraev *Tez. Dokl. Mezhdunarodnogo Simpoziuma po Makromolekulyarnoi Khimii* (Abstracts of Reports of the International Symposium on Macromolecular Chemistry), Budapest, 1969, p. 18
151. A A Berlin, B I Liogon'kii, G M Shamraev *Usp. Khim.*, 1971, **40**(3) 513 [English translation in *Russ. Chem. Rev.*, 1971(3)]
152. V V Korshak, A L Rusanov, A M Berlin, T V Polina, Author's Certificate No. 788 689, USSR, 1980; *Byull. Izobret.*
153. G C Berry, T G Fox *Polymers in Space Research* (Edited by L Segal, M Shen, E N Kelley), Marcel Dekker, New York, 1970, p. 91
154. G C Berry, T G Fox *J. Macromol. Sci., A*, 1969, **3** 1125

Translated from *Uspekhi Khimii* **61** 865–882 (1992) U.D.C. 541.5

Stereoelectronic effects in silicon, phosphorus, and sulphur molecules. Quantum-chemical calculations and qualitative orbital models

A A Korkin
Institute of Physiologically Active Substances, Russian Academy of Sciences, Chernogolovka

ABSTRACT. The results of non-empirical quantum-chemical calculations for silicon, phosphorus, and sulphur compounds of different structure are discussed. Qualitative orbital models, which establish a relation between the distribution of electrons and molecular structure and properties, are analysed. A general definition of stereoelectronic effects is presented.

The bibliography includes 176 references.

Contents

I. Introduction 473
II. *d* Orbitals in the chemistry of silicon, phosphorus, and sulphur 474
III. Structural and energetic manifestations of hyperconjugation 475
IV. Multiple bonds and conjugation 477
V. Hypervalent molecules and radicals 479

I. Introduction

The comparative study of the structure and the electronic and energetic characteristics of silicon, phosphorus, and sulphur molecules has been traditional in quantum chemistry in view of the existence of many similar relations, problems, and trends in the chemistry of these elements.[1–23]

The concept of the "stereoelectronic effect" is widely used in both experimental and theoretical studies in organic and organoelement chemistry.[24–31] Until recently, stereoelectronic effects were indissolubly linked to ideas concerning hyperconjugation in its broad interpretation, involving the interaction of lone pairs (LP) with unoccupied σ^* and π^* orbitals. The need to introduce a general concept is associated with the fact that it has been quite firmly established that conformational effects are common to different classes of compounds.[24,32–34] The stability of certain conformations, the changes in the structural parameters and relative reactivities in a series of related compounds, as well as other characteristics can be explained in many instances and treated systematically on the basis of models which include as the initial postulates the "classical" ideas concerning localised electron pairs with allowance for the interaction between these pairs and the antibonding orbitals of neighbouring, mainly vicinal bonds. Deslongchamps[24] defined stereoelectronic effects as "the stereochemistry of particular electron pairs—bonding and anti-bonding".

It is quite evident, however, that, if one considers particular electron pairs as localised pairs, then, within the framework of the above definition, one can discuss only the molecular characteristics which have come to be referred to as cooperative: energies, dipole moments, polarisabilities, vibration frequencies in spectra, structural parameters, etc. We emphasise the term "have come to be referred to as cooperative" because one-electron characteristics such as ionisation potentials, electron affinities, and electronic transition energies are also in essence functions of the entire multielectron system of the molecule. However, the one-electron characteristics and different "effects" coupled with them are not embraced by the definition of "stereoelectronic effects" if the latter are considered within the framework of the model of localised electron pairs, because one-electron characteristics are determined by the properties of delocalised molecular orbitals or, more rigorously, by the behaviour of an individual electron in the field of other electrons and nuclei of the molecule (see also Dewar[35]).

If one abandons the idea that the isolated electron pairs should be regarded from the start as localised, then the definition of stereoelectronic effects includes also the energetic and spatial changes in the frontier molecular orbitals, which occur when the molecular conformations change, this being manifested in the electronic,[36] photoelectron,[37] and X-ray electronic[38] spectra.

In the present review, we shall discuss the literature data in the context of a broader definition (compared with that given by Deslongchamps[24]), in which the stereoelectronic effect is understood as the "deviations of the characteristics of molecules from the values predicted by the base model which can be explained as a result of disregarded interactions and represented in the form of fine details of the spatial distribution of electrons".[39] This definition includes explicitly the concept of the "base model", whose equivalent in the Deslongchamps definition is "isolated electron pairs". Base models can be different in the work of different workers depending on the selected method of study and the ideas concerning the structure and properties of molecules, so that in certain cases it is important to consider beforehand the initial postulates (null approximation) on the basis of which the orbital models of stereoelectronic effects are constructed.

Orbital models of molecules with participation of Third Period atoms are constructed as a rule on the basis of analogous models of the structural analogues, including atoms of the Second Period referring to the same Group in the Periodic Table. Here account is taken of the difference between the electronegativities, the sizes of the valence orbitals, and the presence of the *d* shell in the Third Period atoms.

On passing from the Second to the Third Period, the difference between the energies of the valence *s* and *p* orbitals diminishes, which should promote the hybridisation of the atomic orbitals. However, the opposite trend, caused by the increase in the size of the atoms and in the difference between the radii of the 3*s* and 3*p* orbitals, exerts a greater influence.[17] The presence of 2*p* electrons in

the inner layer results in a greater size of the valence 3*p* orbitals than that of the 3*s* orbitals, which lowers in its turn the effectiveness of hybridisation.[40] The relative increase in the size of the 3*p* orbitals makes the 3*s* orbital "quasi-inner" and, in the presence of non-bonding electron pairs in the atom, the latter are predominantly of the *s* type (see, for example, Magnusson[41] and Korkin[42,43]). Accordingly, the contribution of *p* electrons predominates in the bonding electron pairs. The stabilisation of the "non-hybridised" state of the Third Period atoms is associated also with increase in the size of the atom and decrease of the repulsion of the ligand and the geminal electron pairs, which leads to a smaller steric strain of the bond angles formed by the "pure" *p* orbitals (~90°).

The above differences in the nature of the orbitals of the Second and Third Period atoms make it possible to explain the characteristic features of the structure and chemical properties of silicon, phosphorus, and sulphur compounds. The aim of the present review is to discuss the general trends and the comparative aspects in the development and use of orbital ideas in the chemistry of these elements. We did not attempt to embrace all the available publications on calculations for the silicon, phosphorus, and sulphur molecules. Their number is very great, which undoubtedly reflects the interest of theoreticians in this field. The review deals to a greater extent with studies in which comparative calculations are presented for silicon, phosphorus, and sulphur molecules in relation to one another and in relation to their structural analogues (carbon, nitrogen, and oxygen) and the results obtained are discussed in the language of qualitative orbital models.

II. *d* Orbitals in the chemistry of silicon, phosphorus, and sulphur

The question of the role of *d* orbitals occupies a special place in the theoretical chemistry of non-transition elements. In order to account for the structure and stability of highly coordinated molecules, Pauling[12,44] put forward the hypothesis of the involvement of *d* orbitals in the formation of hybrid atomic orbitals (sp^3d, sp^3d^2). However, whereas in the case of transition metal atoms one is concerned with the hybridisation of *ns*, *np*, and $(n-1)d$ orbitals which have similar energies, the excitation of an electron to the 3*d* shell in the silicon, phosphorus, and sulphur atoms requires an energy of the order of 10 eV, which is close to the ionisation potential of 3*p* electrons.[17,45] In neutral atoms the 4*s* orbitals have lower energies under these conditions than the 3*d* orbitals by an amount of the order of 2eV.[46] When electrons are abstracted, the energy of the 3*d* orbitals decreases to a greater extent than that of the 4*s* orbitals and in the dication M^{2+} the positions of the 4*s* and 3*d* orbitals are reversed.[46] The abstraction of electrons is accompanied by a decrease in the diffuseness of the 3*d* orbitals and their sizes approach those of the valence 3*s* and 3*p* orbitals.

The increase in the coordination number and the increase in the electronegativity of the substitutuent entail an increase in the effectiveness of the charge on the central atom. In this case, as in ionisation, the effective charge of the 3*d* orbitals diminishes and their population increases.[1,17,47]

The fraction of electrons occupying *d* orbitals depends not only on the molecular structure but also on the initial basis set and the exponents of the Gaussian or Slater functions. Since the *d* orbitals of silicon, phosphorus, and sulphur atoms in the ground state are unoccupied, the choice of the exponents of the *d* functions is usually made by optimising the energies of a series of molecules.[47,48] Depending on the nature of the problem and the computational facilities available to the investigator, the *d* orbitals are added to all the atoms of the Second and Third Period or only to those of the Third Period (for further details, see Clark[49]).

The question arises whether one should consider the *d* orbitals of silicon, phosphorus, and sulphur atoms as "normal" valence orbitals, as in the case of transition elements, or as polarisation functions. This problem has been discussed to some extent in numerous publications devoted to non-empirical calculations for silicon, phosphorus, and sulphur molecules. In the general case, an unambiguous answer is apparently not available to this question, because, firstly, the role of the *d* orbitals depends significantly on the molecular structure and the nature of the characteristic investigated and, secondly, the very concept of "valence orbital" permits different interpretations.

Comparative non-empirical calculations in terms of *sp* and *spd* basis sets have shown (see, for example, Refs. 1, 2, 6, and 48–50) that the influence of the *d* orbitals on different molecular characteristics increases with increase in the coordination number of the atom, but the populations of the *d* orbitals are then much smaller than the values which are attributed to the sp^3d^n hybridisation and do not exceed 0.3 of an electron even for SF_6.[51]

The influence of *d* orbitals on molecular geometry has been studied most thoroughly. Calculations using the 3-21G* and 6-31G* basis sets make it possible to determine the bond lengths and bond angles, on average, to within 0.01 Å and 1° respectively,[48] while the 3-21G and 6-31G basis sets lead to much too high bond lengths. This applies to both single bonds in molecules of the type PF_5 or SF_6 and to semipolar or multiple bonds of the type of the phosphoryl or sulphoxide bonds, for example, in the F_3PO and F_2SO_2 molecules. The multiplicity of the P=O abnd S=O bonds in these molecules is due to the reverse transfer of electron density from the O atom to the P or S atom, the contribution of *d* orbitals in this bond not exceeding 25%.[1,52]

The majority of conformational effects in silicon, phosphorus, and sulphur molecules can be described satisfactorily at a qualitative level also without taking into account *d* orbitals, within the framework of hyperconjugation ideas (see the next Section), but the quantitative results as a rule agree best with experimental data when account is taken of *d* orbitals.[48] Exceptions may arise as a consequence of the cancelling of errors due to the incompleteness of the basis set and failure to take into account correlation effects. The presence or absence of *d* orbitals in the basis set can alter the relative stabilities of conformations, but their role is then related to non-specific electrostatic and van der Waals interactions, which depend on bond lengths, bond angles, and electron populations of the atoms.[53–62] For example, allowance for 3*d* orbitals lead indirectly to an increase in the relative stability of the *cis*-conformation of the H_2NSH molecule, because the nitrogen atom becomes less pyramidal,[59] and to a decrease of the relative stabilities of the eclipsed conformation of methyl alcohol and of its S, Se, and Te analogues as a result of the increase in the steric repulsion caused by the decrease in the C–X bond length.[61] The overall populations of *d* orbitals depend only slightly on the molecular conformations.[62]

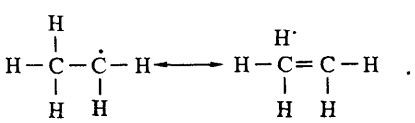
The inclusion of *d* orbitals in the basis set improves the quantitative description of electronic characteristics such as the dipole moments and ionisation potentials. Since, as already mentioned, the bond lengths calculated in terms of *sp* basis sets exceed the experimental values, dipole moments are also found to be too high.[48,62] The electronic characteristics associated with direct electron transfer to unoccupied orbitals, such as UV spectra[63,64] and

electron affinity,[65,66] are more sensitive to the quality of the basis sets and a satisfactory quantitative description of these characteristics requires the inclusion of diffuse functions and functions with a high multiplicity in the basis set. The requirements imposed on the basis set in such cases are also due to the fact that quantitative calculation of the energies of excited states and anions requires allowance for electron correlation effects whose calculation using small basis sets does not lead in many instances to an increase in the accuracy of the results.[48,49] However, it is of interest to note that, as shown by the results of calculations by the X_α method, the lowest-energy states of the SiH_4^-, PH_3^-, HCl^-,[67] R_3SiPh^-,[68] and $RSPh^-$ [69] anions correspond to the presence of an additional electron in the σ^* orbital in the initial molecules, while the σ^* orbitals of the structural analogues of these anions, containing the atoms of Third Period elements, have higher energies than the Rydberg orbitals and do not correspond to stationary states of the anions.

The idea that *d* orbitals are involved in chemical bonding has undergone a significant evolution as computational quantum-chemical methods developed. At the present time, it is possible to test directly many postulates and corollaries of qualitative orbital theories, including also "*d*-orbital effects", by calculating molecular characteristics in terms of *sp* and *spd* basis sets. At the same time, the usual practice in the organic chemistry of silicon, phosphorus, and sulphur is to formulate orbital ideas on the basis of the analysis of molecular characteristics (obtained from experimental studies) using correlation analysis. If any molecular characteristics do not vary in conformity with linear relations of the Hammett–Taft type under these conditions, then this is explained by the effects of $p_\pi-d_\pi$ conjugation, a decrease in the diffuseness of the *d* orbitals under the influence of electronegative substituents, the involvement of *d* orbitals in chemical bonding on the grounds of symmetry considerations, etc. (see, for example, Refs. 23 and 70–75 and the literature quoted therein). Attempts are then made at a quantitative determination of the contribution of *d* orbitals to the measured characteristics and at a comparative estimation of the reliability of alternative orbital models (for example $d_\pi-p_\pi$ or n,σ^* conjugation) from the results of experimental studies.[76–79] Such empirical models can undoubtedly be useful for the classification of particular sets of experimental data, but their importance for the theoretical justification of ideas concerning the nature of chemical bonding should not be overestimated. The majority of "*d*-orbital effects" can be explained in a different way within the framework of models taking into account only valence *s* and *p* orbitals.[27,45]

III. Structural and energetic manifestations of hyperconjugation

The idea of the involvement of C–H σ-bonds in resonance interactions was put forward in the middle of the 1930s[80–82] to explain the structural features and reactivity of hydrocarbons. Wheland[80] attributed the increased stability of the ethyl radical relative to the methyl radical to the resonance stabilisation of the $CH_3CH_2^\cdot$ radical with participation of the so called "non-bonded structures":



Similar structures but with resonance of the ionic type were put forward by Baker and Nathan[81] to explain the reactivity in the series of *p*-alkyl-substituted bromotoluenes. The orbital model for the description of the resonance interaction of this type was developed by Mulliken,[83] who suggested that the term hyperconjugation be used for the description of the resonance interaction of C–H σ-bonds with unsaturated fragments. From the standpoint of the molecular orbital method, hyperconjugation arises as a consequence of the non-orthogonality of the σ and π orbitals, which leads to their mutual delocalisations. For the coplanar disposition of the sp^3 and p_π orbitals of two carbon atoms forming a chemical bond, their overlap amounts to 80% of the $p_\pi-p_\pi$ overlap.[84] However, the energetic and structural manifestations of hyperconjugation in the molecules of unsaturated hydrocarbons are not quite so pronounced as those of the formation of π-bonds in the ethylene molecule or of the conjugation in the benzene or even butadiene molecule, which is associated with the large energy gap between the occupied (σ) and unoccupied (π^*) orbitals.

Immediately after its appearance, the idea of hyperconjugation gained wide currency for the interpretation of various features observed experimentally, which, as shown in Dewar's critical review,[84] were either incorrectly interpreted or were susceptible to an equally acceptable qualitive description within the framework of other models. Dewar's review[84] resulted in appreciable cooling of the chemists' enthusiasm as regards hyperconjugation ideas, the development of which underwent a fresh start only after the appearance of modern computer programmes for non-empirical LCAO-MO calculations with automatic optimisation of the geometry. In particular, many structural features and spectroscopic and chemical properties of silicon, phosphorus, and sulphur compounds, which had been previously explained within the framework of the *d*-orbital model, could be interpreted as hyperconjugation effects.[1,18,85–90]

Three types of resonance stabilisation are considered within the framework of the hyperconjugation ideas: radical (I), cationic (II), and anionic (III):

$$\underset{\text{(I)}}{Y-E-\dot{X}\longleftrightarrow\dot{Y}\ E=X}\ , \qquad \underset{\text{(II)}}{Y-E-\overset{+}{X}\longleftrightarrow Y\ E=X}\ ,$$

$$\underset{\text{(III)}}{Y-E-\bar{X}\longleftrightarrow Y\ E=\bar{X}}\ .$$

For molecules with a closed shell, the direction of the shift of electron density [resonance of type (II) or (III)] is determined to a first approximation by the deficiency or excess of electron density on the group X and the polarised bond E–Y.

The general structural and chemical consequences of hyperconjugation have not been discussed in detail in the studies quoted above and we shall consider here the characteristic features of its manifestation in non-empirical calculations for silicon, phosphorus, and sulphur molecules and their structural analogues containing Second Period atoms.

One of the ways of investigating hyperconjugation effects involves the calculation of the energies of isodesmic reactions. This method was used by Schleyer, et al.[91] to calculate the energies of isodesmic reactions involving disubstituted methanes CH_2XY (X, Y = NH_2, OH, F, PH_2, SH, Cl):

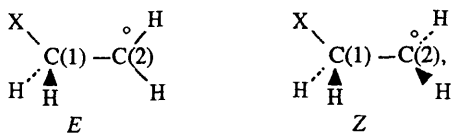
$$CH_4 + XCH_2Y = CH_3X + CH_3Y + \Delta E.$$

According to their data,[91] the stabilisation energy diminishes following the replacement of the group X and/or Y containing Second Period atoms by its structural analogue containing Third Period atoms. When X, Y = PH_2 or SH, the stabilisation energy is small ($0 < \Delta E < 0.5$ kcal mol^{-1}), whereas in the case where X = Cl and Y = PH_2, SH, or Cl, ΔE assumes negative values. A more detailed analysis shows that hyperconjugation involving the lone pairs of the Second Period atoms X predominates (NH_2 > OH > F), decreasing with decrease in the electronegativity of Y (F > OH > NH_2 > Cl > SH > PH_2).

Another way of estimating the effectiveness of hyperconjugation involves the study of the behaviour of structural parameters and molecular energies in the study of conformations. Such study has been described by Magnusson[92] for the series of molecules $X-CF_3$ (X = SiH_3, SiH_2^-, PH_3^+, PH_2, PH^-, SH_2^+, SH) and their structural analogues (X = CH_3, CH_2^-, NH_3^+, NH_2, NH^-, OH_2^+, OH). As in the study of Schleyer, et al. mentioned above, it was concluded here that hyperconjugation weakens on passing from Second Period atoms to Third Period atoms.

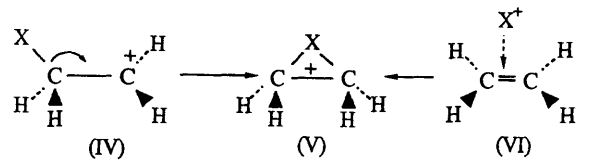
This conclusion is not, however, universal. For example, in the cations $X-CH_2^+$ the π-donor capacity of X = SH and Cl is higher than that of X = F and OH, whereas in the neutral molecules Ph−X, HC≡C−X, and $H_2C=CH-X$ the opposite picture is observed.[93] The authors[93] explained this by the fact that in neutral molecules the resonance integral of the interaction of the lone pair of X and the *p* orbital of the carbon atom of the unsaturated fragment is decisive, its values being higher for Second Period atoms, whereas in the cations the energy gap between the occupied orbital (*n* orbital of X) and the unoccupied orbital (*p* orbital of the carbon atom) is decisive, diminishing on passing from Second Period atoms to Third Period atoms.

The structural and energetic manifestations of hyperconjugation are well illustrated by the relative stabilities of (*E*)- and (*Z*)-conformations of β-substituted ethyl cations, radicals, and anions:[60,93,94]



where the circle denotes "plus" and "minus" signs or the "radical". The cation is stabilised as a result of the interaction of the σ_{CH} and σ_{CX} orbitals with the unoccupied *p* orbital of the C(2) atom. An increase in the electronegativity of the substituent *X* diminishes the contribution of the atomic orbital of the C(1) atom to the σ_{CX} orbital and hence weakens the conjugation with participation of the C−X bond. As a result, the (*E*)-conformation, where σ_{CH} orbitals are involved in conjugation, is more stable for electronegative substituents.[94] The opposite picture is observed in the anions, because in this case stabilisation is achieved as a result of $n-\sigma^*$ interaction. An increase in the electronegativity of the substituent X increases the contribution of the atomic orbital of the C(1) atom to the σ_{CX} orbital and increases the effectiveness of its interaction with the occupied *n* orbital of the C(2) atom.[94,95] In radicals, the interaction of the singly occupied *p* orbital of the C(1) atom with both σ and σ* orbitals is stabilising.[32,96] As a result of this, the electronegativity of X has only a weak influence on the relative stabilities of the (*E*) and (*Z*)-conformations. If X includes Second period atoms, then virtually free rotation about the C(1)−C(2) bond is observed in radicals,[60,97–99] but if X contains Third Period atoms[60] the (*Z*)-conformation is more stable owing to the greater polarisability of the C−X bonds. Analysis showed that under these conditions an increase in the electronegativity of the group X entails a decrease in the contribution of the $\sigma_{CX}-p_C^*$ interaction to the stabilisation of the (*Z*)-conformation, while the contribution of the $\sigma_{CX}^*-p_C^*$ interaction increases.[60]

However, in reality, the situation is more complex. For example, high level *ab initio* calculations with complete optimisation of the geometry (see, for example, Ford and Raghuver[100] and the references therein) have shown that in cations a competition is observed between the "classical" structure (IV) and the "non-classical" structure (V):



Structure (V) can apparently be regarded as a result of very effective $\sigma_{CX}-p_C$ interaction, although at a qualitative level the model of the complex of X^+ with the molecule of ethylene (VI) is no less justified. In β-substituted ethyl anions with electropositive substituents X, the (*Z*) conformation is additionally stabilised as a result of the overlap of the unoccupied atomic orbitals of the atom X (Li, Be, Na, Mg) and the doubly occupied orbital of the carbon atom.[95]

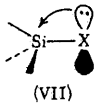
In the Introduction, we already noted that one of the important elements of the construction of orbital models of the structure of molecules containing atoms of non-transition elements of the Third and subsequent Periods is the idea of the decrease of the effectiveness of hybridisation for heavy atoms.[17] This is perhaps most clearly manifested when the structures of molecules comprising tricoordinate nitrogen and phosphorus atoms are compared. In the molecules of tetracoordinate silicon, the "enforced" sp^3-hybridisation of the atomic orbitals is observed by virtue of symmetry, which brings it closer to carbon. In the molecules of dicoordinate sulphur, as in those of oxygen, there is, apart from the predominantly *s*-type hybridised lone pair, a second lone pair formed by the pure *p* orbital capable of participating effectively in conjugation.[56,89,101–103]

The lone pairs of the nitrogen and phosphorus atoms differ significantly in their capacities for $n-\sigma^*$ and $n-\pi^*$ interactions.[41–43,103–107] In the ammonia molecule, the lone pair of the nitrogen atom is localised predominantly in the *p* orbital of the nitrogen atom, whereas in the phosphine molecule the lone pair is localised mainly in the *s* orbital of the phosphorus atom.[43] The energy expenditure on the transition from the pyramidal tricoordinate nitrogen atom to the planar atom, in which the hybrid orbital of the lone pair becomes a pure *p* orbital, is readily "made good" by the energy gain as a result of conjugation with the low-lying unoccupied σ* or π* orbitals of the substituents at the nitrogen atom. On the other hand, the phosphorus atom in the structurally analogous molecules always retains a pyramidal structure. In terms of localised orbitals and hybridisation, this can be explained at a qualitative level by the fact that energy factors are unfavourable for the planar structure involving tricoordinate phosphorus in which the lone pair occupies a *p* orbital. Within the framework of the qualitative molecular orbital theory, the same result is attributed to the smaller (compared with nitrogen) energy gap between the HOMO and the LUMO in the planar PH_3 molecule

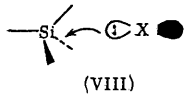
and to its instability as regards pyramidal distortion.[108] The stability of the pyramidal structure of phosphorus-containing molecules is associated, in addition, with the decrease in the steric repulsion of the ligands on passing from Second Period atoms to Third Period atoms due to the increase in size of the central atom.

The difference in the nature of the hybrid orbitals of the lone pairs of the nitrogen and phosphorus atoms is manifested in the protonation of the aminophosphine (H_2NPH_2) molecule.[42,109] The addition of H^+ to the nitrogen atom lengthens the P–N bond, whilst its addition to the phosphorus atom shortens it. This result can be explained by the different capacities of the lone pairs of the nitrogen and phosphorus atoms for $n-\sigma^*$ interaction and is used in the consideration of the mechanism of the acid catalysis of the dissociation of the P–N bond in aminophosphines.[110] The lengthening of the P–N bond on protonation of the nitrogen atom is caused by the inhibition of the $n_N-\sigma^*_{PH}$ interaction and by the increase in the steric repulsion in the coordination sphere of the nitrogen atom. When the phosphorus atom is protonated, the shortening of the P–N bond is explained by the rehybridisation of the valence atomic orbitals of phosphorus (by the increase in the contribution of the *s* orbital to the hybrid atomic orbitals participating in the formation of bonds) and by the strengthening of the $n_N-\sigma^*_{PH}$ interaction in the cation $H_2NP^+H_3$. Such qualitative analysis makes it possible to explain the influence of various substituents on the basicity of amines and phosphines.[43,105,111,112]

The π-acceptor effect of the silyl group is well known (see, for example, Egorochkin[86] and Pitt [87] and the references therein). Previously, this effect was explained by the $p_\pi-d_\pi$ conjugation, but this interpretation was not confirmed by modern non-empirical calculations, which indicate the decisive role of the σ^*_{SiX} orbitals in the π-acceptor capacity of SiX_3 groups[55,56] [$n-\sigma^*$ interaction, structure (VII)]. Another form of the manifestation of the increased acceptor capacity of the SiX_3 groups is $n_\sigma-\sigma^*$ interaction [structure (VIII)], which leads to the formation of *trans*-annular bonds in linear, cylic, and bicyclic silicon-containing molecules.[113–116]



(VII)

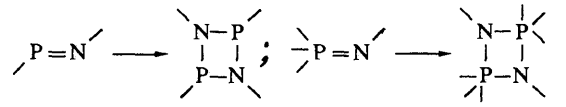


(VIII)

The influence of substituents on the length and strength of the *trans*-annular bond has been studied thoroughly in relation to silatranes.[117,118] A model calculation by the MNDO method[119] showed that the main factor determining the strength of this bond is the energy gap between the n_N and σ^*_{SiX} orbitals. Steric interactions, determining the energy of the transition from the tetrahedral structure of the silicon atom to the bipyramidal structure, also play an important role. The formation of dative bonds as a result of the $n_\sigma-\sigma^*$ interaction has been observed also in molecules of tricoordinate phosphine[120,121] and dicoordinate sulphur,[90,122,123] although not on such a broad scale as for silicon.

IV. Multiple bonds and conjugation

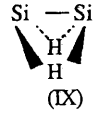
Multiple bonds can be divided into two types depending on whether the octet rule is fulfilled or infringed in the structural formula of the molecule. The first type of multiple bonds are observed in compounds of "normal" valence, in the structural formula of which the octet rule is fulfilled for each atom. For example, the P=N double bond in the iminophosphine (HP=NH) molecule is consistent with this definition, whereas the P=N bond in the iminophosphorane ($H_3P=NH$) molecule, which is usually represented as a double bond, has a different nature.[124] The difference in the nature of the P–N bonds in HP=NH and $H_3P=NH$ is manifested in the analysis of localised molecular orbitals calculated by the Boys method.[125] In the former case, the calculation leads to two equivalent localised "banana" molecular orbitals in the region of the P=N bond, whereas in the second, the presence of two lone pairs at the nitrogen atom, somewhat displaced in the direction of the phosphorus atom, is demonstrated.[124] At the same time, it is essential to note that, despite the difference in the nature of the electron distribution in the region of the PN bonds in iminophosphines and iminophosphoranes, there are also considerable structural (similarity of bond lengths) and chemical similarities between these compounds.[126,127] In particular, the dimerisation reaction



is characteristic of both.

In fact the boundary between the double bonds in "normal" and hypervalent molecules is to some extent arbitrary. For example, the SiO bond in the H_2SiO molecule is so polar that it corresponds to a large extent to the formula $H_2Si^+-O^-$; this brings it close to the PO bond in the H_3PO molecule.[52] On the other hand, hypervalent molecules of the type HPX_2 (X = CH_2, NH, O)[128–131] have a planar structure in which the double bonds are formed as a result of the overlap of the coplanar p_π orbitals, as in the ethylene molecule. At the same time, the polarity of the bonds in the HPX_2 molecules is high, so that their electron distribution is to a large extent consistent with ionic structures.

Compounds containing double bonds involving silicon and trivalent phosphorus remained for a long time chemically "exotic" in view of their instability, which was in its turn determined by the instability of the $p_\pi-p_\pi$ bonds in these compounds. The weakening of the π-bonds in the molecules involving Third Period atoms is caused by the appearance of inner *p* shells in the electronic structure of these atoms.[17,132] The instability of the π-bonds involving Third Period elements has a multiplicity of structural manifestations. For silicon-containing molecules, a series of interesting examples have been quoted in the review of Gordon and co-workers.[133] The replacement of a C atom by a Si atom increases the relative stability of the isomers containing a smaller number of multiple bonds involving silicon. For example, the main isomer of disilaacetylene has the bridged structure (IX) and disilaethylene (X) is more stable than silylsilylene (XI) only to the extent of 3.5 kcal mol^{-1}, while the structural analogue of silapropene has no minimum on the potential energy surface corresponding to the structural formula (XII).



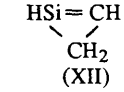
(IX)

$H_2Si=SiH_2$

(X)

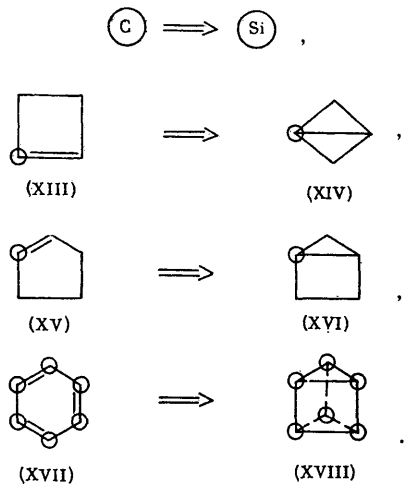
$H_3Si-\dot{S}iH$

(XI)



(XII)

In cyclic molecules the replacement of a C atom by a Si atom diminishes the stability of the unsaturated cyclic compounds (XIII), (XV) and (XVII) compared with the condensed compounds (XIV), (XVI), and (XVIII).

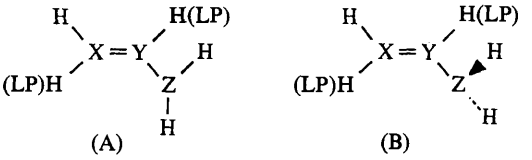


As already mentioned, on passing from Second Period to Third Period atoms, the relative contribution of *p* electrons to the hybrid atomic orbitals participating in the formation of bonds increases and there is a corresponding increase in the *s* electron fraction in the non-bonding orbitals. This factor makes the sp^2-hybridised state of the silicon atom, in which the contribution of *s* orbitals to bonding is large, unfavourable on energy grounds.[134]

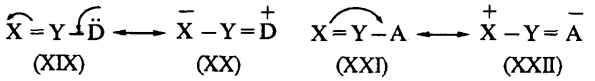
As a result of the endeavour of the unpaired electrons in this instance to occupy the *s* orbital, SiH_2 has a singlet ground state, while CH_2 has a triplet ground state. The stability of the singlet state relative to the triplet state in the X_2E (E = C, Si, Ge, Sn) molecules increases with increase in the relative electronegativity of the substituents X.[135] The strength of the double bonds involving the X_2E fragment and the stability of the planar molecular structure are inversely related to the energy of the singlet–triplet transition in X_2E:.[136,137] The stability of the planar structures of unsaturated molecules involving Group IV atoms has been attributed[137] to the competition between the "triplet" and "singlet" mechanisms of the formation of the double bond:

In the former case the optimum overlap of the interacting orbitals is achieved in the planar molecular structure, while in the latter it is achieved in the non-planar structure. The triplet mechanism describes best the formation of the double bond in the ethylene molecule, whereas in the disilene molecule there is a considerable contribution of the structure with dative bonding, which leads to the instability of the planar structure.[138–141]

In our view, the question of the characteristic features of conjugation with participation of double bonds involving Third Period atoms compared with the analogous bonds involving Second Period atoms is of undoubted interest. Calculations have been carried out[142] in terms of the 3-21G* basis set for the molecules $H_nX{=}YH_m{-}ZH_2$ (X, Y = C, N, Si, P; Z = B, N; n = 1, 2; m = 0, 1) in two conformations: (A) and (B).

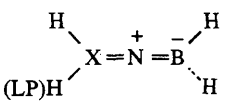


The structural, energetic, and electronic effects, associated with the conformational transitions (A)⟷(B) were analysed. The "classical" ideas concerning the conjugation of the donor (acceptor) group with the double bond are reflected in the form of the resonance of the structures (XIX)⟷(XX) and (XXI)⟷(XXII):



They can be formulated as three main corollaries: (1) conjugation lengthens the double bond and shortens the single bond participating in the conjugation (structural effect); (2) the electron density on the donor (acceptor) group diminishes (increases) in the conformation favouring conjugation (electronic effect); (3) in the absence of steric hindrance, the conformation where the p_π orbitals of the double bond in the substituent overlap to the maximum extent is energetically preferred (energetic effect).

When Y = C, conjugation takes place in conformity with the above rules when account is taken of the polarity of the X=C bond. When Y = N and Z = B, the stronger dative interaction of the lone pair of the nitrogen atom and the unoccupied *p* orbital of the boron atom is superimposed on the conjugation effect, which leads in conformation (B) to the linearisation of the molecule with formation of the allene-like structure (XXIII).

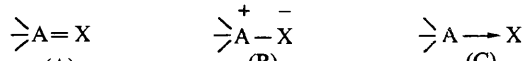


(XXIII)

When Y = Si or P, the effects of the conjugation and polarisation of the σ- and π-bonds under the influence of conformational transitions are similar in magnitude and, depending on their direction, can strengthen one another or cancel out. For example, in the conformational transition (B)→(A) in the $HN{=}P{-}NH_2$ molecule a shortening and not a lengthening of the P=N bond is observed. Similar results were detected also in X-ray diffraction studies on substituted aminoiminophosphines.[143] Analysis of the Mulliken populations has shown that the transition to the conformation (A) is accompanied by an increase in the polarity of the PN bond, as a result of which the latter is shortened. Similar effects had been observed earlier in the study of the influence of the substitution of H by F in the $HN{=}CH_2$ and $HP{=}CH_2$ molecules.[144]

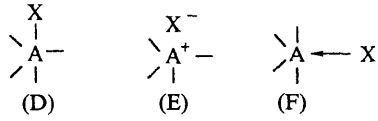
V. Hypervalent molecules and radicals

The concept of hypervalence in the chemistry of non-transition elements is associated with the description of molecular structure in which the octet rule breaks down. This means that in the structural formulae of such molecules the number of ligands and lone pairs surrounding the central atom is greater than four. Compounds containing multiple bonds of the phosphoryl or sulphoxide type (R_3PO, R_2SO, R_2SO_2, etc.) are also classified as hypervalent. Although the number of ligands in these molecules does not exceed four, the multiplicity of the bonds presupposes the involvement of more than four electron pairs in their formation [structure (A)]. The octet rule can be formally fulfilled if the structural formulae of such molecules are written using mesoionic (B) or dative (C) bonds.



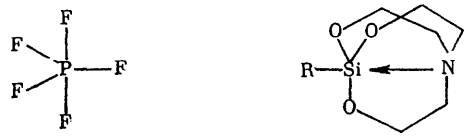
(A) (B) (C)

In many respects, the multiple bonds in the usual and hypervalent compounds exhibit similar properties (see also the previous Section). At the same time, the structural formulae (B) and (C) also reflect definite specific features of these bonds. The formulae (D)–(F), analogous to (A)–(C), are used to represent the structures of molecules in which the hypervalence is due to the increase in the number of ligands linked to the central atom.



(D) (E) (F)

As in the usual molecules, the nature of the chemical bonds in hypervalent molecules is extremely varied: ranging from weak to strong and from covalent to ionic bonds. The use of a particular formula for the representation of hypervalent molecules is determined to a large extent by the specific situation and the wish of the author to emphasise particular properties of the compound. The molecule of phosphorus pentafluoride is usually represented by the formula (XXIV), despite the high polarity of the P–F bonds, whereas in silatranes the *trans*-annular bond between silicon and nitrogen is represented by the dative formula (XXV).

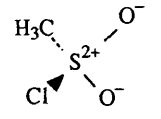


(XXIV) (XXV)

The structural formula (XXV) does not reflect the increase in the positive charge on the silicon atom on formation of a bond with nitrogen, which is observed in calculations for model molecules of pentacoordinate silicon.[145,146]

The wide variety of different types of chemical bonds in hypervalent molecules hinders the selection of the structural, energetic, or electronic parameters which could reflect quantitatively the degree of "hypervalence" of the atom in the molecule. The population of the 3*d* orbitals has been usually employed as such a parameter, although recently this criterion has been subjected to serious criticism (see Reed and Schleyer[1] and the references therein). At the same time, the important role of *d* orbitals in the description of the properties of hypervalent molecules has been emphasised in a number of studies (see, for example, Refs. 147–150). It appears evident nowadays that the quantitative description of the structural, energetic, and spectroscopic characteristics of hypervalent molecules can be achieved only using wide basis sets including 3*d* orbitals. At the same time, qualitative concepts such as that of the model of the reverse transfer of π-electron density from the ligands to the *d* orbital of the central atom (for the description of the multiplicity of bonds of the phosphoryl type) or the model of hybridisation with participation of *d* orbitals in highly coordinated molecules have not been confirmed by the results of modern non-empirical calculations.

According to the data of Reed and Schleyer,[1] based on the results of NBO (Natural Bond Orbitals) analysis,[151,152] the molecule of chlorosulphone and structurally similar hypervalent molecules have a predominantly ionic character corresponding to the Lewis structure (XXVI). The increased multiplicity of the S–O bond is due mainly to the effect of negative hyperconjugation with participation of the lone pair of oxygen and the antibonding bond orbitals σ^*_{SCl} and σ^*_{SC}:



(XXVI)

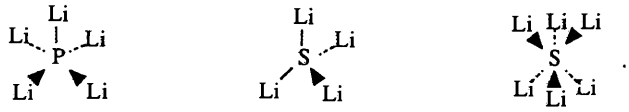
In pentacoordinate and hexacoordinate molecules, the three-centre four-electron bond model is more consistent with the qualitative concept of the hypervalent bond than the model of hybridisation with participation of 3*d* orbitals.

The method of correlation diagrams, proposed previously by Shaik[153] for the analysis of nucleophilic substitution reactions, was used to explain the stability of SiH_5^-,[154,155] sulphuranes, and sulphuranyl radicals.[156] In contrast to Walsh diagrams, in which the dependence of the molecular orbital energies on structural parameters is analysed, the Shaik diagram method is based on the analysis of the energies of the Lewis structures obtained by the valence bond method. The qualitative difference between CH_5^- (transition state in the S_N2 reaction between CH_4 and H^-) and SiH_5^- (a relatively stable intermediate[157]) can be explained by the stabilisation of the latter as a result of the involvement of the σ^* orbital of the equatorial SiH_3 fragment in bonding.

The σ^* orbital of the SiH_3 fragment has less antibonding character, in contrast to the analogous orbital in the carbon analogue, and is localised predominantly on the silicon atom. Although the *d* orbitals do in fact increase the relative stability of the bipyramid in this case, nevertheless they do not determine the qualitative nature of the effect.[158]

The stability of hypervalent molecules as a rule increases with decrease in the electronegativity of the ligands, which is consistent with the ideas based both on the molecular orbital theory and on the valence bond diagram method. At the same time, calculations for the hypervalent phosphorus- and sulphur-containing molecules with the most electropositive ligands (lithium atoms), namely PLi_5, SLi_4, and SLi_6,[159] are in our view of considerable interest.[159] When the geometry is optimised in terms of the HF/3-21G* approximation (with *d* orbitals only in the S and P atoms), all the above molecules have energy minima corresponding to the "non-classical" (from the standpoint of the Gillespie–Nyholm model[160]) structures

(XXVII)–(XXIX), which are stable as regards decomposition into atoms and the segregation of the Li_2 molecule. Such behaviour is caused mainly by two factors: the increase in electron density on the central atom and the effective bonding of neighbouring lithium atoms via diffuse *p* orbitals:

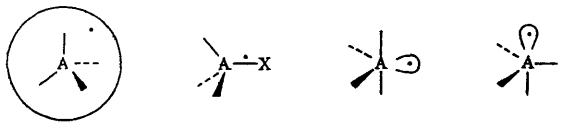


C_{4v} (XXVII) C_{3v} (XXVIII) D_{3d} (XXIX)

All three molecules are structurally non-rigid. The $SiLi_4$ molecule, whose energy minimum corresponds to the C_{2v} structure, exhibits a similar behaviour.[161]

Until recently quantum-chemical calculations for molecules containing unpaired electrons were predominantly qualitative (estimates). Modern non-empirical programs for high-speed computers make it possible in many instances to calculate quantitatively the structures and energies of radical species. This increases in its turn the predictive and conceptual value of orbital models based on modern non-empirical calculations for such systems.

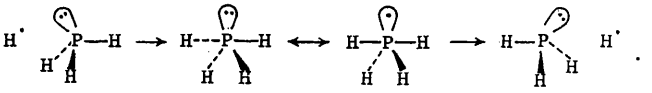
From the standpoint of orbital ideas, the excess electron in hypervalent radicals can be located in the diffuse Rydberg orbital (A) or the antibonding bond orbitals (B) or can occupy one of the coordination sites in the manner of a lone pair [(C) and (D)].



(A) (B) (C) (D)

According to non-empirical calculations, the unpaired electron in the metastable radicals $\dot{N}H_4$[162–165] and $\dot{O}H_3$[166,167] is located in the Rydberg orbital, while the radical $\dot{C}H_5$ is a transition state in the reaction of methane with a hydrogen atom.[168,169] On passing from Second to Third Period elements, the energies of the antibonding orbitals diminish and the "capacity" of the coordination sphere of the central atom increases.

The structure of phosphoranyl radicals (PX_4) is intermediate between (B), (C), and (D) and depends on the nature of the substituents. In radicals of the $Ar_3\dot{P}Cl$ type, the excess electron is located, according to EPR data, in the σ^* orbital of the P–Cl bond.[170–172] On the other hand, according to the results of *ab initio* calculations,[173] such radicals should have a trigonal-bipyramidal structure with the excess electron on the phosphorus atom in the apical position. In the $H_3P-\dot{X}$ (X = PH_3, SH_2, ClH) series, the first member is a σ^* radical with the excess electron localised on the P–P bond, whilst the third has a trigonal-bipyramidal structure, the difference between the apical and equatorial positions of the unpaired electrons amounting to only 0.15 kcal mol^{-1} in terms of the MP2/4-31G* approximation.[174] The radical $H_3P-\dot{S}H_2$ has an intermediate configuration both from the standpoint of its structure and of the distribution of the unpaired electron density. The stabilities of the radicals $\dot{S}iH_5$, PH_4, and $\dot{S}H_3$ have been analysed[175] by the method of correlation diagrams for valence bonds.[153] The phosphoranyl radical is most stable as regards decomposition with evolution of atomic hydrogen. Analysis[175] showed that the stability of hypervalent radicals increases with decrease in the A–H bond energies. The phosphoranyl radical is traditionally stabilised as a result of the involvement of the lone pair of the phosphorus atom in the redistribution of electron density on formation of the trigonal bipyramid:



In $\dot{S}H_3$ such stabilisation is less effective, owing to the greater energy of the abstraction of the lone pair electron from the H_2S molecule.

The radicals $H_2\dot{P}=X$ (X = O, S), investigated by the *ab initio* method,[176] are also hypervalent like the initial $H_3P=X$ molecule. The abstraction of a hydrogen atom from $H_3P=X$ is accompanied by lengthening of the P–X bond and an appreciable decrease in the HPX bond angles. The P–X bond lengths are intermediate under these conditions between the lengths of double ($H_3P=X$) and single (H_2P-XH) bonds. The distribution of spin density also shows that the unpaired electron in the radicals H_2PX is delocalised between the P and X atoms. Thus the structure of radicals of this kind is intermediate between $H_2\dot{P}=X$ and $H_2P-\dot{X}$.

- - - o0o - - -

Modern non-empirical calculations are a source of a wide variety of qualitative and quantitative information, which makes it possible to rethink the existing ideas and formulate new ones concerning the structure of chemical bonds (especially in silicon, phosphorus, and sulphur compounds). This stimulates in its turn the development of experimental research and the synthesis of chemical compounds of new classes.

References

1. A E Reed, P v R Schleyer *J. Am. Chem. Soc.*, 1990, **112** 1434
2. C S Ewig, J R Van Wezer *J. Am. Chem. Soc., 1989,* **111** 1552
3. F Volatron *J. Mol. Struct. Theochem.*, 1989, **186** 167
4. R S McDowell, A Streitwieser *J. Am. Chem. Soc.*, 1985, **107** 5849
5. R Hoffmann, J M Howell, E L Muetterties *J. Am. Chem. Soc.*, 1972, **94** 3047
6. I Mayer *J. Mol. Struct. Teochem.*, 1987, **149** 81
7. R H Holmes *J. Am. Chem. Soc.*, 1984, **106** 3745
8. G Trinquier, J-P Daudey, G Caruanna, Yv Madauli *J. Am. Chem. Soc.*, 1984, **106** 4794
9. H Wallmeier, W Kutzelnigg *J. Am. Chem. Soc.*, 1979, **101** 2804
10. L G V Petterson, P E M Siegbahn *J. Chem. Phys.*, 1985, **83** 6467
11. R Haddon *Chem. Phys. Lett.*, 1985, **120** 372
12. L Pauling *J. Am. Chem. Soc.*, 1931, **53** 1367
13. H Kwart, K King *d-Orbitals in the Chemistry of Silicon, Phosphorus and Sulfur*, Springer, Berlin, 1977
14. G C Pimental *J. Chem. Soc.*, 1951, **19** 446
15. R J Hach, R E Rundle *J. Am. Chem. Soc.*, 1951, **73** 4321
16. J J Masher *Angew. Chem., Int. Ed. Engl.*, 1969, **8** 54
17. W Kutzelnigg *Angew. Chem., Int. Ed. Engl.*, 1984, **23** 272
18. E N Tsvetkov, A A Korkin *Teor. Eksp. Khim.*, 1985, **21** 39, 159, 536

19. P Jutzi *Angew Chem., Int. Ed. Engl.*, 1975, **14** 232
20. L E Gusel'nikov, N S Nametkin *Chem. Rev.*, 1979, **79** 529
21. A H Cowley *Acc. Chem. Res.*, 1984, **17** 386
22. N Wiberg *J. Organomet. Chem.*, 1984, **273** 141
23. L N Markovskii, V D Romanenko, A V Ruban *Khimiya Atsiklicheskikh Soedinenii Dvukhkoordinirovannogo Fosfora* (The Chemistry of Acyclic Compounds of Dicoordinate Phosphorus), Naukova Dumka, Kiev, 1988
24. P Deslongchamps *Stereoelectronic Effects in Organic Chemistry*, Pergamon Press, Oxford, 1984
25. J M Lehn, G Wipff *J. Chem. Soc. Chem. Commun.*, 1975, 800
26. M V Sigalov, V A Pestunovich, V M Nikitin, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 1180
27. D G Gorenstein, B A Luxon, E M Goldfield *J. Am. Chem. Soc.*, 1980, **102** 1757
28. R Kluger, G R J Thatcher *J. Am. Chem. Soc.*, 1985, **107** 6006
29. E Magnusson *Aust. J. Chem.*, 1985, **38** 23
30. D G Gorenstein *Chem. Rev.*, 1987, **87** 1047
31. W M Wolf, T J Bartzak *Z. Kristallogr.*, 1988, **185** 255
32. N D Epiotis, W R Cherry, R L Yates, et al. *Top. Curr. Chem.*, 1977, **70**
33. L Radom *Progress in Theoretical Organic Chemistry* (Edited by I G Csizmadia), Elsevier, Amsterdam, 1982, Vol. 3, p. 1
34. A J Kirby *The Anomeric Effect in Oxygen-Containing Compounds* (Translated into Russian), Mir, Moscow, 1985
35. M J S Dewar *J. Am. Chem. Soc.*, 1984, **106** 669
36. A M Panov, G V Ratovskii, T V Lipovich, et al. *Zh. Obshch. Khim.*, 1982, **52** 1761
37. L V Ermolaeva, V V Zverev *Zh. Strukt. Khim.*, 1983, **24** 37
38. A M Panov, G V Ratovskii, G N Dolenko, V I Dmitriev *Zh. Obshch. Khim.*, 1985, **55** 2243
39. A A Korkin *Metalloorg. Khim.*, 1990, **3**(5) 969 [English translation in *Organomet. Chem. USSR*, 1990(5)]
40. E Magnusson *J. Am. Chem. Soc.*, 1984, **106** 1177
41. E Magnusson *Phosphorus Sulfur*, 1986, **28** 379
42. A A Korkin, E N Tsvetkov *Bull. Soc. Chim. Fr.*, 1988, 335
43. A A Korkin, E N Tsvetkov *Zh. Neorg. Khim.*, 1989, **34**(2) 290 [English translation in *Russ. J. Inorg. Chem.*, 1989(2)]
44. L Pauling *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, New York, 1960
45. D A Bochvar, N P Gambaryan L M Epshtein *Usp. Khim.*, 1976, **45**(7) 1316 [English translation in *Russ. Chem. Rev.*, 1976(7)]
46. L G Vanquickenborne, K Pierloot, D Devoghel *Inorg. Chem.*, 1989, **28** 1805
47. M E Dyatkina, N M Klimenko *Zh. Strukt. Khim.*, 1973, **14** 173
48. W J Hehre, L Radom, P v R Schleyer, J A Pople *Ab initio Molecular Orbital Theory*, Wiley-Interscience, New York, 1986
49. T Clark *A Handbook of Computational Chemistry* (Translated into Russian), Mir, Moscow, 1990
50. P v R Schleyer, J S Binckley *J. Chem. Phys.*, 1976, **64** 5142
51. A E Reed, F Weinhold *J. Am. Chem. Soc.*, 1986, **108** 3586
52. M W Schmidt, S Yabushita, M S Gordon *J. Phys. Chem.*, 1984, **88** 382
53. M Aida, C Nagata *Theor. Chim. Acta*, 1986, **70** 73
54. E Magnusson *J. Am. Chem. Soc.*, 1986, **108** 11
55. A E Reed, C Schade, P v R Schleyer, et al. *J. Chem. Soc., Chem. Commun.*, 1988, 67
56. E Magnusson *Tetrahedron*, 1985, **41** 2939, 2945, 5235
57. A A Korkin *Int. J. Quant. Chem.*, 1990, **38** 245
58. A E Reed, P v R Schleyer *J. Am. Chem. Soc.*, 1987, **109**, 7362; *Inorg. Chem.*, 1988, **27** 3969
59. F Bernardi, A Bottoni, A Mangini, C Tonachini *J. Mol. Struct. Theochem.*, 1981, **86** 163
60. F Bernardi, A Bottoni, J Fossey, J Sorba *Tetrahedron*, 1986, **42** 5567
61. V K Yadav, A Yadav, R A Poirier *J. Mol. Struct. Theochem.*, 1989, **186** 101
62. E Magnusson *Aust. J. Sci. Res.*, 1986, **39** 735
63. V A Godik, G G Konoplev, A I Rodionov, D I Shigorin *Teor. Eksp. Khim.*, 1982, **8** 80
64. F Bernardi, A Bottoni, A Venturini, A Mangini *J. Am. Chem. Soc.*, 1986, **108** 8171
65. J Baker, R H Nobes, L Radom *J. Comput. Chem.*, 1986, **7** 349
66. J V Ortiz *J. Chem. Phys.*, 1987, **86** 308
67. J A Tossel, J H Moore, J C Giordan *Inorg. Chem.*, 1985, **24** 1100
68. J C Giordan, J H Moore *J. Am. Chem. Soc.*, 1983, **105** 6541
69. G Mauzizio, D Giuseppe, J Dezek, et al. *Chem. Phys.*, 1984, **91** 383
70. R F Hudson *Structure and Mechanism in Organophosphorus Chemistry* (Translated into Russian), Mir, Moscow, 1967
71. A F Wells *Structural Inorganic Chemistry*, 5th Ed., Clarendon, Oxford, 1984
72. F A Cotton, G Wilkinson *Advanced Inorganic Chemistry*, 5th Ed., Wiley, New York, 1988
73. D E C Corbridge *Phosphorus* (Translated into Russian), Mir, Moscow, 1982
74. A V Fokin M A Landau *Ftoridy Fosfora i Ftorolefiny* (Phosphorus Fluorides and Fluoro-olefins), Nauka, Moscow, 1989
75. N N Greenwood, A Earnshaw *Chemistry of the Elements*, Pergamon Press, Oxford, 1984
76. I N Jung, P R Jones *J. Organomet. Chem.*, 1975, **101** 27
77. W Adcock, G L Aldous, W Kitching *Tetrahedron Lett.*, 1978, 3387
78. B G Zykov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2230
79. E N Tsvetkov, A A Korkin *Trudy VIII Vsesoyuznogo Soveshchaniya po Khimii Fosforganicheskikh Soedinenii* (Proceedings of the VIIIth All-Union Conference on the Chemistry of Organophosphorus Compounds), Nauka, Moscow, 1987, p. 211
80. G W Wheland *J. Chem. Phys.*, 1934, **2** 474
81. J W Baker, W S Nathan *J. Chem. Soc.*, 1935, 1844
82. L Pauling, H S Springall, K J Palmer *J. Am. Chem. Soc.*, 1939, **61** 927
83. R S Mulliken *J. Chem. Phys.*, 1939, **7** 339
84. M J S Dewar *Hyperconjugation* (Translated into Russian), Mir, Moscow, 1965
85. R P Arshinova *Usp. Khim.*, 1984, **53**(4) 595 [English translation in *Russ. Chem. Rev.*, 1984(4)]
86. A N Egorochkin *Usp. Khim.*, 1984, **53**(5) 772 [English translation in *Russ. Chem. Rev.*, 1984(5)]
87. C G Pitt *J. Organomet. Chem.*, 1973, **81** 49
88. R Ponec, L Dejmek, V Chalovsky *Collect. Czech. Chem. Commun.*, 1981, **46** 2663
89. L B Krivdin, V I Donskikh, G A Kalabin, B A Trofimov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1053
90. A Kucsman, I Kapovits, L Parkanyi, et al. *J. Mol. Struct.*, 1984, **125** 331

91. P v R Schleyer, E D Jemmis, G W Spitznagel *J. Am. Chem. Soc.*, 1985, **107** 6393
92. E Magnusson *Aust. J. Sci. Res.*, 1936, **39** 747
93. F Bernardi, A Mangini, N D Epiotis, et al. *J. Am. Chem. Soc.*, 1977, **23** 7465
94. R Hoffman, L Radom, J A Pople, et al. *J. Am. Chem. Soc.*, 1972, **94** 6221
95. A Pross, L Radom *Aust. J. Chem.*, 1980, **33** 241
96. M J S Dewar *The PMO Theory of Organic Chemistry* (Translated into Russian), Mir, Moscow, 1977
97. J Pacansky, M Dupuis *J. Chem. Phys.*, 1979, **71** 2095
98. F Delbecq, J M Lefour *Tetrahedron Lett.*, 1983, 3613
99. H B Schlegel *J. Phys. Chem.*, 1982, **86** 4878
100. G P Ford, K S Raghuver *Tetrahedron*, 1988, **44** 7489
101. R Kimmelma *Acta Chem. Scand., Ser. B*, 1988, **42** 592
102. L I Belenkii (Editor) *Khimiya Organicheskikh Soedinenii Sery* (The Chemistry of Organic Compounds of Sulphur), Khimiya, Moscow, 1988
103. Yu L Frolov, Abstract of Doctoral Thesis in Chemical Sciences, Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences, Irkutsk, 1982
104. E N Tsvetkov, M I Kabachnik *Usp. Khim.*, 1971, **40**(2) 177 (Translated into English from *Russ. Chem. Rev.*, 1971(2)]
105. S Ikuta, P Kebarle *Can. J. Chem.*, 1983, **61** 97
106. H Schmidt, A Schweig, F Mathey, G Muller *Tetrahedron*, 1979, **31** 1287
107. C Schade, P v R Schleyer *J. Chem. Soc., Chem. Commun.*, 1987, 1399
108. C C Levin *J. Am. Chem. Soc.*, 1975, **97** 5649
109. D Gonbeau, G Pfister-Guillouzo *Can. J. Chem.*, 1985, **63** 3242
110. A A Korkin, E N Tsvetkov *Zh. Obshch. Khim.*, 1987, **57** 2155
111. S Ikuta, P Kebarle, G M Bancroff, et al. *J. Am. Chem. Soc.*, 1982, **104** 5899
112. C Glidewell, C Thompson *J. Comput. Chem.*, 1982, **3** 495
113. M G Voronkov, A A Kashaev, E A Zel'bst, et al. *Dokl. Akad. Nauk SSSR*, 1979, **147** 1147
114. E Lukevics (Editor) *Kremniiorganicheskikh Proizvodnye Aminospirtov* (Organosilicon Derivatives of Aminoalcohols), Zinatne, Riga, 1987
115. I D Kalikhman, O B Bannikova, L I Belousov, et al. *Metalloorg. Khim.*, 1988, **1**(3) 683 [English translation in *Organomet. Chem. USSR*, 1988(3)]
116. L Parkanyi, J Nagy, K Simon *Metalloorg. Khim.*, 1975 **101** 11
117. V A Pestunovich, V F Sidorkin, O B Dogaev, M G Voronkov *Dokl. Akad. Nauk SSSR*, 1980, **251** 1440
118. E Lukevics, L A Pudova, R Ya Sturkovich *Molekulyarnaya Struktura Kremniiorganicheskikh Soedinenii* (Molecular Structure of Organosilicon Compounds), Zinatne, Riga, 1988
119. A A Korkin, N A Aksinenko, E N Tsvetkov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2061
120. G Bettermann, D S Schomburg, R Schmutzler *Phosphorus Sulfur*, 1986, **28** 327
121. R R Holmes *J. Phys. Chem.*, 1960, **64** 1295
122. C P Huber, P R Carey, Hsi Shi-Chuan, et al. *J. Am. Chem. Soc.*, 1984, **106** 8263
123. Iwasaka, et al. *Acta Crystallogr., Sect. C*, 1986, **42** 121, 124
124. A N Chernega, A A Korkin, M Yu Antipin, Yu T Struchkov *Zh. Obshch. Khim.*, 1989, **58** 2045
125. S F Boys *Quantum Theory of Atoms, Molecules and Solid State* (Edited by P O Löwdin), Wiley-Interscience, New York, 1967, p. 253
126. A S Tarasevich, I E Boldeskul, V P Kukhar' *Usp. Khim.*, 1986, **55**(8) 1344 [English translation in *Russ. Chem. Rev.*, 1986(8)]
127. L N Markovskii, V D Romanenko, A V Ruban *Khimiya Atsiklicheskikh Soedinenii Dvukhkoordinirovannogo Fosfora* (The Chemistry of Acyclic Compounds of Dicoordinate Phosphorus), Naukova Dumka, Kiev, 1988
128. R Jaquet, W Kutzelnigg, V Staemmler *Theor. Chim. Acta*, 1980, **54** 205
129. W W Schoeller, J Niemann *J. Am. Chem. Soc.*, 1986, **108** 22
130. W W Schoeller, C Lerch *Inorg. Chem.*, 1986, **25** 576
131. A Streitwieser, Jr., A Rajca, R S McDowell, R Claser *J. Am. Chem. Soc.*, 1987, **109** 4184
132. M W Schmidt, P N Truong, M S Gordon *J. Am. Chem. Soc.*, 1987, **109** 5217
133. K K Baldridge, J A Boatz, S Koseki, M S Gordon *Annu. Rev. Phys. Chem.*, 1987, **38** 211
134. H Sun, D A Hrovat, W T Borden *J. Am. Chem. Soc.*, 1987, **109** 5275
135. E R Davidson *Diradicals* (Edited by W T Borden), Wiley-Interscience, New York, 1982, p. 73
136. E A Carter, W A Goddard *J. Phys. Chem.*, 1986, **90** 998
137. G Trinquier, J-P Malrieu *J. Am. Chem. Soc.*, 1987, **109** 5303
138. K Krogh-Jespersen *J. Phys. Chem.*, 1982, **96** 1492
139. G Raabe, J Michl *Chem. Rev.*, 1985, **85** 419
140. G Olbrich *Chem. Phys. Lett.*, 1986, **130** 115
141. K Somasundran, R D Amos, N C Handy *Theor. Chem. Acta*, 1986, **70** 393
142. A A Korkin *Int. J. Quantum Chem.*, 1990, **38** 245
143. A N Chernega, A A Korkin, M Yu Antipin, et al. *Zh. Obshch. Khim.*, 1989, **59** 2243
144. H-G Mack, B Steger, H Oberhammer *Chem. Phys. Lett.*, 1986, **129** 582
145. Yu L Frolov, S G Shevchenko, M E Voronkov *J. Organomet. Chem.*, 1985, **292** 159
146. G N Kartsev, N M Klimenko, Zh E Grabovskaya, G M Chaban *Zh. Strukt. Khim.*, 1988, 126
147. I Mayer *Theochem*, 1987, **149** 81
148. J G Angyan, R A Poirier, A Kucsman, I G Csizmadia *J. Am. Chem. Soc.*, 1987, **109** 2237
149. V G Smeyers, J J Randez, F J Randez, et al. *Theochem*, 1988, **166** 141
150. Y Maouche, M C Brianso, B Maouche *Theochem*, 1988, **166** 449
151. A E Read, F Weinhold *QCPE Bull.*, 1985, **24** 2702
152. A E Read, F Weinhold, L A Curtiss *Chem. Rev.*, 1988, **88** 899
153. S S Shaik *Prog. Phys. Org. Chem.*, 1985, **15** 197
154. G Sini, P C Hiberty, S S Shaik *J. Chem. Soc., Chem. Commun.*, 1989, 772
155. G Sini, G Ohanessian, Ph C Hiberty, S S Shaik *J. Am. Chem. Soc.*, 1990, **112** 1407
156. F Volatron *J. Mol. Struct.*, 1989, **186** 167
157. D J Hadjasz, R R Squires *J. Am. Chem. Soc.*, 1986, **108** 3139
158. A E Read, P v R Schleyer *Chem. Phys. Lett.*, 1987, **133** 553
159. C J Marsden *J. Chem. Soc., Chem. Commun.*, 1989, 1356
160. R J Gillespie *Molecular Geometry* (Translated into Russian), Mir, Moscow, 1975
161. P v R Schleyer, A E Read *J. Am. Chem. Soc.*, 1988, **110** 4453
162. B N McMaster, J Mrozer, V H Smith *Chem. Phys.*, 1982, **73** 131
163. H Cardy, D Liotard, A Dargelos, E Pognet *Chem. Phys.*, 1983, **77** 287

164. J Kaspar, H V Smith, B N McMaster *Chem. Phys.*, 1985, **96** 81
165. E Kassab, E M Elveth *J. Am. Chem. Soc.*, 1987, **109** 1653
166. R A Gangi, R F W Bader *Chem. Phys. Lett.*, 1971, **11** 216
167. K S E Niblaes, B O Ross, P E M Siegbahn *Chem. Phys.*, 1977, **25** 207
168. K Morokuma, R E Davis *J. Am. Chem. Soc.*, 1972, **94** 1060
169. K S E Niblaes, B O Ross, P E M Siegbahn *Chem. Phys.*, 1977, **26** 59
170. T Berclez, M Geoffroy, E A C Lucken *Chem. Phys. Lett.*, **1975, 36** 677
171. M C R Symons *Chem. Phys. Lett.*, 1976, **40** 226
172. G W Eastland, M C R Symons *J. Chem. Soc., Perkin Trans. 2*, 1977, 2883
173. R A J Janssen, G J Visser, H M Buck *J. Am. Chem. Soc.*, 1984, **106** 3429
174. T Clark *J. Comput. Chem.*, 1983, **4** 404
175. A Demolliens, O Eisenstein, P C Hiberty, et al. *J. Am. Chem. Soc.*, 1989, **111** 5623
176. M T Nguen, Ha Tae-Kyu *Chem. Phys.*, 1989, **131** 245

Translated from *Uspekhi Khimii* 61 883–909 (1992) U.D.C. 541.15:547.898

Radiation chemistry of crown-compounds

V V Makhlyarchuk, S V Zatonskii
Faculty of Chemistry, Lomonosov Moscow State University

ABSTRACT. **The results of studies on the radiation-chemical reactions in various systems containing crown-ethers and their analogues are surveyed and analysed in the review. The use of crown-compounds as extractants for the selective isolation of radionuclides is considered from the standpoint of radiation chemistry. Data concerning the radiolysis of individual crown-ethers as well as their aqueous and non-aqueous solutions are described. Good prospects for the application of macrocyclic compounds and their complexes in the study of the mechanisms of radiation-chemical processes are demonstrated.**

The bibliography includes 142 references.

Contents

I. Introduction 484
II. Crown-compounds as extractants for radionuclides. Radiation-chemical aspects 484
III. Radiolysis of macrocyclic polyethers 489
IV. Radiation-chemical reactions in solutions of crown-compounds 493

I. Introduction

Crown-compounds are macrocyclic compounds containing in their structures electron-donating heteroatoms such as those of oxygen (crown-ethers), nitrogen, or sulphur and possessing the ability to form with a high degree of selectivity stable "guest-host complexes" with cations and neutral molecules. Polycyclic compounds consisting of two (cryptands) and more rings can also be included among crown-compounds.[1–3] The chemistry of crown-compounds has been developing vigorously and the synthesis of numerous new macroheterocycles with unusual properties has stimulated studies not only in the field of organic chemistry but also in adjacent fields where these substances have found important practical applications.[4–6] The first studies concerning the radiation chemistry of crown-ethers were published in 1984.[7–12]

The capacity for the selective binding, separation, and transport of metal cations stimulated the use of crown-compounds as extractants for the selective isolation of radionuclides in radiochemical technology,[13] which in fact induced the initial practical interest in the radiation chemistry of macrocyclic polyethers and their solutions. The complex of a crown-ether and an inorganic salt is formed as a result of the ion–dipole interaction between the cation and the negatively charged oxygen atom of the polyether ring. The stability of the complex formed then depends on the relative diameter of the cavity within the crown-compound and the diameter of the cation. The complex-forming capacity is also influenced by the charge and hardness of the cation and the nature of the electron-donating heteroatoms of the crown-compounds and the substituents in the macrocycle.[1,3,14–16] As a result of the formation of a complex with a crown-compound, the relatively small alkali metal or alkaline earth metal ion is converted into a bulky organic cation capable of dissolving in the organic phase. Thus inorganic salts are solubilised in weakly polar organic solvents, which is favoured by the highly lipophilic properties of the ligand skeleton.[3,17] The weakly solvated, almost "bare" anions formed on complex formation in weakly polar solvents differ appreciably from their solvated analogues. The electron-donating properties of the weakly solvated anion are enhanced and it becomes a potentially strong base and nucleophile. Such an anion is activated by the crown-compound and its reactivity increases.[18] The degree of activation depends on the nature of the anion, the solvent, and the macrocyclic ligand.

The ability of crown-compounds to transport ionic reactants from the solid or aqueous phase to the organic phase and to act on the state of ion pairs in the solution influences the kinetics and stereochemistry of many reactions. Under these conditions, certain reactions can be carried out only in the presence of macrocyclic compounds.[19] This permits the application of these substances in the study of reaction mechanisms in organic chemistry. By virtue of the ability of crown-ethers and cryptands to dissolve alkali metals even in weakly polar organic solvents such as benzene and toluene,[20–23] it becomes possible to extent significantly the range of solvents in which the solvated electron and related species, which are the objects of study in radiation chemistry, may be obtained.[24] The weakly solvated alkali metal anions, present in such solutions, have very powerful reducing properties.[17] Strong oxidants, insoluble in the majority of organic solvents, such as potassium dichromate and permanganate, dissolve even in benzene in the presence of crown-ethers.[25–28] Thus a powerful instrument becomes available for the study of the oxidation-reduction processes occurring in the radiolysis of non-aqueous solutions.[29,30] Crown-compounds, which make it possible to alter the state and reactivity of not only ionic reactants but also of ionic reaction intermediates, can serve as an effective means for the study of the mechanisms of radiation-chemical reactions.[31,32] Macrocyclic polyethers and their analogues give rise to the possibility of increasing appreciably the number of compounds soluble in weakly polar media, which helps to create new antiradiation agents or reagents and phase-transfer catalysts for radiation-chemical synthesis.

II. Crown-compounds as extractants for radionuclides. Radiation-chemical aspects

Extraction is one of the most important fields in which macrocycles are used.[33] In particular, the employment of crown-compounds for the selective isolation of radionuclides is extremely

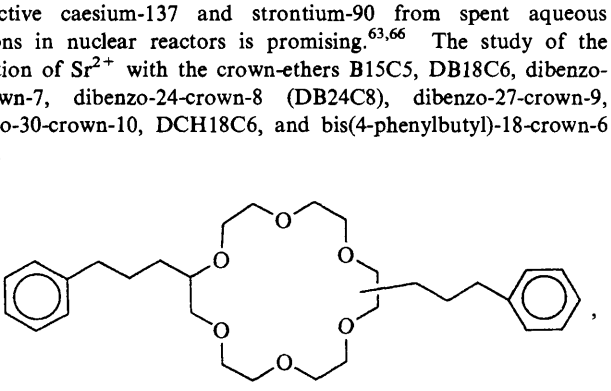
promising.[34,35] In the processing of spent nuclear fuel,[36] the extractant can receive a dose of the order of 0.4–40 kGy in one cycle depending on the organisation of the extraction process, while under conditions of multiple employment of the extractant the integral radiation dose received by the latter can reach tens of megagrays.[37] The radiolysis of extraction systems can also have negative consequences important for technology such as the degradation of the extractant and the decrease in the efficiency of the extraction, the formation of radiolytic products influencing unfavourably the selectivity of the extraction and the phase separation, and the formation of corrosive acids and oligomers which hinder the regeneration of the extractants. For this reason, the radiolytic reactions of organic compounds and of two-phase aqueous organic systems, the search for new more effective and radiation-resistant extractants which are satisfactorily compatible with the organic liquids used as diluents, as well as the behaviour of salts of the actinide elements, which are the main components of nuclear fuel, have been the subject of vigorous studies.[13,37–39]

Numerous studies have been devoted in this connection to crown-ethers. For example, a review[40] quotes data on the extraction of tervalent actinides by crown-compounds and their linear analogues. Another review[41] reports the complexes of divalent actinides with crown-ethers and their physicochemical properties and demonstrates the similarity to and differences from alkaline earth elements. The uranium(III) complexes of a series of crown-ethers have been investigated.[42] The processes involving the extraction of uranium, thorium, neptunium, and plutonium from nitric acid solutions by crown-ethers have also been studied.[43–46] A wide variety of compounds can be used as extractants and diluents, for example: 15-crown-5 (15C5) and dicyclohexano-18-crown-6 (DCH18C6) in nitrobenzene and 1,2-dichloroethane for uranium(VI), neptunium(IV), and americium(III); DCH18C6 in nitrobenzene for neptunium(IV);[47] 12-crown-4 (12C4), 15C5, 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), and DCH18C6 with 4-benzyl-3-methyl-1-phenylpyrazolone in toluene for uranium(VI), americium(III), and thorium(IV);[48] five different crown-ethers in 1,2-dichloroethane for uranium(VI),[49] DCH18C6, DB18C6, and 18C6 with thenoyltrifluoroacetone in benzene[50] and 12C4, 15C5, 18C6, DB18C6, and DBH18C6 in chloroform[51,52] for americium(III); DCH18C6 or benzo-15-crown-5 (B15C5) with 3-methyl-1-phenyl-4-trifluoroacetyl-5-pyrazolone in chloroform for trivalent americium, curium, californium, and europium.[53] The application of 18C6 makes it possible to carry out the selective extraction of thorium in the form of the picrate complex from a mixture containing cerium, uranium, zirconium hafnium, yttrium, and lead.[54]

The use of crown-ethers (for example, DCH18C6 or DB18C6) as extractants in the processing of irradiated nuclear fuel permits the isolation of uranium and plutonium from aqueous solutions containing nitric acid.[55,56] It has been shown that DCH18C6 (especially the *cis*, *syn*, *cis*-isomer of this macrocycle) is an effective extractant for plutonium present in highly radioactive solutions resulting from the processing of nuclear fuel. This crown-ether is more radiation-resistant and selective in the isolation of plutonium(IV) than tri-n-butyl phosphate (TBP) usually employed. Thus, in a study of a 10% solution of DCH18C6 in chloroform irradiated from a ^{137}Cs source (absorbed dose 168 kGy) by UV, IR, and ^{1}H and ^{13}C NMR spectroscopic methods as well as high performance liquid chromatography (HPLC), no products of the radiation-chemical reactions of the crown-ether were detected. In addition, a comparative study has been made of the extraction of plutonium from moderately active solutions by commercial DCH18C6 (mixture of isomers) and with the crown-ether subjected to preliminary washing with nitric acid. The extractant was irradiated during its contact with the solution containing plutonium(IV), uranium(VI), and fission products in the course of eight months. In this case, the overall absorbed energy was 611 kJ mol^{-1}, including 80.5 kJ mol^{-1} as the α-emission energy, which corresponds to 5000 cycles involving extraction from highly active solutions. It has been shown that, even if the selectivity in the isolation of plutonium does actually decrease as a result of the strong irradiation of the polyether, the decrease is extremely insignificant. The amount of extracted plutonium is 92 and 90% respectively for the commercial products and the irradiated DCH18C6. Thus, according to the authors,[56,57] the use of crown-ethers as extractants makes it possible to create a new industrial technology for the processing of nuclear fuel.

Apart from actinides, other radioactive elements and isotopes can be extracted with crown-ethers. The extraction of technetium(IV) with DB18C6 and 18C6 has been investigated in a study,[58,59] where the organic phase was nitrobenzene, benzene, and acetylacetone; the extraction of astatine-211 with crown-ethers from various media and its mechanism have been discussed.[60] The selective isolation of iodine-131 from irradiated uranium and tellurium oxides can be achieved with a high efficiency using DB18C6 in 1,2-dichloroethane as the extractant.[61] The equilibria in the extraction system involving the extraction of radium from an aqueous medium containing sodium nitrate and hydroxide into a solution of dicyclohexano-21-crown-7 in toluene in the presence of 2-heptyl-2-methylnonanoic acid has been investigated.[62] The possibility of the selective separation of radium from other alkali and alkaline earth elements was demonstrated.

The use of crown-ethers in the technology of the extraction of radioactive caesium-137 and strontium-90 from spent aqueous solutions in nuclear reactors is promising.[63,66] The study of the extraction of Sr^{2+} with the crown-ethers B15C5, DB18C6, dibenzo-21-crown-7, dibenzo-24-crown-8 (DB24C8), dibenzo-27-crown-9, dibenzo-30-crown-10, DCH18C6, and bis(4-phenylbutyl)-18-crown-6 (I), i.e.



(I)

for nitric acid solutions containing $NaNO_3$ showed that the crown-ethers (I) and DCH18C6 (mixture of two *cis*-isomers) can be used for this purpose. The latter extractant is more effective and the best diluent is 1,1,2,2-tetrachloroethane.[67] Similar results were obtained by Filippov, et al.,[68] who investigated the extraction of magnesium, calcium, strontium, and barium nitrates from nitric acid solutions with the crown-ether DCH18C6 in dichloroethane. The possibility of the selective extraction of Sr^{2+} was demonstrated, the crystalline complex $Sr(NO_3)_2$.DCH18C6 was isolated, and its IR spectroscopic characteristics were obtained. It has been noted[69] that DCH18C6 is an effective extractant not only for Sr^{2+} but also for Tl^{+} (diluent – 1,1,2,2-tetrachloroethane and trichlorobenzene).

A method is available for the isolation of strontium from spent solutions in the nuclear reactors in atomic power stations,[70] where ^{90}Sr is extracted with a solution of crown-ether in chloroform, benzene, toluene, or alkanes at pH 2–6 after adding picric acid, trialkylphenol, or phenyltetrazoline-5-thione. This method makes it possible to separate strontium from potassium, lead, silver, and mercury usually present in the solutions.

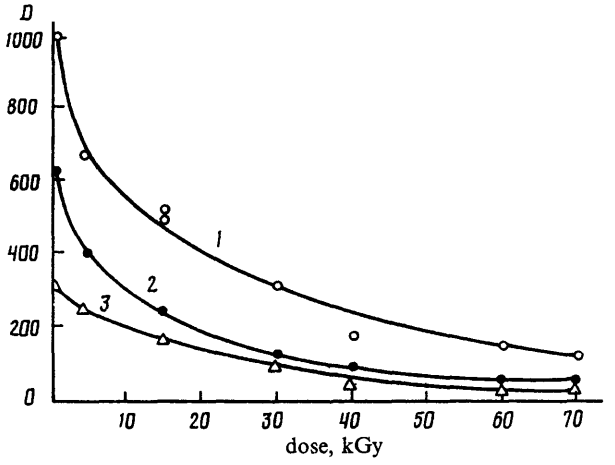


Figure 1. The effect of the absorbed radiation dose on the partition coefficient in the extraction of strontium by irradiated solutions of DCH18C6 in chloroform. Molar crown-ether concentration: *1*, 0.05; *2*, 0.01; *3*, 0.005. ^{60}Co γ-radiation dose rate 24 Gy s^{-1}.[71]

The results of a study[71] of the extraction of strontium from aqueous solutions of picric acid with solutions of crown-ethers in chloroform subjected to ^{60}Co γ-irradiation are of interest in this connection. It was established that the partition coefficient *D* decreases significantly in the dose range up to 70 kGy for DCH18C6 (Fig. 1). Similar relations were observed also for solutions of 18C6 (Fig. 2), DB18C6, DB24C8, and D15C5 in chloroform, the effectiveness of the extractant decreasing in the sequence DCH18C6 > 18C6 > DB24C8 > DB18C6 > B15C5. This effect is due to the radiolytic reactions of chloroform, since the radioactive degradation or dehydrogenation of the crown-ether was not observed.

Comparison of the ^1H NMR spectra of pure DCH18C6 and of the crown-ether irradiated in chloroform (70 kGy) shows that either chlorination (1 or 2 halogen atoms) takes place or the complex H^+DCH18C6)Cl^- is formed under the influence of irradiation. However, later results of the study of γ-radiolysis of solutions of B15C5 in chloroform[72] failed to confirm the occurrence of radical reactions of the crown-ether and Cl atoms with formation of products mono- or di-chloro-substituted in either the aromatic or the polyether ring. On the basis of NMR and mass-spectrometric data, it was postulated that the radiolysis of chloroform containing B15C5 results in the formation of complexes of the type (H^5B15C5)Cl^- and (H^+B15C5)Cl^-_2 (the appearance of the red-violet colour on irradiation of the solution is attributed to this). The macrocycle decomposition products were not identified, although the appearance of carbonyl groups resulting from the opening of the polyether ring was detected by IR spectroscopy.

After the chloroform has been removed by evaporation from the irradiated DCH18C6 solution, the residue, dissolved in a fresh portion of choroform, was used to extract strontium.[71] In this case, the partition coefficient (D = 442) proved to be much higher than that obtained in the extraction of strontium with a solution of DCH18C6 in irradiated chloroform (D = 54). Evidently the decrease in the partition coefficient *D* is not a result of the reactions of the extractant. The data obtained[71,72] show that the main factor inducing the sharp decrease in the partition coefficient is the formation of HCl in the radiolytic decomposition of chloroform. Other products of the radiolysis of the latter influence the partition coefficient to a lesser degree. The formation of C_2Cl_6 diminishes the dielectric constant of the solvent, leading to a lower value of *D* at high concentrations. Comparison of the dose dependence of the partition coefficient *D* for 18C6 dissolved in irradiated chloroform and for the irradiated solution of this crown ether (Fig. 2) emphasises yet again that the decisive factor in the decrease of the effectiveness of the extraction is radiation-chemical processes occurring in the diluent.

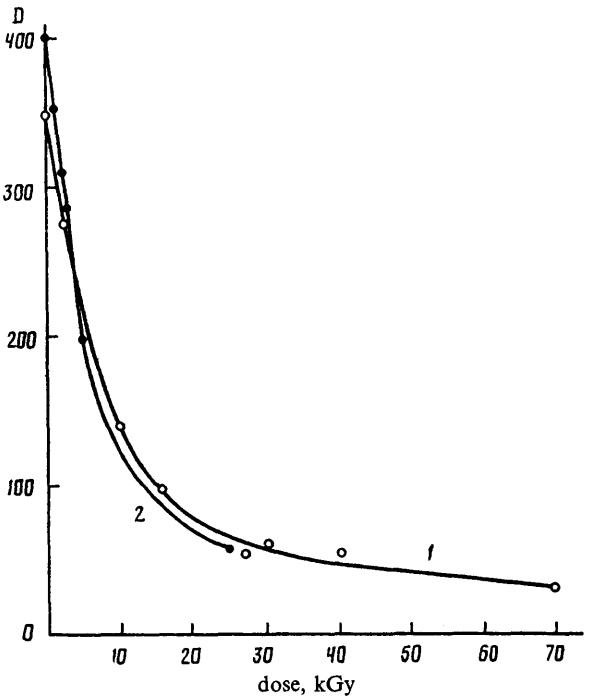


Figure 2. The effect of the absorbed γ-radiation dose on the partition coefficient in the extraction of strontium by an irradiated 0.1 M 18C6 solution in chloroform (curve *1*) and 0.13 M solution of 18C6 in chloroform subjected to preliminary irradiation (curve *2*).[71]

Interesting results were obtained in the study of the influence of γ-radiation on the ionophoric capacity of the ligand in the transfer of alkali and alkaline earth metal ions through a liquid membrane consisting of a 1×10^{-3} M solution of 18C6 in chloroform.[73] The

irradiated membrane has the greatest effect on the transport of cations in the case of caesium and barium (Table 1). The selectivity in the transport of ions shifts from K^+ to Cs^+ and from Sr^{2+} to Ba^{2+} under the influence of radiation. A similar effect has also been noted for another ligand—1,10-phenanthroline. The authors[73] have not reached unambiguous conclusions concerning the causes of the observed phenomenon and note that it can be due both to radiolytic reactions of the ligand and to a change in the properties of the organic phase, in particular the formation of HCl. The rate of the membrane transport is related directly to the extraction properties of the metal ion in the systems considered.

Table 1. The effect of γ-irradiation on the membrane transport of cations from 1×10^{-3} M aqueous solutions of picrates.[73]

Cation	Concentration of cation transferred to the aqueous phase 10^6C, M		$10^6\Delta C$, M
	non-irradiated 18C6–$CHCl_3$ system	irradiated* 18C6–$CHCl_3$ system	
Li^+	0.044	0.196	0.152
Na^+	0.399	0.458	0.115
K^+	8.900	11.970	3.070
Cs^+	7.640	21.840	14.200
Mg^{2+}	0.135	1.00	0.865
Ca^{2+}	0.360	3.990	3.650
Sr^{2+}	5.120	10.330	5.210
Ba^{2+}	6.790	18.680	9.100

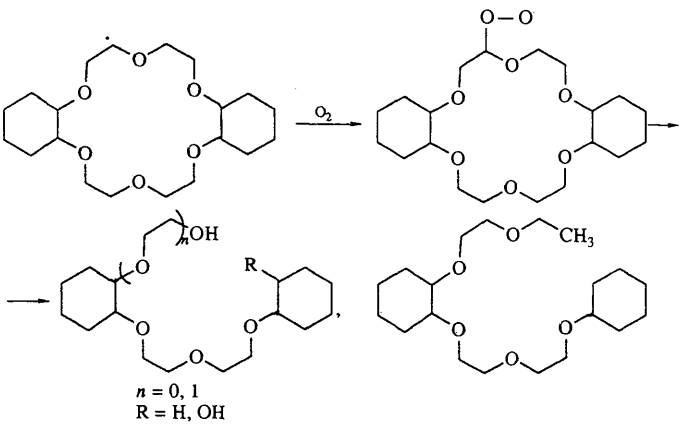
*The 1×10^{-3} M 18C6 solution in chloroform was irradiated from a ^{60}Co γ-source. Dose rate 1.5 Gy s^{-1}, absorbed dose 450 Gy.

An appreciable increase in the radiation-chemical yield $G(HCl)$ on passing from the individual compounds to two-phase aqueous organic systems has been noted for trichlorobenzene and tetrachloroethane.[74] The presence of the crown-ether DCH18C6 or DB18C6 leads under these conditions to an appreciable decrease in $G(Cl^-)$. This can be explained by the proton-solvating properties of the crown-ethers and their ability to form complexes of the type DCH18C6.HCl.

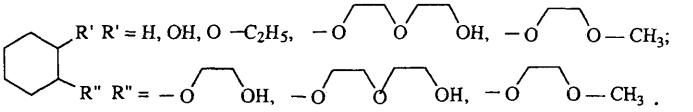
The presence of lanthanum(III) nitrate does not affect the accumulation of Cl^- ions in the 0.1 M crown-ether in tetrachloroethane–3 M HNO_3 extraction system.[75] The radiation-chemical reactions of DCH18C6 and DB18C6 in such aqueous organic systems have been examined.[76] The products of the radiolysis of the crown-ethers after irradiation from a ^{60}Co γ-source (absorbed dose ~100 kGy) were identified with the aid of UV, IR, and ^1H NMR spectroscopy. On the basis of the data obtained, in combination with the results of elemental analysis, the authors[76] proposed a probable mechanism of the formation of nitro- and chloro-derivatives of the products of the radiolysis of macrocyclic polyethers in the extraction system containing tetrachloroethane.

Further studies of the qualitative composition and of the pathways leading to the formation of the products of the radiolysis of DCH18C6 forming part of the 0.1 M DCH18C6 in 1,1,2,2-tetrachloroethane–3 M HNO_3 model extraction system by chromatograph-linked mass spectrometry[77,78] made it possible to refine the process mechanism. More than 40 products of the reactions of the crown-ether were identified and it was established that their structure is determined to a large extent by the nature of the diluent and the composition of the aqueous phase of the extraction system. The proposed mechanism of the radiation-chemical reactions of DCH18C6 includes five main product formation pathways.

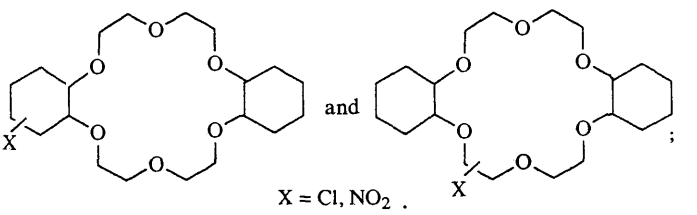
The radical with the unpaired electron localised on a carbon atom of the macrocycle, produced in the first stage, can interact with oxygen, further reactions of the peroxide radical formed leading to the appearance of degradation products (pathway *1*) with partial retention of the polyether bridge between the cyclohexane rings.



Further degradation to products containing only one cyclohexane fragment is postulated (by analogy with the behaviour of the peroxide radicals of ethers).

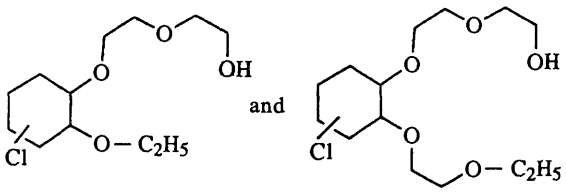


The formation of different chloro- and nitro-substituted crown-ethers



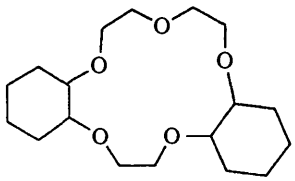
is a result of the reactions of the products of the radiolysis of tetrachloroethane and HNO_3 with DCH18C6 (pathways *2* and *3*).

For the chloro-derivatives, degradation with formation of structures of the type

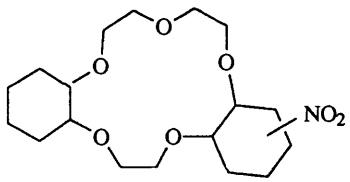


is also postulated.

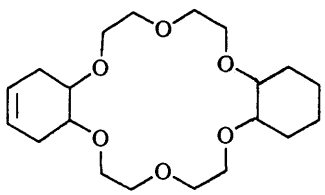
The decomposition of the crown-ether with loss of the epoxyethane fragment and retention of the ring



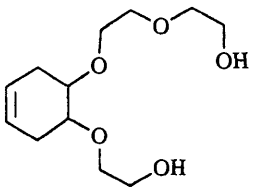
in the case of the liquid-phase radiolysis of DCH18C6 (pathway *4*) is probably analogous to the previously observed process occurring under electron impact in the mass spectrometer[79] and also leads, according to the authors,[78] to the appearance of nitro-substituted cyclic structures.



The partial dehydrogenation of the cyclohexane ring in the DCH18C6 molecule (pathway *5*) leads to the corresponding unsaturated compounds

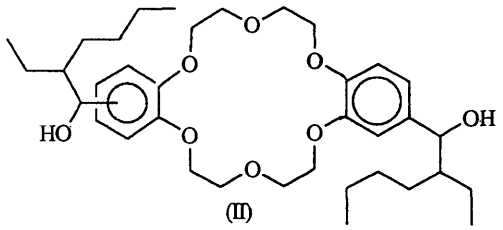


and subsequent fragment of the type



In addition, monocyclohexyl-substituted crown-ethers and the products of the methylation of DCH18C6 were identified in the irradiated extraction system.

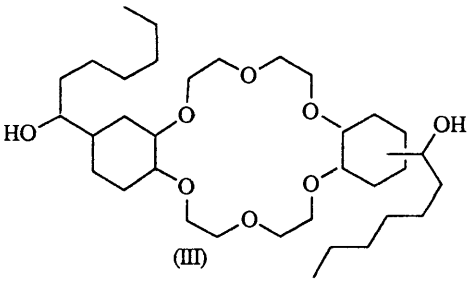
Another approach to the extraction of caesium and strontium from solution in nitric acid with the aid of crown-ethers has been used by Schulz and Bray[80] and Bowers and co-workers.[81,82] They used for the extraction four-component organic systems containing tributyl phosphate (28 vol.%), dinonylnaphthalenesulphonic acid (NNS) or didodecylnaphthalenesulphonic acid (5 vol.%), a macrocyclic polyether (0.05 M), and a hydrocarbon diluent (kerosene, 68 vol%). In these systems, dinonylnaphthalenesulphonic acid is used to substitute the relatively hydrophilic nitrate by a much more lipophilic anion, which increases the partition coefficient of strontium. Tributyl phosphate acts as a modifying agent, inhibiting the formation of a third phase and increasing the solubility of the crown-ether and dinonylnaphthalenesulphonic acid. It is recommended that 4,4′(5′)-bis(2-ethyl-1-hydroxyhexyl)benzo-18-crown-6 (II) be used for the effective extraction of caesium.



(II)

In this case, about 60% of the caesium is transferred from the spent model solution to the organic phase, whereas for solutions of a number of other crown-ethers the above quantity is only approximately 30%.[82]

Similarly, the selective extraction of strontium is promoted by the presence of 0.02 M 4,4′(5′)-bis(1-hydroxyheptyl)cyclohexano-18-crown-6 (III) in the four-component system.



(III)

It was established in comparative experiments that, when the TBP–NNS–crown-ether (II) or (III)–kerosene system is irradiated from a ^{60}Co γ-source up to an absorbed dose of 100 kGy, the partition coefficient of caesium falls from 1.6 to 1.0 and that of strontium diminishes from 2.0 to 1.6.[81]

The selective isolation of Sr^{2+} and Cs^{+} from nitric acid solutions with the aid of liquid membranes containing dinonylnaphthalenesulphonic acid and DCH18C6 dissolved in n-dodecane has been described.[83] The likely usefulness of immobilised liquid membranes for the regeneration and separation of strontium and caesium ions in industry and in analytical chemistry has been demonstrated. The crown-ether DCH18C6 and its derivatives have found applications in the extraction[84–87] and extraction-chromatographic[88–90] isolation and concentration of strontium radioisotopes in the analysis of waste waters, biological samples, and objects in the environment. With the

aid of DB24C8 and dichloromethane as the diluent, it is possible to separate caesium not only from alkali and alkaline earth metals but also from zirconium, hafnium, thorium, lead, bismuth, and other elements usually present in fission products.[91] Sorbents and membranes based on crown-ethers immobilised on different carriers and designed for the extraction and concentration of the ^{137}Cs and ^{90}Sr radionuclides from the alkaline waste produced by atomic power stations have been investigated[92,93] and optimum conditions for the selective transport of the $^{137}Cs^+$ ions through the crown-ether-containing membrane have been developed.

The latest studies by Horwitz and co-workers[94,95] showed that strontium can be effectively extracted from nitric acid by the crown-ether DCH18C6 or its derivatives in various oxygen-containing aliphatic diluents (for example, in alcohols and ketones), which are less toxic than chlorine-containing solvents and do not form corrosive HCl on radiolysis.

Table 2. The effect of radiolysis on the extraction system of the SREX process.[95]

Absorbed dose*, kGy	Partition coefficient of strontium D	
	0.01 M HNO_3	3 M HNO_3
0	0.020	39.6
116	0.056	41.5
244	0.080	36.3
317	0.038**	27.0**
321	0.12	18.5
386	0.11	14.1

* γ-radiation dose rate from a ^{60}Co source 0.7 Gy s^{-1}.
** The values obtained for a 0.2 M solution of DBC18C6 in 1-octanol subjected to preliminary irradition are presented.

In a new process,[95] called SREX, which has many advantages over the methods proposed earlier, the selective extraction of strontium from acid spent solutions is achieved using a 0.2 M solution of di-t-butylcyclohexano-18-crown-6 (DBC18C6) in 1-octanol. It has been shown experimentally that 99.7% of the strontium present initially in the solution can be extracted after only three extraction cycles. Table 2 summarises the results of the study of the influence of γ-radiolysis on the effectiveness of the SREX process. For absorbed doses not exceeding 240 kGy, the partition coefficient of strontium between the organic phase and 3 M HNO_3 does not change appreciably, but for higher doses D falls significantly and at ~390 kGy it diminishes by a factor of almost three compared with the initial value. On the other hand, the data obtained for 0.01 M HNO_3 show that, even for the lowest absorbed radiation dose investigated, the system undergoes radiolytic reactions leading to an almost threefold increase in the partition coefficient. It has been noted that radiolysis does not impair the selectivity of the strontium extraction process.

In connection with the high radiation stability of crown-ethers noted in a number of studies,[7,12,71,72] Horwitz, et al.[95] decided to check whether the observed change in the partition coefficient is merely a consequence of the radiation-induced degradation of the diluent. For this purpose, a 0.2 M solution of DBC18C6 was prepared in 1-octanol subjected to preliminary irradiation (317 kGy) and the strontium partition coefficients were determined. The measured values of D for 0.01 and 3 M HNO_3 occupy an intermediate position between the values obtained for the initial solution and the irradiated solution used in the extraction process. Thus the radiolysis of the system entails the degradation of both the diluent and the extractant. In the absence of other data apart from the measured partition coefficients, it is impossible to establish definitely the nature of the influence of the irradiation on the extraction system, although the rupture of the crown-ether ring and the formation of hydrocarbons with a smaller chain length and low-molecular-weight alcohols and aldehydes from 1-octanol is likely. It is important to note that the absorbed radiation doses used in the experiments appreciably exceed the values which may be expected in the processing of real radioactive liquid waste. Consequently, the radiation-chemical reactions do not create serious obstacles to the extraction process over a long period.

The complexity of the radiation-chemical behaviour of crown-compounds in multicomponent two-phase aqueous organic extraction systems used under the conditions of the industrial processing of radioactive materials necessitates a profound study of the mechanisms of the formation of the main products of the radiolysis of the extractants on the basis of simpler systems,[96] which may permit the determination of the details of the reaction mechanisms presented above as well as similar mechanisms.

It is therefore useful to examine in the Sections below the radiolysis of individual crown-compounds as well as their aqueous and non-aqueous solutions.

III. Radiolysis of macrocyclic polyethers

As a rule, the description of the radiation-chemical reactions in various systems is usually begun with the consideration of the primary radiolysis products and the reactive intermediates participating in such reactions. It has been shown that the products of this kind in liquid polar media are solvated electrons, various ions, free radicals, and excited molecules.[24] However, the available information about the primary products of the radiolysis of crown-ethers and their analogues is so far scanty and does not permit the formulation of a detailed picture of the primary processes occurring.

The formation of solvated electrons in the radiolysis of liquid crown-ethers has been observed by a pulse method in relation to 12C4 and 12C5.[97,98] The optical spectrum of e^-_{solv} in 12C4, obtained in the pulse radiolysis of the pure crown-ether, is illustrated in Fig. 3. The assignment of the peak in the wavelength range between 1100 and 1500 nm to e^-_{solv} is based on the complete disappearance of this peak when the solution is saturated by the N_2O electron acceptor. The wavelength at the absorption maximum of the solvated electron in 12C4 is close to the corresponding wavelength in ammonia (1504 nm).[97]

When 15C5 is subjected to pulse radiolysis and also when metallic potassium and caesium are dissolved in it, a very broad absorption band (from 0.8 to 1.8 μm) predominates in its near IR optical spectrum. By analogy with pulse radiolysis data for pure 15C5, the band was assigned to the solvated electron e^-_{solv}. The spectra of the

potassium solutions show a shoulder at 0.85 μm, which is characteristic of the K^- anion. On the other hand, solutions of alkali metals in 12C4 do not exhibit an appreciable absorption due to the solvated electron (Fig. 4). Instead, the presence of appreciable concentrations of the alkali metal anion is manifested in the spectrum. It is of interest to note that solutions of metals in 15C5 are less stable than their analogues in 12C4. Studies by pulse radiolysis showed that the rate constant for the first-order reaction involving the disappearance of the electron in 15C5 ($\sim 5 \times 10^6$ s^{-1}) is appreciably lower than in 12C4 ($\sim 2.5 \times 10^7$ s^{-1}).,[98] i.e. the solvated electron is longer-lived (or is more solvated) in liquid 15C5 than in the smaller ionophore 12C4.[99]

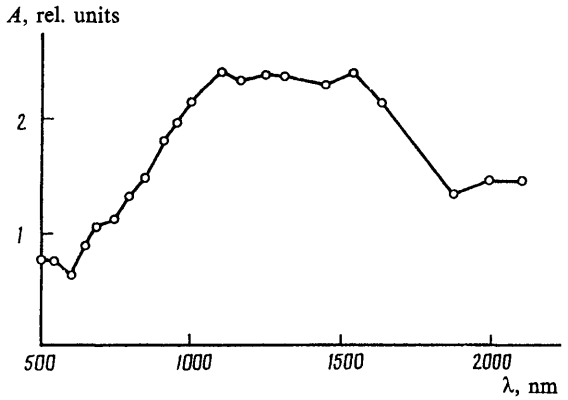


Figure 3. The optical spectrum of the solvated electron obtained on pulse radiolysis (0.2 μs) of 12C4 at room temperature.[97]

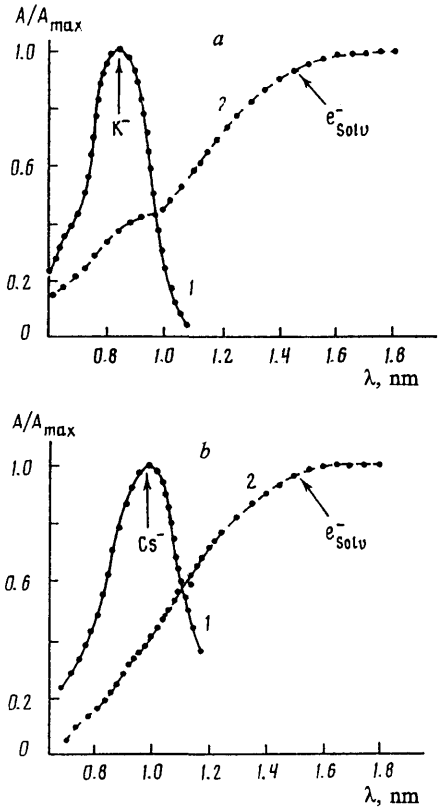


Figure 4. The optical absorption spectra at room temperature of metallic potassium (*a*) and caesium (*b*) dissolved in 12C4 (curves *1*) and 15C5 (curves *2*).[98]

Table 3. The radiation-chemical yields of molecular hydrogen and stabilised paramagnetic species in crown-ethers (absorbed doses 10–180 kGy).[101]

Crown-ether	$G(H_2)$	G(R)		
	T_{irr} = 77 K	T_{irr} = 77 K	after UV irradiation	T_{irr} = 300 K
18C6	0.3	5.7	5.7	0.8
DCH18C6	0.2	3.3	3.0	0.2
DB18C6	0	1.9	1.6	–

The radical intermediates formed in the low-temperature γ-radiolysis of a number of crown-ethers and their analogues with different ring sizes[100] as well as crown-ethers having an 18-membered macroheterocycle with different substituents[101–103] have been investigated by EPR spectroscopy. The results of the study of the primary products of the radiolysis of the polyethers 18C6, DCH18C6, and DB18C6 as well as mass-spectrometric data are presented in Table 3.

The introduction of substituents into the macrocycle leads to an appreciable change in the EPR spectra of the irradiated compounds and the specimens become coloured brown. The effect of UV radiation leads to the decolorisation of the specimen and to the disappearance of one of the spectral lines, which permits its assignment to stabilised electrons. After the "annealing" of the stabilised electrons, the concentration of the paramagnetic species does not increase. On raising the temperature to the melting point of the crown-ethers, the EPR spectra vanish. The appearance of a yellow colour and the presence of stabilised electrons in the irradiated 12C4, 15C5, DCH18C6, and their analogues tetrahydrofuran (THF) and 1,4-dioxane (the smallest member of the family of cyclic epoxyethane oligomers), has also been observed in the study of Kuruc and Sersen,[100] who also noted the instability of the radical intermediate at temperatures above 297 K.

The inconsistency between the radiation-chemical yields of molecular hydrogen and of the paramagnetic species formed (Table 3) and also the complexity of the EPR spectra of the irradiated crown-ethers are a consequence of the simultaneous occurrence during radiolysis of several primary processes, the main one being, according to the authors,[101–103] the rupture of the macrocycle at the C–O bonds. However, Kuruc and Sersen[100] believe that the formation of radicals containing the $-O-\dot{C}H-CH_2-$ fragment is more likely in the given instance, by analogy with the reactions in dioxane and THF.

The EPR study of γ-irradiated solutions of 1,4-dioxane in Freon matrices permitted the conclusion that the primary radical-cation undergoes an ion-molecule reaction with a neutral molecule and leads to the formation of a radical, resulting from the α-abstraction of hydrogen, and of a protonated dioxane molecule.[104] Other data[105] show that the THF radical-cations in the ground state, generated in freon matrices, are resistant to ring rupture reactions, but in the parent compound matrix the radical-cations, having an excess energy, are capable of forming radicals as a result of ring rupture.

In the case of mono- and di-alkyl derivatives of DB18C6, the abstraction of a H atom from the CH_2 groups of the macrocycle and the alkyl substituents in the crown-ether has been postulated.[102,103] The C-centred nature of the radicals is confirmed by the results of a study by the spin trapping method,[106] since it was established that the EPR spectra of the radical adducts formed on capture by the spin-trapping agent of the crown-ether radicals (generated at 77 K) on heating the specimen and measuring the spectrum at room temperature as well as the spectra of the radical adducts observed on irradiation at room temperature are identical. The EPR spectra of the radicals generated at 77 K, measured at the same temperature in the presence of a spin-trapping agent are consistent with the spectra of the pure crown-ethers.

The analysis of the EPR spectra obtained after irradiating the crown-ethers 12C4, 15C5, DCH18C6, as well as THF and 1,4-dioxane in the presence of a spin-trapping agent established the formation of spin adducts with H atoms and C-centred radicals. Under these conditions, it cannot be that the radical centre is located on the polyether or cyclohexane ring of the substituted macrocycle. We may note that in the case of THF two spin adducts are detected, which indicates the formation of both α- and β-radicals.[105]

Table 4. The radiation-chemical yields of free radicals in organic compounds at 77 K.[109]

Compound	*G*(R), radical/100 eV
Ethanol	4.0
Ethylene glycol	5-6
Diethyl ether	3.7
THF	1.7
Furan	1.1
Trioxane	1.1
Tetrahydropyran	4
Cyclohexane	3.8
Benzene	0.15

The introduction of substituents, especially aromatic rings, into the polyether ring increases the radiation stability of the crown-ethers as a result of the intramolecular energy transfer from the macrocycle to the substituent.[100-103]

The effect of γ-radiation on solid complexes of crown-ethers with metal salts has been investigated by EPR spectroscopy.[107,108] The radiation-chemical yields of the radicals were measured for $MgCl_2$.18C6, $CaCl_2$.18C6, and $CaCl_2$.15C5. They are 3.3, 8.1, and 3.1 radical/100 eV respectively. The presence of atomic hydrogen was detected in the irradiated specimens of $FeCl_3$.18C6 and $FeCl_3$.15C5.[108] It was noted that the radiation-chemical processes in the molecular complexes of the crown-ethers are determined not only by the nature of the macrocyclic ligand but to a large extent by the properties of the metal cation.

Comparison of the yields of radicals (Table 3) in crown-ethers irradiated at 77 K with the analogous values obtained at the same temperature for a number of other organic substances[109] (Table 4) does not indicate any kind of unusually high radiation stability of the crown-ethers. Their properties are similar to those of ethers and alcohols. The yields of the final radiolytic products are extremely important for the characterisation of the radiation stability of the compounds (as the factor influencing their practical employment).

The γ-radiolysis of DB18C6, DCH18C6, and 18C6 in the condensed phase in the presence and absence of air has been investigated in a series of studies[7,9,79,101] by gas–liquid chromatography and UV and NMR spectroscopy. No radiolysis products were found under these conditions in the condensed phase in the range of absorbed doses up to 640 kGy. Mass spectrometry of the gas phase of the irradiated crown-ethers made it possible to detect the formation during radiolysis of molecular hydrogen and of traces of epoxyethane (Table 5), but the yields of these products were not quoted.[7,9] Since the irradiation of DB18C6 and DCH18C6 results in the formation of $\sim 7 \times 10^{-5}$ and $\sim 8 \times 10^{-3}$ mol of H_2 per mole of the crown-ether,[7] it was possible to estimate the radiation-chemical yield of hydrogen taking into account the molecular weights of the crown-ethers and the absorbed dose of ionising radiation (~640 kGy). It amounts to ~0.003 molecule/100 eV for DB18C6 and ~0.3 molecule/100 eV for DCH18C6. In a later study by the same workers,[79] yields of hydrogen, amounting to 0.12, ~0.01, and ~0.01 molecule/100 eV were obtained respectively for DCH18C6, DB24C8. The upper limits of the decomposition are ~0.004 and ~0.2 molecule/100 eV for DB18C6 and DCH18C6 respectively.[7]

Table 5. Mass spectra of the gas-phase products of the radiolysis of DCH18C6 and DB18C6 (absorbed dose rate 0.51 Gy s^{-1}, dose ~640 kGy).[7]

m/e	Peak intensity, rel. units		Proposed structure of fragments
	DB18C6	DCH18C6	
2	70	1000	H_2^+
15	10	20	CH_3^+
26	10	10	$C_2H_2^+$
28	10	20	$C_2H_4^+$, CO^+
44	60	50	$C_2H_4O^+$, CO_2^+

In the proposed radiolysis mechanism,[7,79] it is assumed that epoxyethane is formed in a small amount from the cyclic polyether as a result of ion-molecule reactions and that, after the elimination of the C_2H_4O fragment from the molecular ion of the crown-ether,

the opening of the macrocycle does not occur, a cyclic structure with a smaller ring size being formed instead. It is assumed that the source of hydrogen in the irradiation of DCH18C6 is the cyclohexyl fragments.

The study by Langrock, et al.[12] was also devoted to the radiation stability of crown-ethers. They investigated the γ-radiolysis of B15C5, DB18C6, DB24C8, and dithio-18C6 in the presence of air in the temperature range 293–313 K (absorbed dose range 0.1–1 MGy). The yields of the gaseous radiolysis products were determined by gas chromatography and those of the decomposition of the polyethers were found by ^{1}H NMR spectroscopy (Table 6). The authors[12] state that the resistance of the crown-ethers to γ-radiation can be regarded as satisfactory in the dose range up to 0.2 MGy and is acceptable up to 1 MGy. The radiation stability diminishes in the sequence DB24C8, B15C5 > DB18C6 > dithio-18C6. Crown-ethers containing only oxygen heteroatoms in the macrocycle are recommended for practical use in radiochemical separation processes.

Table 6. The yields G of the products of the γ-radiolysis of crown-ethers for an absorbed dose of 0.1 MGy.[12]

Crown-ether	Yields of gaseous products			Yield in the decomposition of the solid substance
	H_2	CH_4	C_2H_6/C_2H_4	
B15C5	0.00145	0.000203	0.000340	0.1428
DB18C6	0.00166	0.000267	0.008193	0.4928
DB24C8	0.00194	0.000239	0.003506	0.1284
Dithio-18C6	0.00206	0.000273	0.069085	0.6466

Table 7. The radiation-chemical yields of the products of the γ-radiolysis of polyethers at different temperatures (dose rate 4 Gy s^{-1}, absorbed doses 2–15 kGy).[110]

Compound	State of aggregation	$G(H_2)$		$G(C_2H_4)$	
		290K	300K	290K	300K
1,4-Dioxane	Liquid	–	1.41	–	0.364
PEG-300	"	1.46	–	0.048	–
PEG-600	Oil	2.06	–	0.043	–
	Liquid	–	1.51	–	0.026
15C5	"	1.60	1.94	0.081	0.158
18C6	Crystalline	2.14	–	0.020	–
	Liquid	1.62	1.85	0.108	0.163
DB18C6	Crystalline	0.175	–	0.014	–
DCH18C6	Oil	1.03	–	0.078	–
	Liquid	0.86	1.18	0.089	0.118

The results of studies on gaseous products of the γ-radiolysis of deaerated specimens of the cyclic polyethers 15C5, 18C6, DB18C6, and DCH18C6, their acyclic analogues—the poly(ethylene glycols) PEG-300 and PEG-600, and also 1,4-dioxane have been described.[110] It was established on the basis of the results of chromatographic analysis that the principal gaseous products are hydrogen and ethylene (Table 7), together with which a small amount of methane (G = 0.012 molecule/100 eV for 15C5) and traces of acetylene and carbon monoxide [G(CO) < 0.002] were detected. The low yield of ethylene formed in the γ-radiolysis of crown-ethers as well as polyglycols, compared with $G(C_2H_4)$, for dioxane is associated with the fact that the probability of the simultaneous dissociation of two C–O bonds in a single $-O-CH_2-CH_2-O-$ unit is greater for the dioxane molecule.

Thus the radiation-chemical behaviour of crown-ethers is similar to that of dioxane and poly(ethylene glycols) and, from the standpoint of radiation stability, macrocyclic polyethers do not differ fundamentally from the acyclic analogues and also from 1,4-dioxane which is in its turn more stable in this respect by a factor of 1.5–2 than, for example, diethyl ether.[109]

Table 8. Kinetic characteristics of the products of the interaction of certain crown-compounds, ethers, and oxygen-containing heterocycles with the primary water radiolysis products.

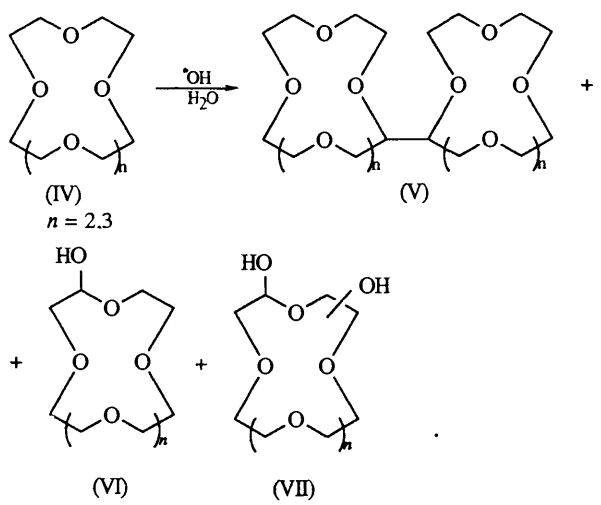
Reaction	Medium	Rate constant, litre mol^{-1} s^{-1}	Rate constant for the recombination of crown-radicals $2k$, litre mol^{-1} s^{-1}	Refs.
18C6+e^-_{aq}	pH 6.7	$4\cdot10^6$	–	[111]
18C6+OH	pH 6.7, sat. N_2O	$6.0\cdot10^9$	$4.0\cdot10^8$	[111]
18C6+H	pH 1.2	$1.9\cdot10^8$	$5.0\cdot10^8$	[111]
18C6+O^-	pH 13.3, sat. N_2O	$5.0\cdot10^9$	$1.0\cdot10^9$	[111]
$KClO_4$.18C6+e^-_{aq}	pH 6.6	$< 10^6$	–	[111]
$KClO_4$.18C6+OH	pH 6.6, sat. N_2O	$1.0\cdot10^{10}$	$5.0\cdot10^8$	[111]
$KClO_4$.18C6+H	pH 1.2	$5.4\cdot10^7$	$5.0\cdot10^8$	[111]
$KClO_4$.18C6+O^-	pH 13.6, sat. N_2O	$9.2\cdot10^9$	$8.0\cdot10^8$	[111]
$NaClO_4$18C6+OH	–	$1.6\cdot10^{10}$		[114]
$NaClO_4$18C6+H	–	$2.5\cdot10^8$	–	[114]
$RbClO_4$.18C6+OH	–	$8.9\cdot10^9$	–	[114]
$RbClO_4$.18C6+H	–	$7.9\cdot10^7$	–	[114]
DCH18C6+e^-_{aq}	pH 6.5	$5.0\cdot10^6$	–	[113]
DCH18C6+OH	pH 6.5, sat. N_2O	$1.0\cdot10^{10}$	$5.0\cdot10^8$	[113]
DCH18C6+H	pH 1.0	$9.0\cdot10^7$	$2.9\cdot10^9$	[113]
DCH18C6+O^-	pH 13.5, sat. N_2O	$3.0\cdot10^9$	$3.6\cdot10^8$	[113]
C[2.2.1]+OH	sat. N_2O	$5.2\cdot10^9$	–	[115]
C[2.2.2]+OH	ditto	$6.0\cdot10^9$	–	[115]
$Cd(ClO_4)_2$C[2.2.1]+e^-_{aq}	–	$1.0\cdot10^{10}$	–	[115]
$Cd(ClO_4)_2$.C[2.2.2]+e^-_{aq}	–	$7.7\cdot10^8$	–	[115]
Ethyl ether+e^-_{aq}	–	$< 10^7$	–	[116]
Ethyl ether+OH	pH 1.2–7	$2.6\cdot10^9$	–	[116]
Ethyl ether+H	pH 1	$4.7\cdot10^7$	–	[116]
Dioxane+H	pH 2–9	$2.2\cdot10^9$	–	[116]
Dioxane+H	pH 1	$1.3\cdot10^7$	–	[116]
THF+OH	pH 9	$2.7\cdot10^9$	–	[116]
THF+H	pH 1	$7.8\cdot10^7$	–	[116]
1,2-Diethoxyethane+OH	pH 9	$2.2\cdot10^9$	–	[116]

IV. Radiation-chemical reactions in solutions of crown-compounds

1. Radiolysis of crown-ethers in aqueous solutions

Aqueous solutions of crown-ethers have been the objects of study by pulse radiolysis.[111–114] The study of the interaction of 18C6 (as well as its complexes with alkali metal perchlorates) and DCH18C6 with the primary water radiolysis products showed that crown-ethers exhibit a high reactivity in relation to hydrogen atoms and OH and O^- radicals and are significantly less reactive in relation to hydrated electrons (Table 8). It has been found[111,113] that at pH 6.5–6.7 the radiation-chemical yield of hydrogen is 0.9 molecule/100 eV both for 18C6 and DCH18C6, i.e. is close to the sum $G(H) + G(H_2) = 1.0$ in the radiolysis of pure water. In acid solutions (pH 1.0), the yield of hydrogen is $G(H_2) = 3.8$ molecule/100 eV for 18C6 and 3.0 molecule/100 eV for DCH18C6, i.e. is close to the sum of the yields $G(H) + G(H_2) + G(e_{aq}) = 4.1$. On this basis, it was concluded that hydrogen atoms interact with crown-ethers in the dehydrogenation reaction.

It follows from the identity of the optical absorption spectra of the short-lived products (λ_{max} = 260 nm) in acid as well as neutral and alkaline solutions of crown-ethers that H atoms, OH radicals, and O^- radical-ions dehydrogenate the polyether molecule with formation of the same radical. On the basis of EPR spectroscopic data, it is claimed[111,113] that both in the radiolysis of aqueous solutions of 18C6 and in the case of DCH18C6 the radical centre is located on the carbon atom of the polyether ring $-O-CH_2-CH-O-$, while the cyclohexyl groups in DCH18C6 are not involved to an appreciable extent. This mechanism has been confirmed also in the study of the dehydrodimerisation of crown-ethers in aqueous solution in the presence of hydrogen peroxide and iron(II) sulphate:[117]



Apart from the dimerisation products (V), the hydroxy-substituted crown-ethers (VI) and (VII) were isolated from the reaction mixture. The formation of the latter is possible as a result of the recombination of the corresponding radicals. Compounds (V)–(VII) are colourless oily substances whose composition and structure have been confirmed by elemental analysis, ^1H NMR, and mass spectrometry.[117]

It has been established[111,114] that absorption with $\lambda_{max} \simeq 260$ nm arises also in the pulse radiolysis of solutions of complexes of alkali metal perchlorates with 18C6. The presence of the potassium ion increases the rate constant for the reaction of the OH radical with the crown-ether but reduces the rate constant for the reaction of the H atom (Table 8). The disappearance of crown-radicals obeys the kinetic equation for second-order reaction (the values of $2k$ are listed in Table 8). Thus the presence of the alkali metal ion does not affect the mechanism of the interaction of OH and H radicals with the macrocyclic ligand and the reaction results in the appearance of analogous crown-radicals. On the other hand, the nature of the cation bound in the complex influences the reactivity of the crown-ether. It follows from the data in Table 8 that the rate constants for the interaction with the OH radical diminish from sodium to rubidium. Such variation is probably associated with the decrease in the energy of the C–H bond in the metal complex of the crown-ether as a consequence of the polarisation of the C–O bonds, which is greater the smaller the ionic radius of the metal.

Table 9. The rate constants for the reactions of complexes incorporating macrocyclic tetraaza-ligands with the primary water radiolysis products in aqueous solutions.

Reaction	Medium	Rate constant, litre mol^{-1} s^{-1}	Refs.
$[Mn(L^2)Cl_2]^+ + OH$	sat. N_2O	$5.2\cdot10^9$ ($125\cdot10^3$)*	[118]
$[Mn(meso\text{-}L^5)Cl_2]^+ + OH$	"	$3.1\cdot10^9$ ($5.0\cdot10^3$)*	[118]
$[Mn(rac\text{-}L^5)Cl_2]^+ + OH$	"	$1.9\cdot10^9$ ($9.0\cdot10^3$)*	[118]
$Ni(L^1)(ClO_4)_2 + OH$	pH 3.3, sat. N_2O	$3.5\cdot10^9$	[119]
$Ni(L^1)(ClO_4)_2 + e^-_{aq}$	pH 6.0, sat. Ar	$3.3\cdot10^{10}$	[120]
$Ni(L^2)(ClO_4)_2 + e^-_{aq}$	"	$3.8\cdot10^{10}$	[121]
$Ni(L^3)(ClO_4)_2 + OH$	pH 3.3 sat N_2O	$4.0\cdot10^9$	[119]
$Ni(L^3)(ClO_4)_2 + e^-_{aq}$	pH 5.5, sat. Ar	$1.2\cdot10^{10}$	[120]
$Ni(L^4)(ClO_4)_2 + e^-_{aq}$	pH 6.0, sat. Ar	$1.2\cdot10^{10}$	[121]
$Ni(meso\text{-}L^5)(ClO_4)_2 + e^-_{aq}$	pH 6–10, sat. Ar	$5.6\cdot10^{10}$	[122]
$Ni(meso\text{-}L^5)(ClO_4)_2 + H$	pH 1.0, sat. Ar	$3.2\cdot10^8$	[122]
$Ni(meso\text{-}L^6)(ClO_4)_2 + e^-_{aq}$	pH 6.0, sat. Ar	$8.7\cdot10^{10}$	[121, 123]**

*The rate constants (k, s^{-1}) for the decomposition of the manganese(IV) complexes formed are indicated in brackets. Their final decomposition reaction product is manganese(IV) oxide.[118]

**Certain spectroscopic characteristics of the complex $[Ni(L^6)]^+$, obtained on γ-irradiation of a solution of $Ni(L^6)(ClO_4)_2$ (saturated with helium at pH 7.6) with a dose of ~0.5 kGy have been published.[124]

Reduction of the cadmium(II) complexes of the cryptands [2.2.1] and [2.2.2] {C[2.2.1] and C[2.2.2]} by hydrated electrons has been investigated by pulse radiolysis.[115] The study of the interaction of

the primary water radiolysis products with cryptands showed that there are reactions of the OH radical (with abstraction of a hydrogen atom from a C—H bond in the cryptand) which are virtually controlled by diffusion (Table 8), while the reactions of the hydrated electron with C[2.2.1] and C[2.2.2] have not been observed. The hydrated electron reacts with the cadmium ion as follows:

$$e^-_{aq} + Cd^{2+} \rightarrow Cd^+.$$

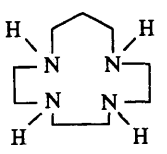
The rate constant for this reaction involving the aqueous $Cd(ClO_4)_2$ solution is $k_{\Psi=0} = 4.8 \times 10^{10}$ litre mol^{-1} s^{-1} after extrapolation to zero ionic strength. In solutions of cadmium(II) perchlorate in the presence of an excess of the cryptand, the disappearance of hydrated electrons via the reactions

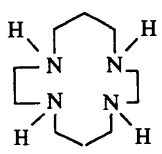
$$e^-_{aq} + [Cd\{C[2.2.2]\}]^{2+} \rightarrow [Cd\{C[2.2.2]\}]^+,$$

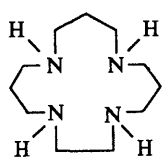
$$e^-_{aq} + [Cd\{C[2.2.1]\}]^{2+} \rightarrow [Cd\{C[2.2.1]\}]^+$$

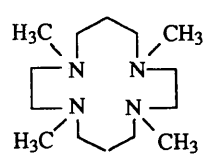
is described by a pseudo-first order kinetic equation; the reaction rate constants are listed in Table 8. The appreciable differences between the reactivities of cadmium cryptates in relation to e^-_{aq} have been related[115] to the crystallographic ionic radii, the size of the cryptand cavity, and the stability constant of the corresponding cryptates.

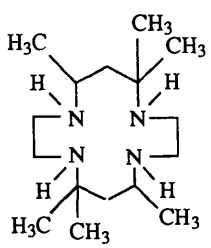
Table 9 lists the kinetic characteristics of certain oxidation-reduction reactions with participation of the primary water hydrolysis products obtained in the pulse radiolysis of solutions of manganese(III) and nickel(II) complexes of cyclam (L^2) and other nitrogen-containing analogues of crown-ethers.

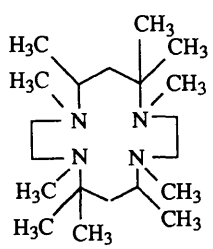

(L^1)


(L^2)


(L^3)


(L^4)


(L^5)


(L^6)

Irradiation of aqueous solutions of 18C6 up to large absorbed doses (0.25 MGy) does not lead to the formation of insoluble products.[113] The formation of compounds containing an aldehyde group with a radiation-chemical yield $G = 0.4$ was established from the results of the chemical analysis of the residue after the removal of water and from IR spectroscopic measurements. The overall yield in the decomposition of 18C6 is 0.6 molecule/100 eV. In aqueous solutions of DCH18C6, starting from a dose of 5 kGy, a pale-yellow deposit is formed. It contains compounds with an aldehyde group which are insoluble in the usual organic solvents. The overall decomposition yield is 0.9 molecule/100 eV for DCH18C6. Since the cyclic structure does not decompose in the stage involving the interaction of the primary water radiolysis products with crown-ethers, it has been suggested[113,114] that the aldehydes are formed in secondary reactions. The aldehydes are probably formed mainly as a result of the interaction of the crown-ether with hydrogen peroxide:

$$-CH_2-\dot{C}H-O-CH_2-CH_2- + H_2O_2 \longrightarrow$$
$$\longrightarrow -O-CH_2-CH_2-O-CHO + \dot{C}H_2-O-CH_2- .$$

Another possible pathway is the disproportionation reaction of the radicals:

$$2\,-CH_2-\dot{C}H-O-CH_2-CH_2- \longrightarrow$$
$$\longrightarrow -CH_2-CHO + CH_2{=}CH-O- +$$
$$+ -CH_2-CH_2-O-CH_2-CH_2- .$$

On irradiation of solutions of DCH18C6, a deposit may appear as a result of the formation of aldehydes and also as a result of the dimerisation of radicals.[113]

We may note that, when poly(ethylene glycols)—high-molecular-weight linear analogues of crown-ethers—are acted upon by radiation in aqueous solutions in the absence of dissolved oxygen, gel formation takes place and the radiation-chemical yield of the cross-linking reaction is 0.27 in 0.5% solution, but the ratio of the cross-linking yield to the polyether chain degradation yield in a neutral medium is 4:1.[125] Degradation predominates in acid solutions. The hydrogen formed in the radiolysis of a 2% solution of poly(ethylene glycol) in D_2O consists mainly of HD (G = 0.59 molecule/100 eV) whereas $G(H_2) = 0.05$ molecule/100 eV. When recalculated in terms of the dose absorbed by the solute, this gives $G(H_2) \simeq 2.5$ molecule/100 eV, which agrees with data[110] for poly(ethylene glycols) (Table 7).

Chain degradation of poly(ethylene glycol) takes place in the presence of oxygen. The reactive products of the radiolysis of the solvent (H, OH) abstract hydrogen from the α-position in the ether linkage and oxygen adds to the macroradical arising in this way and gives rise to a peroxide radical. The chain propagation reaction is that between the peroxide radical and the initial molecule with formation of a hydroperoxide:

$$-CH_2-\underset{\displaystyle O-O^{\cdot}}{\overset{|}{CH}}-O- + -CH_2-CH_2-O- \longrightarrow$$
$$\longrightarrow -CH_2-\underset{\displaystyle O-OH}{\overset{|}{CH}}-O- + -CH_2-\dot{C}H-O- .$$

The decomposition of the hydroperoxide and the recombination of the peroxide radicals afford the alkoxyl radicals $-CH_2-\underset{\displaystyle O}{\overset{|}{CH}}-O-$, which rapidly decompose with rupture of the molecular skeleton.[125,126]

The radiation-chemical reactions of the macrocyclic polyethers examined above may be compared with the behaviour in 0.1 M aqueous solutions of heterocyclic compounds such as 1,3-dioxolans,

1,3- 1,4-dioxanes, etc.[127] The main products of the radiolysis of these compounds are ethylene, carbon monoxide (or dioxide), and aldehydes. The radicals, formed predominantly as a result of the dissociation of the C–H bond in the α-position relative to the heteroatom by the H and OH radical species into five- and six-membered oxygen-containing heterocycles, can rearrange to linear radicals on ring cleavage. However, among the products of the radiolysis of dioxanes, there are substances whose formation cannot be explained by the occurrence of the above processes. The initial radical species derived from dioxanes can decompose, as in the case of 1,3-dioxolans, in accordance with a concerted mechanism (with the simultaneous dissociation of two bonds), which results in the formation of the degradation products. The occurrence of this process in the radiolysis of 1,4-dioxane leads to the formation of acetaldehyde (G = 0.03 molecule/100 eV). Other products of the radiolysis of this compound are ethylene and CO. Under these conditions, $G(C_2H_4)$ = 0.07 and $G(CO)$ = 0.0014 molecule/100 eV in 0.1 M aqueous solution.[127] The radiation-chemical yields of ethylene and carbon monoxide exceed respectively by one and two orders of magnitude the values which would be expected in the case of the formation of the given compounds as a result of the direct action of γ-radiation on the dissolved 1,4-dioxane (the calculation was performed using the values of G for pure dioxane quoted by Zatonsky and Povolotskaya[110]). Thus the radiation-chemical degradation of the cyclic and macrocyclic ethers in aqueous solutions is associated with the indirect action of ionising radiation.

2. Radiolysis of solutions of crown-compounds in aromatic hydrocarbons

Together with the systems, examined in Section II, based on organochlorine solvents, numerous studies, concerned with the radiation-chemical reactions in non-aqueous solutions of crown-compounds, have been devoted to the radiolysis of their solutions in arenes. Aromatic hydrocarbons are much more reactive than aliphatic compounds and solutions of DCH18C6 and other crown-ethers in toluene and benzene are used for the effective extraction isolation from nitric acid solutions of radioactive elements such as uranium(VI) and plutonium(IV).[128]

Table 10. The radiation-chemical yields of the gaseous products of the γ-radiolysis of benzene solutions of crown-ethers.

Crown-ether	Concentration, M	G, molecule/100 eV				Refs.
		H_2	C_2H_2	C_2H_4	CH_4	
–	0	0.038	0.016	–	–	[129]
18C6	0.05	0.046	0.013	0.0010	0.00015	[129]
18C6	0.1*	0.009	–	0.005**	0.002	[130]
18C6	0.05	0.064***	–	0.0020***	0.00018***	–
DBB18C6	0.05	0.045	0.014	0.0027	0.0058	[129]

* Solution of crown-ether in C_6D_6; irradiation in the presence of air.

** The sum of $G(C_2H_4)$ and $G(C_2H_6)$ is quoted.

*** Calculated taking into account the direct effect of radiation on the solute using the corresponding values of G for 18C6 in the liquid state taken from the literature.[110]

Table 10 presents data characterising the radiolytic formation of gaseous products in benzene solutions of crown-ethers. The presence of crown-ethers has only a slight effect on the gas evolution caused by the radiolysis of solvents; the increase in the radiation-chemical yield of hydrogen and the appearance of ethylene and methane are associated in this instance with the direct action of ionising radiation and the solute. This is confirmed by the results of the study of the γ-radiolysis of a solution of 18C6 in fully deuteriated benzene[130] and also by the calculated values of G presented in Table 10. The presence of t-butyl substituents in the molecule of 4,4′(5′)-di-t-butyldibenzo-18-crown-6 (DBB18C6) is responsible for the high yields of ethylene and methane—the polyether degradation products—in a benzene solution of DBB18C6 compared with 18C6.[129] The yield in the radiation-chemical decomposition of 18C6 on γ-irradiation of its solution in C_6D_6 (initial concentration 0.435 M) is ~1.25 molecule/100 eV,[130] which corresponds to the decomposition of about 15% of the compound on absorption of a dose of 1 MGy.

Table 11. The influence of crown-compounds and their complexes on the formation of dimeric benzene γ-radiolysis products.

Additive	Concentration of crown-compound, M	Yield of products G, molecule/100 eV		Refs.
		biphenyl	phenylcyclohexadienes	
–	0	0.120	0.050	[131]
15C5	0.01	0.096	0.052	[131]
	0.1	0.090	0.054	[131]
18C6	0.05	0.080	0.045	[31]
	0.1	0.069	0.037	[31]
DB18C6	0.0001	0.097	0.050	[131]
	0.001	0.101	0.052	[131]
DCH18C6	0.01	0.091	0.042	[131]
	0.1	0.089	0.042	[131]
DBB18C6	0.05	0.091	0.048	[29]
	0.075	0.072	0.032	[132]
DB24C8	0.01	0.106	0.057	[131]
	0.05	0.072	0.044	[131]
C[2.2.2]	0.05	0.060	0.043	[31]
18C6+K	0.05*	0.096	0.000	[31]
	0.1*	0.088	0.000	[31]
18C+KOH	0.1*	0.134	0.000	[132]
18C6+KO_x	0.1*	0.201	0.000	[132]
C[2.2.2]+K	0.05*	0.035	0.000	[31]
DCH18C6+KBr	0.1*	0.118	0.051	[32]
DCH18C6+KI	0.1*	0.115	0.038	[32]
DCH18C6+KOH	0.1*	0.141	0.000	[32]
DBB18C6+$KMnO_4$	0.05**	0.218	0.000	[29]
DBB18C6+KOH	0.05*	0.090	0.051	[132]

* Saturated solution of the inorganic component.

** $KMnO_4$ concentration 0.013 M.

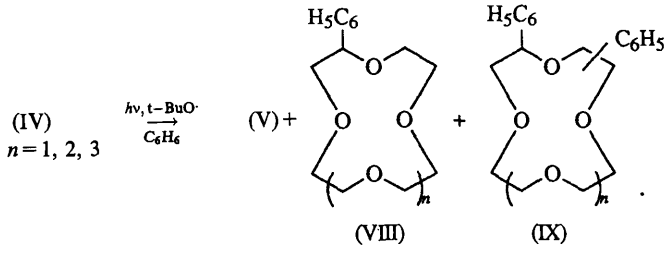
Thus from the standpoint of gas evolution processes and also the degradation of crown-ethers dissolved in benzene, macrocyclic polyethers are extremely radiation-resistant compounds for absorbed

doses not exceeding 200 kGy and can be used for many radiochemical separation processes as selective extractants.

Another process determined by radiolysis and inducing an impairment of the extraction-technological characteristics of the system is the formation of high-boiling products. Studies of the formation of dimeric products of the radiolysis of aromatic hydrocarbons in the presence of various crown-ethers have shown[8,131] that crown-compounds do not induce an additional reaction of the matrix via this pathway. On the contrary, in most cases, they, as it were, protect the solvent against the action of radiation. Examples of a decrease in the yield of biphenyl and phenylcyclohexadienes — the main benzene radiolysis products — in the presence of crown-compounds are presented in Table 11. This effect of crown-ethers agrees with the model of the formation of high-boiling products via the cationic polymerisation mechanism (including the addition of primary arene radical-cations to neutral molecules).[30,31]

Bearing in mind the powerful proton-accepting properties of crown-ethers,[133,134] one may expect the occurrence of reactions involving proton transfer from the molecular arene ion to the polyether molecule. The introduction of benzene rings into the polyether molecule lowers its proton affinity[133] and the effect of dibenzocrown-ethers on the yield of dimeric products is therefore much weaker than that of, for example, 18C6. On the other hand, a cryptand acts more effectively than crown-ethers because it is a stronger proton-solvating agent.

We may note that, although phenyl radicals are in fact formed as a result of the deprotonation of the benzene radical-cation, they may react further with the crown-ether without giving rise to biphenyl and phenyl cyclohexadienes. Thus the decrease in the yield of dimers in the radiolysis of benzene solutions of 1,4-dioxane has been explained[135] by the interaction of phenyl radicals with solute molecules leading to α-abstraction of a hydrogen atom. In the study of the dehydrodimerisation of 12C4, 15C5, and 18C6 in benzene in the presence of t-butyl peroxide, whose decomposition was initiated photochemically, phenyl-substituted crown-ethers (VIII) and (IX), formed on recombination of the corresponding radicals, were isolated and characterised in addition to the expected dimerisation products (V):[117]



Similar processes occur in the radiolysis of toluene in the presence of crown-ethers. Since the deprotonation reaction

$$C_6H_5CH_3^+ \longrightarrow C_6H_5CH_2^{\cdot} + H^+$$

is extremely important for the toluene radical-cations in the liquid phase while the benzyl radicals formed are less reactive than phenyl radicals and are destroyed predominantly as a result of recombination, in the presence of 18C6 there is some increase in the yield of the dimeric radiolysis products. In the case of a solution of DB24C8, the yield of bibenzyl falls somewhat, although the overall yield of the dimers remains unchanged.[131]

Another aspect of the use of crown-compounds in radiation-chemical studies is associated with attempts to act on the processes involving the radiolysis of liquid matrices of aromatic hydrocarbon,[29–32,132,136–138] based on the hypothesis that electron-donating agents present in solution should diminish the probability of the formation of radiolysis products, whereas electron-accepting agents (i.e. substances with oxidising properties) should promote radiolysis. The unique properties of crown-ethers, which make it possible to solubilise inorganic substances of different nature in organic (including hydrocarbon) solvents, provide very extensive possibilities for this purpose.

For example, dissolution of metallic potassium in arenes containing a crown-ether or a cryptand results in the formation of systems with a homogeneous distribution of electron-donating species, namely K^- anions or electrons, which are present in the form of crown-separated pairs $[K^+, L]K^-$ or $[K^+, L]e^-_{solv}$, where L is the macrocyclic ligand. On irradiation of such benzene solutions, the yield of biphenyl is extremely low, while phenylcyclohexadienes are not formed at all (Table 11). The yield of bibenzyl is also significantly reduced in the toluene–18C6–potassium system, while benzylmethylcyclohexadienes are detected only in trace amounts. The inhibition of the formation of dimeric products in the radiolysis of aromatic hydrocarbons, induced by the charge-transfer process (the transfer of an electron to the parent radical-cation)

$$ArH^+ + K^- \longrightarrow ArH + K$$

probably proceeds extremely effectively, because the reactant with a low ionisation potential (the reductant) is not simply the neutral solute molecule but an active weakly solvated electron-donating species bearing a negative charge.[31]

Potassium hydroxide and halides solubilised by crown-ethers do not manifest pronounced reducing or oxidising properties and do not lead to such appreciable inhibition of the formation of dimers,[136,137] while additives with oxidising properties induce the opposite effect. Thus the presence of $KMnO_4$ suppresses the formation of phenylcyclohexadienes, but increases appreciably (by 80%) the yield of biphenyl.[29,138] The electrons arising in the primary radiolytic steps interact with additives of this type, being converted into chemically more inert species and increasing thereby the lifetime of the benzene radical-cations and hence the probability of the occurrence of ion–molecule reactions. The absence of phenylcyclohexadienes is caused by the complete oxidation of their precursors to biphenyl by permanganate ions.

Combination of additives of different types, for example, crown-ethers and spin-trapping agents[139] or crown-ethers and transition metal acetylacetonates,[140,141] in the radiolysis of aromatic hydrocarbons can serve as an extremely effective instrument for the study of the mechanism of the formation of the products. Investigation of the latter systems is of independent importance because the combination of the crown-ether–β-diketone–diluent components is encountered in real extraction systems used for the isolation of radionuclides.[59,142]

References

1. M Hiraoka *Crown-compounds. Their Characteristics and Applications* (Translated into Russian), Mir, Moscow, 1986, 363 pp
2. A V Bogatskii, N G Luk'yanenko, T I Kirichenko *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1985, **30** 487
3. E Weber, F Voegtle, R Hilgenfeld, et al. *Host Guest Complex Chemistry. Synthesis, Structures, Applications* (Edited by F Voegtle, E Weber) (Translated into Russian), Mir, Moscow, 1988, 511 pp
4. I P Shestakova, L V Darda, O V Ivanov *III Vsesoyuznaya Konferentsiya po Khimii i Biokhimii Makrotsiklicheskikh Soedinenii: Tezisy Dokladov. Ivanovo* (The IIIrd All-Union Conference on the Chemistry and Biochemistry of Macrocyclic Compounds. Abstracts of Reports. Ivanovo), Ivanovo, 1988, Part 2, p. 314
5. S Quici, P Anelli *Chim. Oggi*, 1989, 7 49; quoted after *Chem. Abs.*, **112** 178720 d
6. T E Kron, E N Tsvetkov *Usp. Khim.*, 1990, **59**(3) 483 [English translation in *Russ. Chem. Rev.*, 1990(3)]
7. T G Myasoedova, A V Ponomarev, P A Zagorets, E A Filippov *Khim. Vys. Energ.*, 1984, **18** 110
8. V V Makhlyarchuk, S V Zatonskii, I E Mikhailenko, V V Saraeva *Vsesoyuznaya Konferentsiya po Teoreticheskoi i Prikladnoi Radiatsionnoi Khimii: Tezisy Dokladov. Moskva* (All-Union Conference on Theoretical and Applied Radiation Chemistry. Abstracts of Reports. Moscow), Nauka, Moscow, 1984, p. 233
9. T G Myasoedova, M Yu Ikonnikov, E A Filippov *Vsesoyuznaya Konferentsiya po Teoreticheskoi i Prikladnoi Radiatsionnoi Khimii: Tezisy Dokladov. Moskva* (All-Union Conference on Theoretical and Applied Radiation Chemistry. Abstracts of Reports. Moscow), Nauka, Moscow, 1984, p. 59
10. O S Povolotskaya, S V Zatonskii *Vsesoyuznaya Konferentsiya po Teoreticheskoi i Prikladnoi Radiatsionnoi Khimii: Tezisy Dokladov. Moskva* (All-Union Conference on Theoretical and Applied Radiation Chemistry. Abstracts of Reports. Moscow), Nauka, Moscow, 1984, p. 297
11. B G Ershov, A F Seliverstov *II Vsesoyuznaya Konferentsiya po Khimii Makrotsiklov: Tezisy Dokladov i Soobshchenii. Odessa* (The IInd All-Union Conference on the Chemistry of Macrocycles. Abstracts of Reports and Communications. Odessa), Odessa, 1984, p. 157
12. E J Langrock, H Langguth, B Plisch *ZFI-Mitt.*, 1984, (98) 548
13. Z I Nikolotova, Handbook. *Ekstraktsiya Neitral'nymi Organicheskimi Soedineniyami. Aktinoidy* (Extraction by Neutral Organic Compounds. The Actinides), Energoatomizdat, Moscow, 1987, 280 pp
14. C J Pedersen *J. Am. Chem. Soc.*, 1967, **89** 7017
15. C J Pedersen, H K Frensdorff *Usp. Khim.*, 1973, **42**(3) 492 [English translation in *Russ. Chem. Rev.*, 1973(3)]
16. A Yu Tsivadze, A A Varnek, V E Khutorskii *Koordinatsionnye Soedineniya Metallov s Kraun-Ligandami* (Coordination Compounds of Metals with Crown-Ligands), Nauka, Moscow, 1991, 387 pp
17. E V Dehmlow, S S Dehmlow *Phase-Transfer Catalysis* (Translated into Russian), Mir, Moscow, 1987, 485 pp
18. N G Luk'yanenko, A V Bogatskii, T I Kirichenko *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1985, **30** 571
19. C L Liotta *The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues* (Edited by S Patai), Wiley, New York, 1980, Part 1, p. 157
20. B Kaempf, S Raynal, A Collet, et al. *Angew. Chem.*, 1974, **86** 670
21. M A Komarynsky, S I Weissman *J. Am. Chem. Soc.*, 1975, **97** 1589
22. G V Neison, A von Zelewsky *J. Am. Chem. Soc.*, 1975, **97** 6279
23. G Schmid *Chem. Lab. Betr.*, 1976, **27** 121
24. A K Pikaev *Khim. Vys. Energ.*, 1976, **10** 107
25. D J Sam, H E Simmons *J. Am. Chem. Soc.*, 1972, **94** 4024
26. D G Lee *The Oxidation of Organic Compounds by Permanganate Ion and Hexavalent Chromium*, Open Court, La Salle (Ill.), 1980, 174 pp
27. D G Lee, H Karaman *Can. J. Chem.*, 1982, **60** 2456
28. V Holba, J Muchova *React. Kinet. Catal. Lett.*, 1986, **32** 365
29. V V Makhlyarchuk, S V Zatonskii, I E Mikhailenko, V V Saraeva *Izv. Vyssh. Uchebn. Zaved. Khim. i Khim. Tekhnol.*, 1987, **30**(4) 26
30. V V Makhlyarchuk, S V Zatonskii, V V Saraeva *Effektivnoe Vozdeistvie Radiatsii na Organicheskie Reaktsii: Sbornik Nauchnykh Trudov NIFKhI* (Effective Action of Radiation on Organic Reactions. Collected Scientific Reports from the NIFKhI [Karpov Moscow Physicochemical Institute?]), Izd. NIITEKhIM, Moscow, 1989, p. 62
31. V V Makhlyarchuk, S V Zatonskii *Dokl. Akad. Nauk SSSR*, 1990, **313** 1468
32. S V Zatonskii, V V Makhlyarchuk *Vsesoyuznoe Soveshchanie "Mekhanizmy Reaktsii Nukleofil'nogo Zameshcheniya i Prisoedineniya": Tezisy Dokladov. Donetsk*, 1990 (All-Union Conference on "The Mechanisms of Nucleophilic Substitution and Addition Reactions". Abstracts of Reports. Donetsk, 1990), 1991, p. 142
33. B N Laskorin, V V Yakshin *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1985, **30** 579
34. K Gloe, P Mühl, A I Kholkin, et al. *Isotopenpraxis*, 1982, **18** 170
35. W J McDowell *Sep. Sci. Technol.*, 1988, **23** 1251
36. V I Zemlyanukhin, E I Il'chenko, A N Kondrat'ev, et al. *Radiokhimicheskaya Pererabotka Yadernogo Topliva AES* (Radiochemical Processing of Nuclear Fuel from Atomic Power Stations), Energoatomizdat, Moscow, 1989, 280 pp
37. G F Egorov *Radiatsionnaya Khimiya Ekstraktsionnykh Sistem* (Radiation Chemistry of Extraction Systems), Energoatomizdat, Moscow, 1986, 208 pp
38. A K Pikaev *Sovremennaya Radiatsionnaya Khimiya. Tverdoe Telo i Polimery. Prikladnye Aspekty* (Modern Radiation Chemistry. Solids and Polymers. Applied Aspects), Nauka, Moscow, 1987, 448 pp
39. A K Pikaev, S A Kabakchi, G F Egorov *Radiat. Phys. Chem.*, 1988, **31** 789
40. P Vanura *Chem. Listy*, 1990, **84** 141
41. N B Mikheev, A N Kamenskaya *Radiokhimiya*, 1989, **31** 95
42. S A Kulyukhin, A N Kamenskaya, N B Mikheev, L N Auerman *Radiokhimiya*, 1991, **33** 10
43. V V Yakshin, E A Filippov, V A Belov, et al. *Dokl. Akad. Nauk SSSR*, 1978, **241** 159
44. A M Rozen, Z I Nikolotova, N I Kartasheva, et al. *Dokl. Akad. Nauk SSSR*, 1982, **263** 1165

45. A M Rozen *Radiokhimiya*, 1984, **26** 346
46. V V Yakshin, Z K Karalova *Sovremennye Metody Razdeleniya i Opredeleniya Radioaktivnykh Elementov* (Modern Methods for the Separation and Determination of Radioactive Elements) (Edited by B F Myasoedov, A V Davydov), Nauka, Moscow, 1989, p. 104
47. A G Godbole, N V Thakur, Swapur Rajendra, S K Patil *J. Radioanal. Nucl. Chem.: Lett.*, 1987, **108** 89
48. C Jonezawa, G R Choppin *J. Radioanal. Nucl. Chem.: Art*, 1989, **134** 233
49. Cao Wenqi, Luo Wenzong *Yuanzineng Kexue Jishu*, 1987, **21** 456; quoted after *Chem. Abs.*, 1988, **108** 211275e
50. G M Nair, D R Prabhu *J. Radioanal. Nucl. Chem.: Art*, 1988, **121** 83
51. P K Mohapatra, V K Manchanda *Symposium on Radiochemistry and Radiation Chemistry, Nagpur, 5–8 February, 1990*, Preprints, Bombay, 1990, P.AL-05-1
52. P K Mohapatra,V K Manchanda *Radiochim.Acta*, 1991, **55** 193
53. J N Mathur, P K Khopkar *Solvent Extra. Ion Exch.*, 1988, **6** 111
54. N V Deorkar, S M Khopkar *J. Radioanal. Nucl. Chem.: Art*, 1989, **134** 437
55. J P Shukla, K V Lohithakshan *Chem. Scr.*, 1989, **29** 341
56. J Foos, P Epherre, A Guy, et al., European P. 347315; *Chem. Abs.*, 1990, **112** 242036q
57. M Lemaire, A Guy, R Chomel, J Foos *J. Chem. Soc., Chem. Commun.*, 1991, (17) 1152
58. Minh Le Tuong, T Lengyel *J. Radioanal. Nucl. Chem.: Lett.*, 1988, **128** 417
59. Minh Le Tuong, T Lengyel *J. Radioanal. Nucl. Chem.: Lett.*, 1989, **136** 363
60. Jin Jiannan, Jin Shushan, Zhang Chuyuan, et al. *Sichuan Daxue Xuebao, Ziran Kexueban*, 1987, **24** 444; quoted after *Chem. Abs.*, 1988, **108** 211273c
61. M A A Al-Janabi, A H M Kadem *Appl. Radiat. Isot.*, 1990, **41** 787
62. W J McDowell, B A Arndsten, G N Case *Solvent Extr. Ion Exch.*, 1989, **7** 377
63. E Blasius, K-H Nilles *Radiochim. Acta*, 1984, **35** 173
64. E Blasius, K-H Nilles *Radiochim. Acta*, 1984, **36** 207
65. I H Gerow, M W Davis, Jr. *Separ. Sci. Technol.*, 1979, **14** 395
66. I H Gerow, J E Smith, M W Davis, Jr. *Separ. Sci. Technol.*, 1981, **16** 519
67. E Blasius, W Klein, U Schön *J. Radioanal. Nucl. Chem.: Art*, 1985, **89** 389
68. E A Filippov, V V Yakshin, V M Abashkin, et al. *Radiokhimiya*, 1982, **24** 214
69. T G Myasoedova, M Yu Ikonnikov, A V Ponomarev, et al. *Radiokhimiya*, 1987, **29** 180
70. E-J Langrock, H Schlegel, H Langguth, et al. DDR P. 265134; *Chem. Abs.*, 1989, **111** 122634r
71. L Màtel, T Bilbao *J. Radioanal. Nucl. Chem.: Lett.*, 1989, **137** 183
72. L Màtel *J. Radioanal. Nucl. Chem.: Lett.*, 1990, **146** 85
73. V Vijayavergiya, A Mookerjee *J. Radioanal. Nucl. Chem.: Art*, 1989, **134** 39
74. T G Myasoedova, G V Dmitrieva, M Yu Ikonnikov, et al. *Vsesoyuznaya Konferentsiya po Teoreticheskoi i Prikladnoi Radiatsionnoi Khimii: Tezisy Dokladov. Moskva* (All-Union Conference on Theoretical and Applied Radiation Chemistry. Abstracts of Reports, Moscow), Nauka, Moscow, 1984, p. 258
75. T G Myasoedova, G V Dmitrieva, P A Zagorets *Soveshchanie-Seminar po Radiatsionnoi Khimii: Tezisy Dokladov. Tbilisi* (Conference-Seminar on Radiation Chemistry. Abstracts of Reports. Tbilisi), Metsniereba, Tbilisi, 1985, p. 61
76. T G Myassoedova, G V Dmitrieva, P A Zagorets, et al. *Proceedings of the 6th Tihany Symposium on Radiation Chemistry, Balatonsceplak, 21–26 Sept. 1986*, 1987, Vol. 1, p. 341
77. T G Myasoedova, Yu M Dunaevskii, G V Dmitrieva *Chromatograph-Linked Mass-Spectrometric Analysis of the Products of Radiolysis of the Extraction System Based on Dicyclohexyl-18-crown-6 (DCH18C6)*, 16 pp.; manuscript deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 13.03.89, N 1600-V89
78. T G Myasoedova, G V Dmitrieva *Khim. Vys. Energ.*, 1991, **25** 244
79. T G Myasoedova, P A Zagorets *Khim. Vys. Energ.*, 1986, **20** 436
80. W W Schulz, L A Bray *Separ. Sci. Technol.*, 1987, **22** 191
81. R G Shuler, C B Bowers, Jr., J E Smith, Jr., et al. *Solvent Extr. Ion Exch.*, 1985, **3** 567
82. M W Dawis, Jr., C B Bowers, Jr. , European P. 216473; *Chem. Abs.*, 1987, **107** 185702z
83. A Ramadan, P R Danesi *Solvent Extr. Ion Exch.*, 1988, **6** 157
84. Z Korenová, J Lesný, J Jagnesákova, et al. *J. Radioanal. Nucl. Chem.: Lett.*, 1990, **144** 145
85. V V Yakshin, B F Myasoedov, O M Vilkova, et al. *Radiokhimiya*, 1989, **31** 67
86. V Mikulaj, L Vaseková *J. Radioanal. Nucl. Chem.: Art*, 1991, **150** 281
87. P Rajec, V Mikulaj, J Macková *J. Radioanal. Nucl. Chem.: Art*, 1991, **150** 315
88. N Y Kremliakova, A P Novikov, B F Myasoedov *J. Radioanal. Nucl. Chem.: Lett.*, 1990, **145** 23
89. N Yu Kremlyakova, A P Novikov *IX Vsesoyuznaya Konferentsiya po Ekstraktsii Tezisy Dokladov. Moskva* (The IXth All-Union Conference on Extraction. Abstracts of Reports. Moscow), Moscow, 1991, p. 201
90. E P Horwitz, M L Dietz, D E Fisher *Anal. Chem.*, 1991, **63** 522
91. R G Vibhute, S M Khopkar *J. Radioanal. Nucl. Chem.: Art*, 1991, **152** 487
92. N I Abakumova, V P Remez, A S Shubin, L R Saksonova *Vtoraya Vsesoyuznaya Konferentsiya po Teoreticheskoi i Prikladnoi Radiatsionnoi Khimii. Tezisy Dokladov. Moskva* (The IInd All-Union Conference on Theoretical and Applied Radiation Chemistry. Abstracts of Reports. Moscow), Izd. NIITEKhIM, Moscow, 1990, p. 5
93. N I Abakumova, M V Gridnevskii, L R Saksonova, V I Kononenko *13 Vsesoyuznyi Seminar "Khimiya i Tekhnologiya Neorganicheskikh Sorbentov": Tesizy Dokladov* (The 13th All-Union Seminar on "The Chemistry and Technology of Inorganic Solvents". Abstracts of Reports), Izd. NII Fiz.-Khim. Probl. Beloruss. Gos. Univ., Minsk, 1991, p. 3
94. E P Horwitz, M L Dietz, D E Fisher *Solvent Extr. Ion Exch.*, 1990, **8** 199
95. E P Horwitz, M L Dietz, D E Fisher *Solvent Extr. Ion Exch.*, 1991, **9** 1
96. S V Zatonskii, V V Makhlyarchuk *IX Vsesoyuznaya Konferentsiya po Ekstraktsii: Tezisy Dokladov. Moskva* (The IXth All-Union Conference on Extraction. Abstracts of Reports. Moscow), Moscow, 1991, p. 212

97. R N Edmonds, D M Holton, P P Edwards *J. Chem. Soc., Dalton Trans.*, 1986, (2) 323
98. A Ellaboudy, D M Holton, R N Edmonds, P P Edwards *J. Chem. Soc., Chem. Commun.*, 1986, (18) 1444
99. D M Holton, A S Ellaboudy, R N Edmonds, P P Edwards *Proc. R. Soc. London, A*, 1988, **415** 121
100. J Kuruc, F Sersen *J. Radioanal. Nucl. Chem.: Lett.*, 1990, **145** 197
101. E I Grigor'ev, T G Myasoedova, S V Nesterov, L I Trakhtenberg *Khim. Vys. Energ.*, 1987, **21** 437
102. E I Grigor'yev, T G Myasoedova, S V Nesterov, L I Trakhtenberg *15th International Symposium on Macrocyclic Chemistry, Odessa, 3–8 Sept. 1990:* Abstracts, Odessa, 1990, p. 144
103. E I Grigoryev, T G Myasoedova, S V Nesterov, L I Trakhtenberg *7th Tihany Symposium on Radiation Chemistry, Balatonscéplak, 9–14 Sept. 1990:* Abstracts, 1990, p. 53
104. V N Belevskii, S I Belopushkin, V I Fel'dman, Yu V Rakitin *Dokl. Akad. Nauk SSSR*, 1985, **282** 1161
105. V N Belevskii, S I Belopushkin *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1990, **31** 473
106. J Kuruc *J. Radioanal. Nucl. Chem.: Lett.*, 1990, **145** 205
107. E I Grigor'yev, L V Ivakina, O V Mikhalitsina, et al. *15th International Symposium on Macrocyclic Chemistry, Odessa, 3–8 Sept., 1990:* Abstracts, Odessa, 1990, p. 143
108. E I Grigoryev, L V Ivakina, O V Mikhalitsina, et al. *7th Tihany Symposium on Radiation Chemistry, Balatonscéplak, 9–14 Sept., 1990:* Abstracts, 1990, p. 51
109. V K Milinchuk, V I Tupikov, B A Briskman, et al. Handbook, *Radiatsionnaya Stoikost' Organicheskikh Materialov* (Radiation Stability of Organic Materials) (Edited by V K Milinchuk, V I Tupikov), Energoatomizdat, Moscow, 1986, 272 pp
110. S V Zatonsky, O S Povolotskaya *J. Radioanal. Nucl. Chem.: Lett.*, 1987, **117** 361
111. B G Ershov, A F Seliverstov, N L Sukhov, A V Gordeev *Khim. Vys. Energ.*, 1987, **21** 119
112. A F Seliverstov, B G Ershov *III Vsesoyuznaya Konferentsiya po Khimii i Biokhimii Makrotsiklicheskikh Soedinenii: Tezisy Dokladov. Ivanovo* (The IIIrd All-Union Conference on the Chemistry and Biochemistry of Macrocyclic Compounds. Abstracts of Reports. Ivanovo), Ivanovo, 1988, Part 1, p. 99
113. A F Seliverstov, B G Ershov *Khim. Vys. Energ.*, 1988, **22** 203
114. A F Seliverstov, B G Ershov *Proceedings of the 4th Working Meeting on Radiation Interaction, Leipzig 21–25 Sept. 1987* (Edited by O Brede, K-H Lubert), 1988, p. 537
115. P Lardinois, I Rebena, B Hickel *New. J. Chem.*, 1988, **12** 21
116. A K Pikaev, S A Kabakchi, Handbook, *Reaktionnaya Sposobnost' Pervichnykh Produktov Radioliza Vody* (The Reactivity of the Primary Water Radiolysis Products), Energoizdat, Moscow, 1982, 200 pp
117. N G Luk'yanenko, A V Lobach, M N Parfenova, et al. *Khim. Geterotsikl. Soedin.*, 1987, (9) 1179
118. T W Hambley, G A Lawrance, D F Sangster, C B Ward *Aust. J. Chem.*, 1987, **40** 883
119. N Jubran, D Meyerstein, J Koresh, J Cohen *J. Chem. Soc., Dalton Trans.*, 1986, (12) 2509
120. N Jubran, H Cohen, D Meyerstein *Isr. J. Chem.*, 1985, **25** 118
121. N Jubran, G Ginzburg, H Cohen, et al. *Inorg. Chem.*, 1985, **24** 251
122. A M Tait, M Z Hoffman, E Hayon *Inorg. Chem.*, 1976, **15** 934
123. N Jubran, G Ginzburg, H Cohen, D Meyerstein *J. Chem. Soc., Chem. Commun.*, 1982, (9) 517
124. N Jubran, D Meyerstein, H Cohen *Inorg. Chim. Acta*, 1986, 117 129
125. P A King, J A Ward *J. Polym. Sci., Part A-1*, 1970, **8** 253
126. U Gröllmann, L Schnabel *Makromol. Chem.*, 1980, **181** 1215
127. E P Petryaev, O I Shadyro *Radiatsionnaya Khimiya Bifunktsional'nykh Organicheskikh Soedinenii* (The Radiation Chemistry of Bifunctional Organic Compounds), Izd. "Universitetskoe", Minsk, 1986, 166 pp
128. J P Shukla, R K Singh, A Kumar *Radiochim. Acta*, 1991, **54** 73
129. V V Makhlyarchuk, S V Zatonskii *Izzledovaniya v Oblasti Radiatsionnogo Materialovedeniya Organicheskikh i Neorganicheskikh Materialov: Mezhvuzovskii Sbornik Nauchnykh Trudov* (Studies in Radiation Materials Science of Organic and Inorganic Materials. Intercollegiate Collection of Scientific Reports), Izd. LTI im Lensoveta, Leningrad, 1986, p. 125
130. H Langguth, E J Langrock *Isotopenpraxis*, 1985, **21** 211
131. V V Makhlyarchuk, S V Zatonskii, I E Mikhailenko, V V Saraeva *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1986, **27** 53
132. V V Makhlyarchuk, Candidate's Thesis in Chemical Sciences, Lomonosov Moscow State University, Moscow, 1989, 153 pp.
133. T N Petrenko *Teor. Eksp. Khim.*, 1984, **20** 633
134. J Jagur-Grodzinski *Isr. J. Chem.*, 1985, **25** 39
135. E A Rojo, R R Hentz *J. Phys. Chem.*, 1965, **69** 3024
136. V V Makhlyarchuk, S V Zatonskii *Materialy Konferentsii Molodykh Uchenykh Khimicheskogo Fakul'teta Moskovskogo Universiteta, Moskva* (Proceedings of the Conference of Young Scientists in the Faculty of Chemistry of Moscow University. Moscow), Moscow, 1985, Part 1, p. 46; manuscript deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 5.12.85, N 8373-V
137. V V Makhlyarchuk, V M Zatonskaya, S V Zatonskii *VI Vsesoyuznoe Soveshchanie po Khimii Nevodnykh Rastvorov Neorganicheskikh i Kompleksnykh Soedinenii: Tezisy Dokladov* (The VIth All-Union Conference on the Chemistry of Non-aqueous Solutions of Inorganic and Complex Compounds. Abstracts of Reports. Moscow), Nauka, Moscow, 1987, p. 335
138. S V Zatonskii, V V Makhlyarchuk, I E Mikhailenko, et al. *III Vsesoyuznaya Konferentsiya po Khimii i Biokhimii Makrotsiklicheskikh Soedinenii: Tezisy Dokladov. Ivanovo* (The IIIrd All-Union Conference on the Chemistry and Biochemistry of Macrocyclic Compounds. Abstracts of Reports. Ivanovo), Ivanovo, 1988, Part 1, p. 58
139. V V Makhlyarchuk, V E Zubarev, S V Zatonskii *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1990, **31** 488
140. S V Zatonskii, V V Makhlyarchuk, V V Saraeva *Vtoraya Vsesoyuznaya Konferentsiya po Teoreticheskoi i Prikladnoi Radiatsionnoi Khimii. Tezisy Dokladov. Moskva* (The IInd All-Union Conference on Theoretical and Applied Radiation Chemistry. Abstracts of Reports. Moscow), Izd. NIITEKhIM, Moscow, 1990, p. 95
141. S V Zatonskii, V V Makhlyarchuk, V V Saraeva *Khim. Vys. Energ.*, 1992, **26** 104
142. B F Myasoedov *IX Vsesoyuznaya Konferentsiya po Ekstraktsii: Tezisy Dokladov. Moskva* (The IXth All-Union Conference on Extraction. Abstracts of Reports. Moscow), Moscow, 1991, p. 14

Translated from *Uspekhi Khimii* 61 910–939 (1992) U.D.C. 541.14:541.124:535.34

The mechanism of photolysis of aromatic azides

N P Gritsan, E A Pritchina
Institute of Chemical Kinetics and Combustion, Siberian Section of the Russian Academy of Sciences
Novosibirsk State University, Novosibirsk

ABSTRACT. A survey has been made of data published in recent years on the nature, spectra and reactivity of intermediates obtained on photolysis of aromatic azides. Aspects requiring further investigations have been highlighted.

The bibliography includes 147 references.

Contents

I.	Introduction	500
II.	The structure, electronic spectra and properties of azides	500
III.	The nature and properties of key intermediates	503
IV.	The reactivity of intermediate singlet species	507
V.	Reactions of triplet aromatic nitrenes	509
VI.	Quantum chemical calculations on the properties of intermediates	513
VII.	Conclusions	514

I. Introduction

The photochemical reactions of organic azides have been a focus of study for more than 60 years, and interest in this field is in no way declining. This is principally because these compounds have many practical applications, e.g. in polymer chemistry, in photolithography, and as light-sensitive agents for use in photographic processes which are not based on silver salts.[1–3] Aryl and heteroaryl azides are also used as reactive reagents in the photoaffinity modification of biopolymers.[4,5] Interest in the photochemistry of organic azides has also developed from mechanistic considerations, many of which are complex and unresolved.

It was towards the end of the 1950s, with the advent of new analytical methods, that exhaustive studies were first made on the structure and reactivity of the intermediates obtained on photolysis of organic azides. The results obtained up to 1983 have been reviewed[6,7] and presented as monographs.[8–10] In the Soviet literature of 1975, there is also a review on the photochemistry of organic azides,[11] together with a number of short surveys published as monographs.[1,2] However, in spite of the enormous interest in the photochemistry of organic azides, many mechanistic details remain unclear, and certain data from a number of authors are contradictory.[10] Significant progress has been made during the last 5–6 years as a result of using new methods[12–14] and applying traditional methods in a more sophisticated way.[15–17]

II. The structure, electronic spectra and properties of azides

1. Structure and electronic spectra of azides

Azides are a class of compound with the general formula, RN_3. The three atoms of nitrogen are linear.[18–21] The atom of nitrogen bonded to substituent R is sp^2-hybridised (the R–N–N angle being close to 120°).[18–22] In aryl azides all three nitrogen atoms are involved in conjugation with the aromatic system, although such interaction is weak.[22] As a consequence there is a similarity between the absorption spectra of azides and those of the corresponding aromatic hydrocarbon.

Table 1. Electronic spectral absorption of phenyl azide derivatives.

Substituent	Solvent	T, K	λ_{max}, nm (lg ε, l(mol^{-1} cm)	Refs.
H	EPA	77	247(3.9), 278 (3.3), 315(1.9)*	[22]
	EtOH	77	252(4.06)	[23]
	EtOH	298	249(4.06), 285(3.22)	[24]
p-Me	EtOH	77	254(4.18)	[23]
	EtOH	298	251(4.12), 291(3.23)	[24]
	hexane	300	250(4.18), 283(3.45), 292(3.34)	[25]
p-NH_2	EtOH	77	280(4.17)	[23]
	hexane	300	267(4.23), 303(3.51)	[25]
p-MeO	EtOH	77	253(4.13)	[23]
p-NO_2	EtOH	77	322(4.18)	[23]
	hexane	300	220(4.08), 299(4.30), 318(4.00)	[25]
p-MeCO	EtOH	77	288(4.35)	[23]
p-Ph	EtOH	77	280(4.31)	[23]
m-Ph	EPA	77	246(4.2), 292(3.5), 320(2.3)*	[22]
o-Ph	EPA	77	267(4.1), 296(3.3), 315(2.2)*	[22]
p,*o*′,*p*-Me_3	EPA	77	213(3.8), 247(3.4), 286(2.8), 300(2.1)*	[22]

* $n\pi^*$-region.

The principal bands in the absorption spectra of aromatic azides have been assigned to $\pi\pi^*$ transitions in the aromatic system. There is also absorption, thought to correspond with $n\pi^*$-type transitions,[22–24] which is not evident in the spectra of the corresponding hydrocarbon. The values of these absorption maxima are approximate because they appear as shoulders on the

absorptions due to the more intense ππ*-transitions. These weak absorptions are not a consequence of complex formation or associations,[26] nor due to impurities.[27] Recently, it was proposed that the extended asymmetric tail in the absorption spectra of aromatic azides is due to their transition into dissociated singlet states.[27] Spectral data for a number of substituted phenyl azides are given in Table 1.

2. Quantum yields for the photo-decomposition of aromatic azides

Azides are unstable compounds, decomposing with elimination of N_2 to form nitrenes on photolysis and thermolysis[6–11]

$$ArN_3 \xrightarrow{h\nu} ArN + N_2.$$

Table 2. Quantum yields (φ) for the photolysis for phenyl azide derivatives on irradiation at 254 nm.

Substituent	Concentration ArN_3, mol/l	Solvent	φ at 298 K	φ at 77 K	Refs.
H		hexane	0.53		[28]
	10^{-5}—10^{-4}	acetonitrile	0.72		[29]
	10^{-4}	acetonitrile	0.56		[30]
		Mcy-Ip*		0.52	[28]
	10^{-4}	3-methylpentane		0.49	[31]
p-Me		ethanol	0.59		[24]
p-MeCO		hexane	1.00**		[28]
		Mcy-Ip*		1.00**	[28]
p-NO_2	10^{-4}	acetonitrile	0.54		[30]
	10^{-3}—10^{-1}	acetonitrile	0.7		[32]
p-NH_2	$4 \cdot 10^{-5}$—$2 \cdot 10^{-4}$	toluene	0.96***		[33, 34]
		toluene-THF		0.8***	[33, 34]
p-Br	10^{-4}	acetonitrile	0.80		[30]
o, *o*', *p*-Me_3		hexane	0.96		[28]
		Mcy-Ip*		0.98	[28]
o, *o*', *p*-Br_3	10^{-4}	acetonitrile	0.16		[30]
m-Ph		hexane	0.37		[28]
		Mcy-Ip*		0.36	[28]
o-Ph		hexane	0.46		[28]
		Mcy-Ip*		0.43	[28]

* Mixture of methylcyclohexane and isopentane (1 : 1).
** Irradiation at 280 nm.
*** Irradiation at 313 nm.

The quantum yields for the photolysis of aromatic azides, presented in Tables 2 and 3, are a consequence of excitation in the ππ*-transition. The values of the quantum yield are not dependent on the temperature. It can be seen that the quantum yields for the photolysis of polynuclear aromatic azides are higher than those for PhN_3 and its derivatives. Quantum yields are also available for the photolysis of di-, tri- and tetra-azides.[24,28] Photo-decomposition of PhN_3 and its derivatives on irradiation with visible light ($\lambda < 430$ nm) has also been observed.[23]

Table 3. Quantum yields for the photolysis of poly-condensed aromatic azides.[28]

Compound	λ_{irr}, nm	φ at 298 K	φ at 77 K
1-Azidonaphthalene	303	1.00±0.02	0.95±0.05
3-Azidoquinoline	303	0.84±0.05	0.87±0.05
1-Azidoanthracene	365	1.00±0.03	1.02±0.05

For quenching of triplet nitrenes by reaction with an azide molecule [Eqn. (1)],

$$^3ArN + ArN_3 \rightarrow ArN{=}NAr + N_2, \quad (1)$$

the quantum yield may exceed 1 (but not 2).[35,36] However, Waddell and Lee Go have found that the quantum yield for the photolysis of PhN_3 in acetonitrile can reach $\simeq 300$.[31] In subsequent work devoted to more detailed studies of the photolysis of PhN_3 and certain of its derivatives, even higher quantum yields (up to 15 300) were recorded, consistent with the following chain mechanism:[29,30,37–39]

$$^3ArN + ArN_3 \rightarrow 2\,^3ArN + N_2. \quad (2)$$

Apart from information reported by Waddell et al.,[29,30,37–39] there are no other data in the literature on the effect of concentration on the quantum yield for the photolysis of aromatic azides, and no other references to quantum yields greater than unity have been reported. The quantum yield for the photolysis of 1-azidonaphthalene does not depend on the concentration of the azide in the range 10^{-5} to 10^{-2} M and is equal to 1.[28] Schuster and Liang[32] were unable to reproduce the results of Waddell et al. for the photolysis of *p*-nitrophenyl azide.[30] According to the latter authors, the quantum yield increased from 0.54, at an azide concentration of 10^{-4} M, to 434 at 10^{-1} M.[32] However, according to Schuster et al., the value is independent of concentration in the interval 10^{-3} to 10^{-1} M, the quantum yield being 0.7 under these conditions. Thus, there are contradictory data on the photolysis of PhN_3 and its derivatives.

3. Initial processes in direct and sensitised photolysis

It is generally accepted that singlet nitrenes are the species obtained initially on dissociation of azides in the excited singlet state, while triplet nitrenes are predominantly formed from azides in the excited triplet state.[10–14,40–42] For all aryl azides which have been studied thus far, the main excited state is the triplet one.[40] This has been verified from the ESR characteristics of the triplet species formed on azide photolysis in glass matrices[43–48] or as single crystals[49–50] at 77 or 4 K.

Mechanistic information on the role of triplet azides and nitrenes has been gained by studying the sensitised photolysis of aromatic azides.[15–17,26–28,41,51–54] Leyshon and Reiser[26] found that PhN_3 and 1-$C_{10}H_7N_3$ quench both the singlet and triplet states of the sensitiser. In kinetic experiments, the rate constants for quenching the triplet state of the sensitiser [$k_q(T)$] have been calculated. Based on the relationship between $k_q(T)$ and the position of the triplet level of the sensitiser, it has been proposed that quenching involves

transfer of energy to a thermally populated non-linear azide [ground] state. It is thus considered that in the excited triplet state the non-linear configuration of the azide has the minimum energy.[26] Quantum chemical calculations have in fact shown that distortion of the terminal nitrogen from the plane of the azido group leads to a decrease in the energy of the lower excited triplet state.[51,55]

It has been established that aromatic ketones (benzophenone, acetophenone) function as triplet sensitisers in the photolysis of PhN_3 and 1-$C_{10}H_7N_3$.[15,53] However, the $k_q(T)$ value for quenching the triplet excited state of benzophenone by phenyl azide was found to be 2×10^9 l/mol/s,[15] which is significantly different from the value reports by Leyshon et al.[26] [$k_q(T) = 1.8 \times 10^6$ l/mol/s]. With such a discrepancy, it would be difficult to draw meaningful conclusions.[26]

The quantum yield (φ) for the sensitised decomposition of *o*-azidobiphenyl in the presence of acetophenone is 0.3 [52] (for PhN_3 $\varphi < 0.1$ [15]). In the triplet-sensitised photolysis of *p*-dimethylaminophenyl azide, the quantum yield is very small (in direct photolysis $\varphi \approx 1$).[14] In the sensitised decomposition of 1-$C_{10}H_7N_3$ with benzophenone[53] and of 1-azidopyrene with biacetyl,[42] quenching of the triplet state of the sensitiser is accompanied by the appearance of the corresponding triplet nitrene. The spectrum of ^{3}PhN was not recorded during the sensitised photolysis of PhN_3.[16] There was no sensitised decomposition of *p*-dimethylaminophenyl azide in the presence of 2-acetonaphthone.[27]

Table 4. Excitation energies for the singlet state E_s and rate constants [k_q(S)] for fluorescence quenching of sensitisers by phenyl and 1-naphthyl azide.[26]

Sensitiser	E_S, kcal/mol	k_q(S), l.mol^{-1} s^{-1}	
		PhN_3	$C_{10}H_7N_3$
Phenanthrene	81.7	$1.3 \cdot 10^{10}$	$1.4 \cdot 10^{10}$
Anthracene	75.1	$6.6 \cdot 10^9$	$1.0 \cdot 10^{10}$
9,10-Dimethylanthracene	70.2	$2.5 \cdot 10^9$	$5.4 \cdot 10^9$
Perylene	64.9	$3.4 \cdot 10^8$	$2.7 \cdot 10^9$
Tetracene	60.0	$2.3 \cdot 10^7$	$3.5 \cdot 10^8$
Rubrene	51.1	$1.0 \cdot 10^5$	$5.5 \cdot 10^6$

The efficiency of singlet sensitisation has been studied by determining the fluorescence quenching of the sensitiser (Table 4). The authors[26] came to the following conclusions:

1) singlet sensitisation is more effective in promoting azide decomposition than triplet sensitisation if the energy of the sensitiser is the same;

2) sensitisation is observed well below the estimated acceptor level of the azide;

3) singlet sensitisation of aryl azides is effected by two competing processes: a) S–S-transfer of energy; and b) transfer of an electron [from the azide to the excited hydrocarbon (sensitiser) molecule]. The latter conclusion was based on indirect information [namely the dependence of the rate constant for quenching $k_q(S)$ on the free energy of the electron transfer (ΔG_{ET}) in accordance with the Rehm–Weller equation[56]].

In studying the sensitised photolysis of *p*-dimethylaminophenyl azide in the presence of a series of aromatic hydrocarbons (pyrene, 1-acetamidopyrene, 9-acetamidoacridine),[27] the authors came to the same conclusion as Leyshon et al.,[26] i.e. that two mechanisms of singlet sensitisation, a) and b) were operative. However, in contradiction to Reiser et al.,[26] Schuster et al. consider that the electron transfer takes place from the excited hydrocarbon to the azide.[27] This is supported by the appearance of absorption corresponding to the pyrene cation. It is thought that the electron transfer may take place on the azide molecule in a dissociated state.[27] Such energy transfer to singlet and triplet repulsive states of organic peroxides has already been reported.[57]

4. The mechanism of photo-dissociation of aromatic azides

Aromatic azides have proved interesting as model compounds for studying photo-dissociative processes. In order to gain information on the initial processes, it is necessary to apply highly sensitive methods to measure the very short relaxation times. Basic information on the mechanism of dissociation can be derived by determining the spatial and energy distribution of the resulting molecular fragments.[58–61] In a picosecond time-resolved study of the flash photolysis of aromatic azides, it was shown that photo-dissociation of *p*-dimethylaminophenyl azide in toluene at room temperature proceeds in the singlet excited state within <6 ps.[14]

In order to ascertain mechanistic details, it is important to measure quantum yields as a function of the excitation wavelength.[58] Reiser and Marley[28] considered three possible mechanisms operative in the preliminary stage:

1) uncoupling of the spin of the electrons forming in the N–N σ-bonds (repulsive state T_{σ^*});

2) transfer into dissociated and pre-dissociated states;

3) supply of kinetic energy in excess of the bond energy to a critical vibrational mode (collapse from a principal "hot" electron state).

The first pathway can be discounted because, on this basis, either an aromatic nitrene or a molecule of nitrogen would be found in the triplet state;[28] as has been demonstrated, dissociation of singlet-excited azides results in the formation of *singlet* nitrenes.[9–14,40–42] The formation of a triplet-excited molecule of nitrogen is also unlikely because the energy of the $^3\Sigma_u^+$ state for nitrogen is 6.224 eV.[19,62] Furthermore, triplet-excited nitrogen has not been detected experimentally.[63]

According to Reiser and Marley, the mechanism of azide photo-dissociation involves a collapse of a vibrationally-excited electron state.[28] In our opinion and those of other authors,[24,55,64,65] this is also unlikely. From an analysis of the relationship between the quantum yield for the photolysis of *p*-azidomalachite green and both wavelength and temperature, it has been concluded that dissociation proceeds from an electronically-excited state.[24,64] Two mechanisms are possible:[24] a non-adiabatic dissociation and a pre-dissociation.[66] It is considered that the latter is more likely.[24,64]

Having analysed absorption spectra and performed quantum chemical calculations, Kondratenko and Shrubovich[65] came to the same conclusion as Shields et al.,[27] namely that the long wavelength absorption in the spectra of aromatic azides was a result of a transfer into a dissociated state ($\pi\sigma^*$-type). In their view, the initial mechanism of photolysis is a dissociative one, although they do not exclude a contribution due to pre-dissociation on excitation to higher electronic states.

From semi-empirical quantum chemical calculations, Tsuda et al. came to the conclusion that the motive forces behind the dissociative process of phenyl azides are involved with the displacement of the terminal nitrogen atom from the plane of the other atoms, which leads to a lowering of the activation barrier.[55] A distortion of the terminal nitrogen atom also leads to a shifting of the lower excited states $^1n\pi^*$ and $^1\pi\pi^*$, excitation of which precedes the dissociation. For aromatic azides it is considered that all the excitation energy is concentrated on the azido group, while the aromatic ring functions as an antenna for the photoabsorption.[55]

III. The nature and properties of key intermediates

The formation of nitrenes on photolysis and thermolysis of azides was first postulated on the evidence of product analyses.[6–11] It was not until 1962 that Wasserman et al. provided, through ESR studies, the first spectroscopic indication of the existence of triplet nitrenes.[46] This was based on the observation of a $\Delta m = 2$ transition in a moderate field and a $\Delta m = 1$ transition in a weak field (at 1620 and 6701 G, respectively, for ^{3}PhN).

1. ESR spectroscopy of aromatic nitrenes

The ESR spectroscopic characteristics of triplet molecules are determined by the spin-spin dipole interaction of unpaired electrons. In the absence of a magnetic field, this leads to a splitting of the triplet levels, as described by the spin Hamiltonian:[67]

$$H_{SS} = D(S_z^2 - {}^1/_3S^2) + E(S_x^2 - S_y^2). \quad (3)$$

The splitting parameters in a zero field, D and E, are given by:

$$D = \left\langle \Phi_k \left| \frac{3g^2\beta^2}{4} \frac{r_{12}^2 - 3z_{12}^2}{r_{12}^5} \right| \Phi_k \right\rangle, \quad (4)$$

$$E = \left\langle \Phi_k \left| \frac{3g^2\beta^2}{4} \frac{y_{12}^2 - x_{12}^2}{r_{12}^5} \right| \Phi_k \right\rangle, \quad (5)$$

where Φ_k is the coordinated part of the wave function of unpaired electrons in the triplet state; g is the g-factor, equal to ~ 2; β is the Bohr magneton; and r_{12} is the inter-electronic distance. The spin Hamiltonian takes the form (3) for a specific system of coordinates relative to the axes of the molecule, which, for high symmetry, coincides with the axes of symmetry.[67]

In an external magnetic field, the spin Hamiltonian becomes:

$$H = g\beta HS + H_{SS}. \quad (6)$$

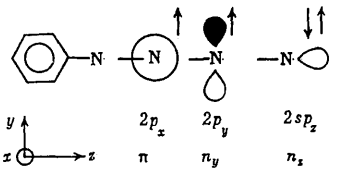
When the applied field is oriented to align with one of the molecular axes, the spin Hamiltonian, as defined by Eqn. (6), can be readily determined.

In the general case, the value of the applied magnetic field strength at absorption depends on the orientation of the field relative to the axes of the molecule. The intensity of the signals in a glass matrix and in the semicrystalline state is noticeably lower than that registered for single-crystals possessing the same number of oriented triplets.[45] The experimentally observed resonances in glass matrices and in the semi-crystalline state are due to the relatively few molecules in which one of the three magnetic axes is approximately aligned with the direction of the applied magnetic field.[45]

For arylnitrenes the main axis z coincides with the C–N bond; the axes x and y are equivalent so that $E \approx 0$.[45,47] The ESR spectra of triplet nitrenes are characterised by a D value which is significantly greater than the microwave quantum of energy.[43,46] From a calculation of the values of the resonance fields for allowed transition with $\Delta m = 1$ when the applied field is oriented to align with one of the axes (using ESR spectrometers where $H < 10\,000$ G), it can be concluded that the recorded signals correspond to an orientation of the applied magnetic field parallel to the plane xy.[45,46] The value of the resonance field can be determined from the equation:

$$H^2 = H_0(H_0 + D), \quad (7)$$

where H_0 is the resonance field for the isolated doublet state, and H is the resonance field for the triplet nitrene (assuming that E = 0).



Mapping of the orbitals of phenylnitrene.[16]

Table 5. Splitting parameters in a zero field (D) for triplet aromatic nitrenes (^{3}RN).

R	D, cm^{-1}
Phenyl	0.998 [47]; 1.003 [68]; 0.999 [48, 49]
Substituted phenyl	0.871—1.065 [47, 48,50,69]
1-Naphthyl	0.789 [47]; 0.798 [68]; 0.79 [71]
2-Naphthyl	1.008 [47]
1-Anthryl	0.663 [47]; 0.65 [72]
2-Anthryl	0.778 [47]; 0.75 [72]
1-Pyrenyl	0.73 [70]

For the simple nitrene, :NH, $D = 1.863$ cm^{-1} (the contribution of spin-spin interaction being 1.595 cm^{-1}, and the contribution of spin-orbital interaction being 0.268 cm^{-1}).[67] The parameter D for various alkylnitrenes lies in the region 1.57–1.66 cm^{-1}.[46] For aromatic nitrenes one of the unpaired electrons is localised in a p_y-orbital of the nitrogen atom (see above), while a second occupies a delocalised π-orbital. Delocalisation leads to a decrease in the spin density at the atom of nitrogen and, correspondingly, to a decrease in the value of D for aromatic nitrenes relative to alkyl nitrenes (Table 5). The following equation may be used for determining the approximate value of the spin density of a π-type unpaired electron on the nitrogen atom:

$$\rho_\pi^N \approx D/D_0 \ , \quad (8)$$

where D is the parameter for an aromatic nitrene, and D_0 for alkyl nitrenes (D_0 = 1.6 cm^{-1}). For arylnitrenes the value ρ_π^N lies in the region of 0.42–0.64.[46]

From ESR spectroscopic data for a series of fourteen para-substituted phenyl azides, recorded under identical conditions hyperfine splitting at the nitrogen nuclei was detected in five instances (a_N = 17 ± 1 G), as well as at the fluorine nucleus (a_F = 17.5 G) and at iodine (a_I = 85 G) in the para-position.[48] The value of D for para-substituted phenylnitrenes lies in the region 0.874–1.008 cm^{-1}, the spin density at the nitrogen nucleus being sensibly independent of the nature of the substituent.[48] Consequently, the simplified Eqn. (8) gives only a rough assessment of the ρ_π^N value. To obtain a quantitative correlation with experimental findings, it is necessary to consider more accurately the effects of delocalisation. The effect of substituents on the value of the parameter D has been studied for 8-substituted 1-naphthylnitrenes[71] and for variously substituted 9-anthracenylnitrenes.[72]

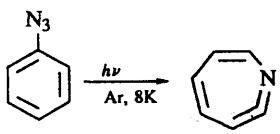
Constrasting with alkyl- and aryl-nitrenes, for which the triplet state predominates, aroylnitrenes fail to provide recordable ESR spectra.[47,73,74] Furthermore, the products obtained by both direct and triplet-sensitised photolysis of aroyl azides ($ArCON_3$) are typical of those obtainable from singlet nitrenes.[73–76] On the basis of these data, one can assume that aroylnitrenes (ArCON) exist principally in the singlet state.[73,74] These are potentially electrophilic, being readily and effectively inserted even into non-activated CH-bonds. Thus, aroyl azides may be used for photo-affinity modification of the lipophilic residues of biopolymers.[77,78]

2. The nature and optical spectra of intermediates

Shortly after the ESR spectra of triplet nitrenes were recorded, Reiser et al. studied the electronic absorption spectra of the species obtained by photolysis of a number of aromatic azides under the same conditions (in oranic glass matrices at 77 K).[22,79,80] They came to the conclusion that the recorded spectra were due to nitrenes in the triplet state. This was based on the following: firstly, the conditions under which the spectra were recorded were the same as those under which the ESR spectra were taken; and, secondly, there was a close similarity between the electronic absorption spectra of [presumed] triplet nitrenes and those of radicals having an unpaired π-electron. For example, the spectrum of ^{3}PhN (λ = 314 and 402 nm) is similar to that of $^2PhCH_2$ (λ = 318 and 463 nm) and, more strikingly, to those of ^{2}PhO (λ = 300 and 403 nm) and ^{2}PhNH (λ = 309 and 403 nm).[22] These results were later reproduced, and low-temperature absorption spectra were recorded for the species obtained from other aromatic azides. Here, too, absorption was assigned to triplet aromatic nitrenes[23,24,40,70,72,81,82] (see Table 6).

a) Photolysis of phenyl azides and its derivatives

In 1978, Chapman et al. showed that 1-aza-1,2,4,6-cycloheptatetraene (1,2-didehydroazepine) was the major intermediate formed on irradiation on PhN_3 in an argon matrix at 8 K.[83] This assumption was based on the appearance of an absorption band at 1895 cm^{-1}, in the IR spectrum, which was characteristic of an intermediate having a cumulene structure.[83]



Similar results were obtained for the photolysis of 3- and 4-substituted phenyl azides.[84] The participation of didehydroazepines and/or azirines in the photochemical conversions of aryl azides had already been suggested on the evidence of product analyses for photolytic reactions in the presence of amines (primary and secondary)[10,85–87] or other nucleophiles.[10,88–91]

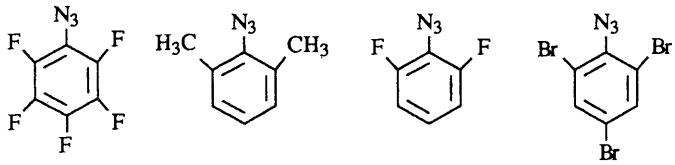
Table 6. Electronic absorption spectra for triplet aromatic nitrenes (^{3}RN) in EPA [22] and ethanol[23] at 77 K.

R	λ_{max}(lg ε, l.mol^{-1} s^{-1})	Refs.
Phenyl	241(3.7), 303(2.8), 368(2.5)	[22]
	243(3.93), 304(3.34), 383(2.93)	[23]
p-Tolyl	250(4.06), 315(3.75), 385(3.04)	—
p-Aminophenyl	309(4.03), 356(3.32), 437(3.48)	—
p-Methoxyphenyl	271(4.21), 330(3.88), 388(3.34)	—
p-Nitrophenyl	312(4.14), 380(2.85), 500(2.57)	—
p-Acetylphenyl	276(4.21), 410(2.94), 508(2.62)	—
p-Biphenylyl	320(4.24), 478(3.04)	—
Mesityl	255(3.7), 320(3.4), 391(2.4)	[22]
m-Biphenylyl	242(4.8), 330(3.5), 393(3.1)	—
o-Biphenylyl	343(3.7), 373(3.0)	—
1-Naphthyl	223(4.5), 321(4.0), 536(3.2)	—
3-Quinolyl	390(3.4), 550(2.3)	[22]
1-Anthryl	240(5.3), 448(4.1), 697(3.2)	—

According to IR spectroscopic data, neither didehydroazepine nor benzazirine intermediates are formed on irradiation of pentafluorophenyl azide[92] or 2,6-dimethylphenyl azide[93] in an argon or nitrogen matrix at 12 K. Here, triplet nitrenes are the key intermediates; however, prolonged irradiation of 2,6-dimethylphenyl azide affords only small amounts of didehydroazepine (ν = 1898 cm^{-1}), presumably as a result of secondary photolysis.[94] An ESR spectroscopy study indicated that irradiation of PhN_3 in an argon matrix at 12 K yields both 1,2-didehydroazepine and ^{3}PhN, while prolonged irradiation affords 2-pyridylmethylene.[94]

After the publications of Chapman et al.[83,94] and Dunkin et al.,[84] some doubts were raised about the authors interpretation of the electronic absorption spectra of azides recorded at 77 K in a glass matrix.[15,16] As a consequence, Platz et al. reproduced the earlier results of low-temperature photolysis (77 K) of PhN_3 and some of its derivatives.[16,95] In this context, low-temperature UV spectra were recorded, and an analysis was made of the product obtained on warming the photolysate to room temperature. The temperature of the photolyses was in the range from room temperature to 77 K. Platz found that, on irradiation of PhN_3 in diethylaniline, the yield of 3*H*-azepine fell from 80% at 273 K to 3% at 153 K and to 0% at 77 K.[95] Irradiation of PhN_3 at 77 K afforded azobenzene and aniline,[95] both of which would be anticipated if photolysis proceeds through triplet nitrenes.[10] There is also reference to the absorption spectra of the products obtained by photolysis of PhN_3 and azides (I–IV) at 77 K, as well as fluorescence spectra and excitation

fluoresecence spectra of the products obtained by photolysis of PhN_3 and azides (I) and (II).[16]



(I) (II) (III) (IV)

The similarity between the absorption spectra and the excitation spectra confirms that the same species is formed.[16] An analysis of results obtained by flash photolysis of PhN_3 in the presence of DEA in a wide temperature interval, [16] as well as the data obtained by Leyva et al.,[95] indicate that the efficiency of didehydroazepine formation decreases as the temperature is reduced, and that ^{3}PhN is the principal species formed on photolysis of PhN_3 at 77 K in a glass matrix.[16] Thus, the electronic spectroscopic interpretations made by Reiser and others are correct.[22–24,40,70–72] (see Table 6).

It should be pointed out that triplet aromatic nitrenes are unstable on prolonged irradiation at 77 K,[16,22,23,79,96,97] which may be associated with the formation of an aniline-solvent radical pair. Recombination of the latter in the gaseous state leads to a substituted amine.[23,96,97] Prolonged photolysis of ^{3}PhN leads to the formation of didehydroazepine.[16] The photochemical reactions of triplet nitrenes also complicate the interpretation of their absorption spectra and make it difficult to determine extinction coefficients (Table 6).

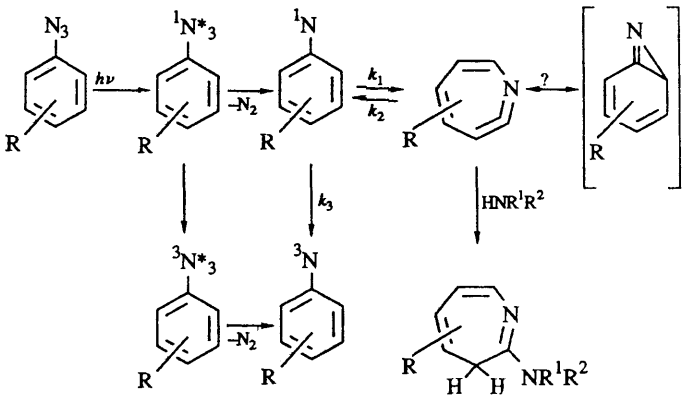
In order to explain why the products obtained by photolysis of aromatic azides at 10 K in an inert gas matrix are different from those obtained in a glass matrix at 77 K, Platz et al.,[16] advanced the hypothesis that at 10 K, in an inert gas matrix, secondary photolysis of the triplet nitrenes takes place to give a didehydroazepine; it is also considered that high-temperature chemistry is manifested in locally heated areas. In recent work, it has been shown that ^{3}PhN is the principal product obtained by photolysis of PhN_3 in a hydrocarbon glass matrix (3-methylbutane at 45 K) and in an inert gas matrix (N_2 or Ar at 12 K).[98] Didehydroazepine has even been detected as the primary species formed on photolysis of ^{3}PhN.[83,84] Hayes et al. argued that didehydroazepine, which had always been formed in small amounts (~20%) on photolysis of ^{3}PhN in a number of matrices, is the result of isomerisation of a vibrationally- or electronically-excited singlet nitrene state, ^{1}PhN.[98]

At present, there are around 20 publications devoted to systematic kinetic studies of the photo-reactions of aryl azides.[12–17,27,32,34,36,42,53,70,82,99–107] In the majority of these, electronic absorption spectra of intermediates were recorded, and, in two instances,[12,13] IR absorption data for the intermediates are available. Essentially, the electronic spectra of the intermediates were interpreted in terms of triplet aromatic nitrene absorption because of the similarity with the absorption spectra of the products obtained by low-temperature photolysis.[36,42,70,99–101]

Flash photolysis of PhN_3 [13,15,16,102,106] and certain of its derivatives[12–14,16,32,102,104–107] has been widely reported. In an early study of azide photolysis in the presence of amines, only the absorption of 1*H*-azepine was detected.[102] Later, the absorption of an intermediate, presumed to be ^{3}PhN, was detected in the absence of an amine.[82,105] However, this was subsequently disputed.[15] A detailed comparison of the absorption spectrum of ^{3}PhN at 77 K with that of the intermediate formed at room temperature showed that the similarity was far from exact. For example, the well-defined splitting in the spectrum of ^{3}PhN with maxima at 490, 382 and 303 nm was absent in the absorption spectrum of the intermediate, which exhibited a broad, poorly-defined band with a maximum at ~350 nm.[16] Only with compound (IV) was there a complete superposition of the spectrum obtained by flash photolysis with that obtained at low temperature. The spectra of compounds (I) and (III) were consistent with absorption of triplet nitrenes, exhibiting a poorly-defined maximum in the region ~340–350 nm.[16] A similar low-intensity absorption in the region 320–380 nm was registered for PhN_3 (λ_{max} ~ 340 nm) [15] and for *p*-dimethylaminophenyl azide (λ_{max} ~ 360 nm).[12] On pulsed excitation of 4,4′-diazidobiphenyl in cyclohexane, an intermediate absorption with λ_{max} = 380 nm ($\Delta\lambda$ = 50 nm) and a life-time of 19 ± 2 ns was detected.[107] This was assigned to a singlet intermediate (a singlet mononitrene or a didehydroazepine).[107]

The IR spectroscopic absorption at 1887 cm^{-1} (and that at 1877 cm^{-1} for the ^{15}N isotope), registered during the photolysis of PhN_3 and its derivatives, provided further evidence that reaction proceeds via didehydroazepines (azacycloheptatetraenes), formed by dehydrogenation of the corresponding 1*H*-azepine;[12,13] this was also consistent with product analyses from photolyses in the presence of amines. The IR spectra of intermediates obtained by pulsed excitation of PhN_3 and its derivatives did not exhibit absorption corresponding to benzazirines. Thus, the following scheme may be proposed for the photolysis of PhN_3 and its derivatives:[10,12–16,40]

Scheme 1



b) Spectral characteristics of intermediates

The electronic spectra absorptions of ^{3}PhN and its derivatives are given in Table 6.[22,23] The data relate only to $\pi\pi^*$-transitions. There is a long-wavelength absorption for ^{3}PhN, but it does not correspond with a specific transition.[23] The absorptions for ^{3}PhN and its derivatives were recorded with the following characteristics: $\lambda_{max} \approx 500$ ($\lg\varepsilon$ ~ 2.5); ~400 (~3); ~320 (~3.5), and ~240 nm ($\lg\varepsilon \approx 4$).[16] It is considered that the long-wavelength absorption of ^{3}PhN (λ_{oo} = 489 nm) corresponds with transitions of the type $n_y \rightarrow \pi^*$ and $\pi \rightarrow n_y$, while $\pi\pi^*$ transitions are primarily responsible for the other absorptions. It is possible that the first absorption peak is due, in part, to a transition of the type $n_z \rightarrow n_y$.

Luminescence is characteristic of triplet aromatic nitrenes which possess neutral or donor substituents. This has been classified as $T_1 \rightarrow T_0$ fluorescence.[16,23,42,108] The fluorescence quantum yield for *p*-tolylnitrene is 0.01 ± 0.02 [24] and for *p*-aminophenylnitrene it is 0.10 ± 0.02.[34]

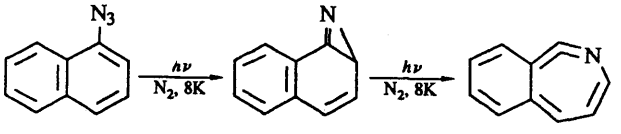
The absorption spectrum of ^{1}PhN is unknown at present. It cannot be ruled out that the broad absorption in the region 400–480 nm, obtained on flash photolysis of *p*-dimethylaminophenyl azide, is due to the presence of singlet *p*-dimethylaminophenylnitrene.[14] It is not clear which singlet species (a didehydroazepine or a singlet mononitrene) is responsible for the absorption at λ_{nm} = 380 nm, recorded on impulse excitation of 4,4′-diazidobiphenyl.[107]

The IR spectra of didehydroazepines (azacycloheptatetraenes) are characterised by absorption with $\nu_{max} \sim 1990$ cm^{-1}; there is also weak, poorly-defined, absorption in the near UV region with a maximum at 340–360 nm. 1*H*-Azepines — the products obtained by addition of primary and secondary amines to didehydroazepines — show significantly higher absorption in this region ($\lambda_{max} \approx 360$ nm). 3*H*-Azepines, formed by subsequent photo-conversion of 1*H*-azepines, absorb in a shorter wavlength region.[15,102]

c. Photolysis of polynuclear aromatic azides

Annelation of azidobenzenes to other aromatic ring systems has a profound effect on the chemical behaviour of the intermediate nitrenes and other species obtained on photolysis.[10] Thus, contrasting with the photolytic behaviour of PhN_3 and its derivatives, the photolysis of polynuclear aromatic azides in the presence of primary and secondary amines leads to aromatic dialkylamines rather than 3*H*-azepines.[10,53,109–111] These products would be anticipated for photolysis via azirines.

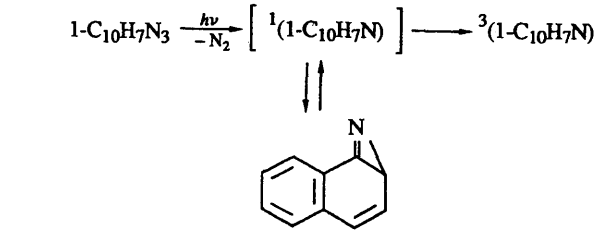
The IR spectra of the products obtained by irradiation of 1- and 2-naphthyl azide in an argon or N_2 matrix at 8 K are characterised by a cluster of absorption bands (typical of tricyclic azirines (1708–1736 cm^{-1}).[112] On prolonged irradiation they disappear and are replaced by a new cluster of bands (1910–1930 cm^{-1}) which possibly correspond to the intermediate didehydroazepines:



However, triplet ^{3}(1-$C_{10}H_7N$) is formed on irradiation of 1-$C_{10}H_7N_3$ in a glass matrix at 77 K.[113]

There are only a few references to flash photolysis of polycondensed azides.[36,42,53,70] Reiser et al. were first to record the absorption of intermediates obtained on flash photolysis of 1-azidonaphthalene and 1-azidoanthracene, and concluded that triplet nitrenes were responsible.[36] Sumitani et al. showed that excitation of 1-azidopyrene using a laser pulse of less than 15 ns produces a species with an absorption maximum in the region 455 n.[42] This was supported later by Schrock et al.[53] After a period of 22 ns at room temperature and 34 ns at 77 K, this species is converted into another with a maximum at 420 nm.[42,53] The latter species was also formed on triplet sensitisation and had an absorption spectrum identical to that of ^{3}(1-PyN) at 77 K. Under the conditions of laser excitation it disappeared in a second-order process to give 1,1′-azopyrene. The Japanese authors assigned the absorption maximm at 420 nm to ^{3}(1-PyN), and that in the region of 455 nm to ^{1}(1-PyN).[42] However, Schrock et al. did not exclude the possibility that the latter absorption was due to the corresponding azirine.[53]

The photolysis of 1-azidonaphthalenes in benzene leads to the formation of 1,1′-azonaphthalene, but in diethylamine a significant amount of 1-aminonaphthalene is formed.[53,109] No absorption was detected in the region 350–650 nm directly after 13 ns laser impulse excitation at this azide in benzene. However, the intensity of the absorption in the near UV region, with a maximum at 370 nm, increased exponentially with time over a period of 2.8 ± 0.2 μs. The species absorbing at 370 nm would appear to be ^{3}(1-$C_{10}H_7N$). It disappeared in a second-order process to give 1,1′-azonaphthalene. The precursor of ^{3}(1-$C_{10}H_7N$), having a lifetime of 2.8 μs, is presumed to be an azirine.[53]

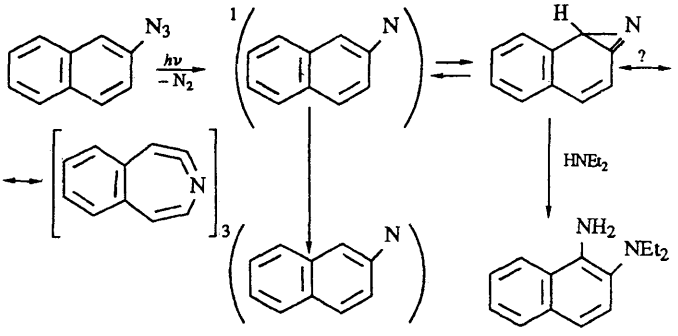


Azo compounds were isolated on irradiation of 2-azidonaphthalene and 2-azidopyrene in benzene, whereas, in the presence of diethylamine, the products were 2-diethylamino-1-naphthylamine and 2-diethylamino-1-pyrenylamine, respectively.[53,113] The triplet-sensitised photolysis of 2-$C_{10}H_7N_3$ in the presence of diethylamine does not lead to the formation of diamines.[53] There was absorption in the region 350–650 nm immediately after laser excitation of 2-$C_{10}H_7N_3$. Then, with a time frame of ~1 ms, azonaphthalene was formed in a second-order process. In the presence of benzophenone as triplet sensitiser, ^{3}(2-$C_{10}H_7N$) was formed with an absorption maximum in the near UV region at 365 nm. This disappeared in a second-order process, more rapidly by direct photolysis, to give azonaphthalene.[53] No novel intermediate species were detected in the presence of diethylamine. However, the yield of azonaphthalene was much lower. The differences in the photochemical behaviour of 1- and 2-azidonaphthalene are evidently associated with the fact that the life-time of the azirine intermediate is significantly longer in the latter case.[53]

After laser pulse irradiation of 2-azidopyrene, an absorption was detected with a maximum at 420 nm, this being assigned to ^{3}(2-PyN_3). The same absorption was evident in diethylamine as solvent. This disappeared after 2.5 μs with the formation of 2-diethylamino-1-pyrenylamine, absorbing in the region 445 nm. Schuster et al. proposed that the conversion of singlet 2-PyN to the triplet form was reversible.[53]

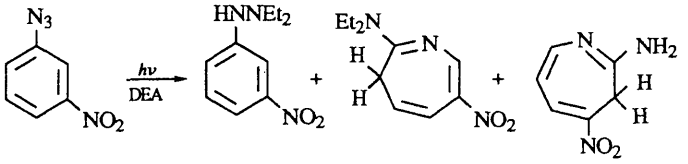
The primary processes involved in the photolysis of polycondensed azides are exemplified by the photo-conversion of 2-azidonaphthalene, as shown below:

Scheme 2

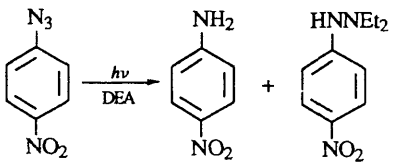


IV. The reactivity of intermediate singlet species

Singlet aromatic nitrenes are not dispersed to insert into C–H bonds or add across double bonds.[10] Compounds which, formally, are products of C–H bond insertion are often obtained as a result of cleavage of hydrogen by triplet nitrenes.[114,115] There are several references to N–H insertion by singlet arylnitrenes having acceptor substituents.[32,116–118] Thus, hydrazine compounds are formed together with 3*H*-azepines by irradiation of 4-cyanophenyl azide in dimethylamine[116,117] and of 3-nitrophenyl azide in diethylamine:[118]



Furthermore, irradiation of 4-nitrophenyl azide in diethylamine affords a mixture of 4-nitroaniline and *N*-(4-nitrophenyl)-*N'*,*N'*-diethylhydrazine (9%):[32]



The yield of the hyrazine falls significantly on triplet sensitisation,[117] and the variation in the yield of hydrazine and azepines,[116,117] or aniline and hydrazine,[32] as a function of the concentration of amine confirms the fact that a singlet nitrene is the precursor of the hydrazine.

1. Isomerisation of singlet aromatic nitrenes

Isomerisation into didehydroazepines (Scheme 1) or into tricyclic azirines (Scheme 2) are the most characteristic reaction of singlet aromatic nitrenes. It is known that these isomerisations take place within 10 ns (the period of the laser pulse).[12–16] The isomerisation is activated thermally, the rate constant for the isomerisation of ^{1}PhN at room temperature being approximately $10^{11\pm1}$ s^{-1}.[16] 3*H*-Azepines were not formed on irradiation of the following aromatic azides in the presence of amines: *p*-nitro=, *o*- and *p*-cyano-, *o*-chloro-, *p*-amino- and *p*-dimethylaminophenyl azide.[10,13,32,119,120]

In contrast to the above-mentioned azides, PhN_3 and the majority of its derivatives are converted into 3*H*-azepines in high yield in the presence of amines.[10,13] The efficiency of formation of the intermediate didehydroazepines was assessed from IR absorption in the region 1887 cm^{-1} relative to that obtained for *p*-chlorophenyl azide[13] (Table 7).

The effect of a heavy halogen atom (Cl, Br, I) on the yield of didehydroazepine is thought to be associated with enhancement of inter-system crossing (ISC) into the initial azide.[13] In our opinion, introduction of a nitro group into the 3- and 4-position of the azidoarene ring has a significant effect on ISC into the azide and is responsible for the low yield of didehydroazepine. With 2-dimethylaminophenyl azide, the efficiency of isomerisation is assumed to be low, as is confirmed by MDNO calculations for the potential barrier to reaction.[13]

Table 7. Relative values for the optical density of the IR absorption of intermediates at 1887 cm^{-1} (ΔD_{rel}) on impulse excitation of para-substituted phenyl azides (p-$XC_6H_4N_3$), and the values of rate constant (k_4) for the reaction of 5-substituted 1,2-didehydroazepines with diethylamine in cyclohexane.[13]

X	ΔD_{rel}	k_4, $l.mol^{-1}\,s^{-1}$
H	0.83	$6.5 \cdot 10^6$
Ph		$3.6 \cdot 10^5$ $(1.4 \cdot 10^4)$*
SMe		$1.6 \cdot 10^5$
OMe	0.48	$2.5 \cdot 10^4$
CO_2H		$3.0 \cdot 10^7$
$CONMe_2$		$4.4 \cdot 10^7$
COMe		$2.8 \cdot 10^8$
NO_2	< 0.05 (0.12**)	
Cl	1.00	$1.3 \cdot 10^8$
Br	1.14	$1.7 \cdot 10^8$
I	0.22	$2.7 \cdot 10^8$

* The rate constant for the reaction of *N*,*N*-diisopropylamine.
** ΔD_{rel} for X = *m*-NO_2.

Table 8. Activation parameters for the effective rate constant $\tilde{k}$ for the conversion of 5-methyl-1,2-didehydroazepine into triplet tolynitrene.[17,25]

Solvent	$\tilde{k}$ (298 K), s^{-1}	$\lg \tilde{k}_0$, s^{-1}	E_{act}, kcal/mol
Hexane	92	9.5±0.2	10.3±0.4
Acetonitrile	$8 \cdot 10^2$	9.6±0.2	9.1±0.3
Ethanol	$5 \cdot 10^3$	8.0±0.1	5.9±0.2

2. Reactions of 1,2-didehydroazepines

It has been shown that the rate of 1,2-didehydroazepine conversion increases with the concentration of PhN_3, the pseudo-first-order rate constant being linearly proportional to the concentration.[13] The bimolecular rate constant for the reaction of didehydroazepine with PhN_3 in heptane at room temperature is 7.5×10^4 l/mol/s.[13] Evidently, this reaction leads to the formation of unidentified polymeric products on both photolysis and thermolysis of PhN_3 as well as its derivatives.[10] The reaction of didehydroazepines with azides may lead to an increase in the quantum yield of azide photolysis as the concentration is increased.[29–31]

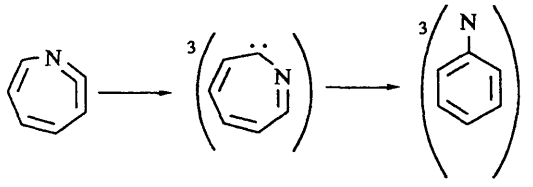
On extrapolation to zero concentration of the azide, the life-time of 1,2-didehydroazepine in heptane at room temperature was found to be 4.8 ms.[13] The life-time (τ) of the 1,2-didehydroazepine formed on impulse photolysis of *p*-tolyl azide was measured in different solvents in the temperature range to 13–60 °C.[17,25] This study of *p*-tolyl azide was undertaken at very low concentration ($< 5 \times 10^{-5}$ M) so that its reaction with the intermediate didehydroazepine does not make a contribution to the measured life-time. The

activation parameters ($\tilde{k}_0$ and E) relating to the effective rate constant for the irreversible conversion of the didehydroazepine into triplet nitene ($\tilde{k} = 1/\tau$) are given in Table 8. The effective constant $\tilde{k}$ is expressed in terms of the rate constants for the individual steps (see Scheme 1) as follows:

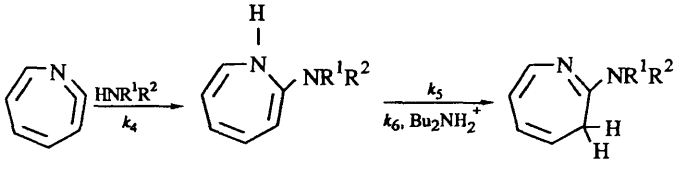
$$\tilde{k} = k_3k_2/(k_1 + k_3) \approx k_3k_2/k_1. \quad (9)$$

Since the rate constant for ISC (k_3) does not normally depend on the temperature, the value of E will equate to the enthalpy of isomerisation of *p*-tolylnitrene into the corresponding didehydroazepine. On conducting the reaction in ethanol, since it was not established whether the didehydroazepine reacts with ethanol under these conditions, it cannot be excluded that the decrease in the value of E is associated with the occurrence of this side-reaction.

Constrasting with the outlined scheme for the irreversible conversion of 1,2-didehydroazepines into triplet nitrenes via singlet nitrenes (Scheme 1),[9,16] an alternative pathway has been proposed on the basis of MNDO calculations:[13]



The reaction of didehydroazepines with amines leads to 1*H*-azepine derivatives which then isomerise into stable 3*H*-azepine derivates.[12,13,15,88,102]



The 1*H*-azepines obtained from a number of ortho-substituted phenyl azides are relatively stable, and their formation has been detected by NMR spectroscopy.[88]

The nature of the solvent and substitution of the phenyl ring affects the rate of formation of 1*H*-azepines (Table 9).[102] When the concentration of the amine is above 3 M the rate of formation of 1*H*-azepine becomes independent of the concentration and nature of the amine.[15] The negative activation energy (Table 9) and the non-linear dependence of the rate on the concentration of amine would suggest that the reaction with amines involves two intermediates.[102]

The rate constant k_4 has been determined by measuring the rate of disappearance of the IR absorption for the intermediate didehydroazepines.[13] It was found that the value of k_4 changes by more than two orders of magnitude on varying the substituent in the 5-position of the 1,2-didehydroazepine (see Table 7) and increases with the electron-accepting properties of the substituent. A reasonable linear dependence (Hammett plot) was found for $\lg k_4$ against the σ-substituent constant.[13]

The rate of isomerisation of 1*H*-azepines to the corresponding stable 3*H*-azepine does not depend on the concentration of the amine and increases significantly in the presence of dibutylammonium ion.[102] The activation parameters relating to the rate constants for the monomolecular and $Bu_2NH_2^+$-catalysed isomerisation of 1*H*-azepines to 3*H*-azepines are given in Table 10.

Table 9. Activation parameters and values of the rate constant for the reaction of didehydroazepines (formed on impulse excitation of derivatives of PhN_3) with dibutylamine (k_4); and the values of the rate constants for the unimolecular (k_5) and $Bu_2NH_2^+$-catalysed (k_6) isomerisation of 1*H*-azepines into 3*H*-azepines in acetonitrile at 21.7 ± 0.3 °C.[102]

Substituent in phenylazide	k_4, l.mol^{-1} s^{-1}	k_4^2, l.mol^{-1} s^{-1}	E_4, kcal/mol	$-k_5$, s^{-1}	k_6, l.mol^{-1} s^{-1}
H	$3.5 \cdot 10^7$			11	$3.1 \cdot 10^6$
H*	$9.7 \cdot 10^5$	$(4.2\pm1.4) \cdot 10^4$	−1.8±0.2	0.11	
o-Me	$7.5 \cdot 10^4$	$(5.9\pm1.3) \cdot 10^5$	1.1±0.2	~10^{-4}**	72
o-Et	$2.9 \cdot 10^4$			~10^{-4}**	
o-CF_3	$7.8 \cdot 10^8$			~$2 \cdot 10^{-3}$	250
p-Me***	$1.6 \cdot 10^6$				

* The value of k and E in hexane.

** k_5 measured in dioxane.

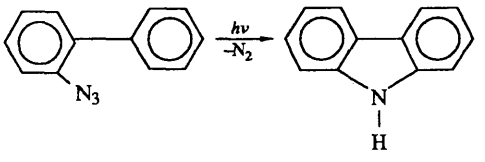
*** The rate constant refers to the reaction with tert-$BuNH_2$ in ethanol.[17]

Table 10. Activation parameters for the rate constants for the monomolecular (k_5) and $Bu_2NH_2^+$-catalysed (k_6) isomerisation of 1*H*-azepines into 3*H*-azepines.[102]

Azide	Solvent	k_5^2, s^{-1}	E_5, kcal/mol	k_6^2, l.mol^{-1} s^{-1}	E_6, kcal/mol
Phenyl azide	hexane	0.7±0.3	1.1±0.4		
	acetonitrile	$(4.2\pm1.0) \cdot 10^2$	2.0±0.2	$(3.8\pm0.7) \cdot 10^8$	2.6±0.2
o-Tolylazide	acetonitrile			$(5.5\pm0.8) \cdot 10^9$	9.9±0.5

3. Cyclisation of ortho-substituted aromatic azides

A large number of photochemical and thermal cyclisation of ortho-substituted aryl azides are known.[10] Only the photochemical cyclisation of *o*-azidobiphenyl (*o*-AB) to carbazole will be examined in this review.



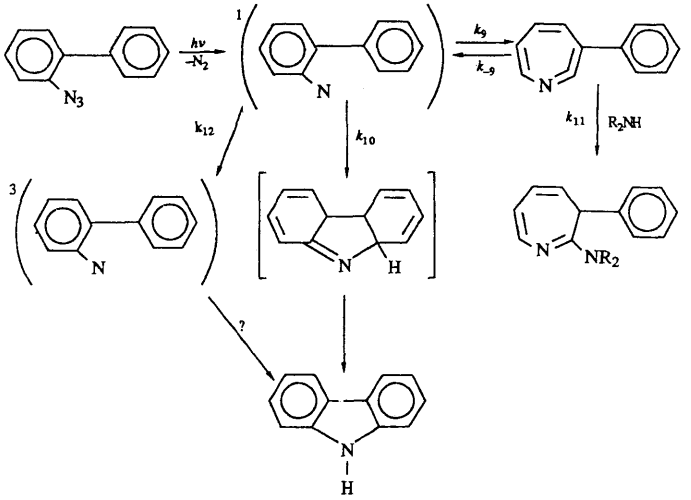
Swenton et al. isolated carbazole (68−74%) and 2,2′-azobiphenyl (8−12%) as a result of photolysis of *o*-AB at a concentration of 10^{-2} M.[52] Triplet quenchers (dienes, pyrene, oxygen) decreased, and triplet sensitisers (benzophenone, acetophenone) increased, the yield

of the azo compound (to 39–49%).[52] A 3*H*-azepine was obtained in addition to carbazole on irradiating *o*-AB in the presence of diethylamine.[101,103,121] The yield of carbazole derivatives was significant on photolysis of *o*-AB and its 2′,3′-disubstituted analogues, even in pure diethylamine (49% for *o*-AB). As the concentration of diethylamine increases the relative proportion of carbazole and 3*H*-azepine begins to fall and then remains sensibly constant.[103]

A kinetic study has been made of carbazole formation (λ_{max} = 289 nm) and of the decay of the intermediate (absorbing at λ_{max} = 342 nm), assumed by the authors to be a triplet nitrene.[100] The rate constant for carbazole formation (k_7) and decay of the intermediate (k_8) in cyclohexane agreed with a factor of 2. On this basis, the authors concluded that a triplet nitrene was a precursor of the carbazole.[100] Later, Sundberg reproduced the results and found that the rate constants k_7 and k_8 in hexane differed by a factor of 2, whereas in other solvents the difference was two orders of magnitude.[101] The intermediate formed during the course of the reaction was not converted into carbazole in significant amount. A kinetic study of the photolysis of 2′,4′,6′-trideuterio-3′,5′-dimethyl- and 3′,5′-bis(trifluoromethyl)-derivatives of *o*-AB (Table 11) has also been undertaken, as a result of which three hypothetical mechanisms were proposed for the formation of carbazole.[101]

The following mechanism for carbazole formation (Scheme 3) may be proposed on the basis of the results obtained for the photolysis of *o*-AB,[52,101,103,121,122] with reference to the conversions of other aryl azides (Scheme 3):

Scheme 3



The reactions of triplet nitrene may lead to the formation of azo compounds.[52] However, it cannot be excluded that a small amount of carbazole is also formed via these species.

The effective rate constant k_7, assuming that k_{12} is negligible, is given by Eqn. (10):

$$k_7 = k_{10}k_{-9}/(k_9 + k_{10}). \quad (10)$$

In the presence of an amine the proportion of carbazole can be expressed by the ratio:

$$\Phi_{min} = k_{10}/(k_{10} + k_9).$$

For *o*-AB, $\Phi_{min} \approx 0.5$, so that $k_{10} \approx k_9$. The activation energy for carbazole formation is evidently close in value to the enthalpy of isomerisation of the intermediate singlet nitrene to didehydroazepine. In cyclohexane, the calculated value of the activation energy (11.5 kcal/mol [100]) is close to the value of that relating to the rate constant ($\tilde{k}$) for the conversion of 5-methyl-1,2-didehydroazepine to triplet tolylnitrene (10.3 kcal/mol [17,25]). The increase in k_7 on passing from hexane to acetonitrile and methanol (see Table 11) coincides with a similar variation in the value of $\tilde{k}$ (see Table 8). The proposed mechanism outlined in Scheme 3 is in reasonable accord with experimental findings, but the nature of the intermediate absorbing in the region $\lambda_{max} \approx 340$ nm has not been established.

Table 11. The values of the effective rate constant for the formation of carbazole (k_7) and the decay of the intermediate (k_8) for the reaction of *o*-azidobiphenyl and its derivatives at 20 ± 1 °C.[101]

Substituent	Solvent	k_7, s^{-1}	k_8, s^{-1}
H	hexane	980	490
	cyclohexane	960*	—
	THF	$5.0 \cdot 10^3$	27
	acetonitrile	$9.8 \cdot 10^3$	—
	methanol	$19.6 \cdot 10^3$	9.9
2,4,6-D_3	cyclohexane	$1.0 \cdot 10^3$*	260*
	THF	$4.9 \cdot 10^3$	11.3
3,5-Me_2	hexane	$1.3 \cdot 10^3$	390
	THF	$6.7 \cdot 10^3$	12.4
	acetonitrile	$7.5 \cdot 10^3$	12.6
3,5-$(CF_3)_2$	hexane	140	~140
	THF	830	—
	acetonitrile	$1.6 \cdot 10^3$	—

* Value at 18 °C.

V. Reactions of triplet aromatic nitrenes

1. Formation of azo compounds

There are two mechanisms by which azo compounds are formed.[32,36,53,70,106]

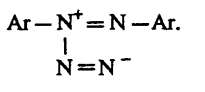
$$^3ArN + Ar'N_3 \xrightarrow{k_{13}} [ArN_4Ar'] \rightarrow ArN{=}NAr' + N_2, \quad (11)$$

$$^3ArN + {}^3ArN \xrightarrow{k_{14}} ArN{=}NAr. \quad (12)$$

The existence of pathway (11) is substantiated by the formation of unsymmetrical azo compounds on irradiation of 1- or 2-azidonaphthalene in the presence of PhN_3.[53] However, no (4-nitrophenyl)azobenzene was detected on photolysis of *p*-nitrophenyl azide

in the presence of PhN_3.[32] Reaction (11) was observed on flash photolysis of 1-azidoanthracene (k_{13} = 0.5 × 10^9 l mol^{-1} s^{-1}) in ethanol.[36]

The yield of azonaphthalene, formed on irradiation of 1-azidonaphthalene with a non-laser source, increases after a few hours in the dark from 22 to 46% (for 2-azidonaphthalene, the increase is from 22 to 45%).[53] This confirms the existence of a relatively stable intermediate adduct. A tetrazene structure, Ar–N=N–N=N–Ar, has been proposed for this compound.[53] It is also possible that it has a 1,2-tetrazene structure:[9,10]



The yield of azobenzene from PhN_3 does not increase when irradiation has been ceased.[15]

The rate of reaction (12) is controlled by diffusion,[36] the approximate value of the rate constant k_{14} being just under the theoretical limit for a diffusion-controlled process (Table 12).

Table 12. Values for the rate constant for recombination (k_{14}) of triplet aromatic nitrenes (^{3}ArN).

Ar	Solvent	$k_{14}.10^{-9}$, l.mol^{-1} s^{-1}	Refs.
1-Naphthyl	hexane	0.55±0.05	[36]
	benzene	0.45	—
	ethanol	0.40	—
	liq. paraffin	0.09	—
1-Pyrenyl	benzene	2.1±0.2	[70]
4-Nitrophenyl	"	1.0	[32]

A third pathway for the formation of azo compounds was examined in Smith's review:[9] dimerisation of aminyl radicals formed by abstraction of an atom of hydrogen from the solvent, substrate or product by a triplet nitrene, followed by dehydrogenation of the resulting hydrazo compound.

2. Abstraction of a hydrogen atom

Amines are often formed together with azo compounds via triplet aromatic nitrenes.[10,36]

$$^3ArN + RH \xrightarrow{k_{15}} Ar\dot{N}H + \dot{R}, \quad (13)$$

$$Ar\dot{N}H + \dot{R} \rightarrow ArNHR, \quad (14)$$

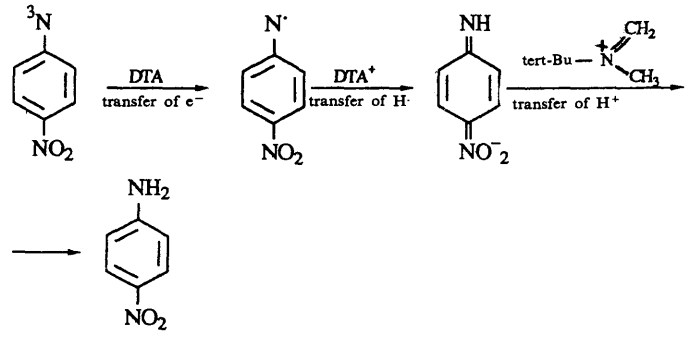
$$Ar\dot{N}H + RH \rightarrow ArNH_2 + \dot{R}. \quad (15)$$

Reaction (13) does not compete with reaction (12) on pulsed irradiation, so that the amount of information on this step is limited. The value of the rate constants for the abstraction of hydrogen from hexane by triplet ^{3}(1-$C_{10}H_7N$) and from ethanol by 4,4′-dinitrobiphenyl† have been evaluated at 2.6 × 10^2 l/mol/s.[36] It is thought that abstraction of hydrogen from the aromatic ring of the azide or the nitrene leads to a polymeric product.[36]

The contribution of pathway (13) predominates in a polymeric matrix, under which conditions amines (principally primary amines) are the main product.

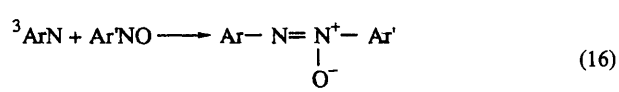
The kinetics of the decay of ^{3}ArN in polymeric matrices cannot be described by a simple kinetic equation.[36] The kinetic curves are characterised by three points in time: τ_0, the estimated time after which the curve starts to slope $\tau_{1/2}$, when the concentration of ^{3}ArN falls by half; and τ_1, the period of the entire process. Time $\tau_{1/2}$ varies between 10^{-3} s in weak polymeric matrices (polystyrene, plasticised toluene) to 0.1–2 s in hard polymeric matrices. The limiting factor in the reaction would appear to be the nature of the surroundings (configurational diffusion). Electron-accepting substituents increase the rate of hydrogen abstraction, the logarithm of the half-life time ($\lg\tau$) being −0.2 (for *p*-morpholinophenylnitrene), −0.8 (for 2,4,6-trimethylphenylnitrene), and −1.5 (for *p*-acetylphenylnitrene).[99]

An alternative pathway for the formation of amine has been proposed for the conversion of *p*-nitrophenyl azide in the presence of *N,N*-dimethyl-tert-butylamine (DTA):[32,106]



3. Photochemical oxidation of aromatic azides

Reiser et al. were first to study the reactions of triplet aromatic nitrenes with oxygen.[22] At 77 K, the reaction is limited by the mobility of oxygen and is associated with the formation of compounds absorbing in the region 400–650 nm. This disappears on thawing the matrix. For a long time, it was thought that nitro compounds were the principal oxygen-containing products formed on photolysis of aromatic azides.[69,70,104,123,124] However, azoxy compounds, arising by interaction of triplet nitrenes with nitroso compounds, have also been detected.[32,124,125]



$$^3ArN + Ar'NO \longrightarrow Ar-N=N^+(O^-)-Ar' \quad (16)$$

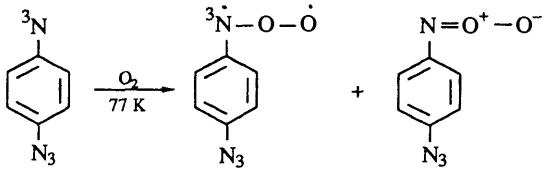
It has been shown that nitrobenzene ($PhNO_2$) is the main product from the oxidative photolysis of PhN_3 in acetonitrile at a high concentration of the azide (1.2 × 10^{-2} M). However, on decreasing the concentration to 10^{-4} M, nitrosobenzene (PhNO) becomes the sole product.[29] The authors propose that PhNO is the initial product, and that $PhNO_2$ is formed therefrom in a secondary photolytic process (a mechanism for formation of PhNO was not proposed).

Shortly after, it was demonstrated that irradiation of *p*-azidoaniline in oxygen-saturated aprotic solvents affords *p*-nitroso- and *p*-nitro-aniline.[126] However, the latter was not considered to arise

† According to Miura et al., pulsed excitation of 4,4′-diazidobiphenyl produces a triplet mononitrene.[107]

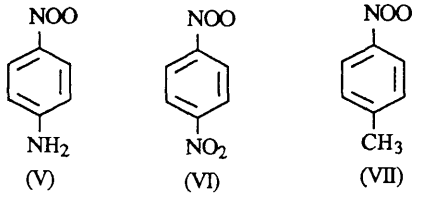
by secondary photolysis. A number of authors reported the simultaneous formation of nitro- and nitroso-compounds on photolysis of PhN_3 and its derivatives.[25,32–34,125] Sawaki et al. also argued that $PhNO_2$ was not formed by secondary photolysis of PhNO.[127]

It has been shown that triplet *p*-azidophenylnitrene reacts in a glass matrix at 77 K with dissolved oxygen to give two types of product: a paramagnetic compound, characterised by ESR spectroscopy (D = 0.11 cm^{-1}) as a triplet species; and a diamagnetic compound, absorbing intensely in the visible region (400–500 nm).[69] By analogy with carbene chemistry, it was proposed that these species are, respectively, a *p*-azidophenylaminodioxide biradical and a bipolar nitroso oxide.



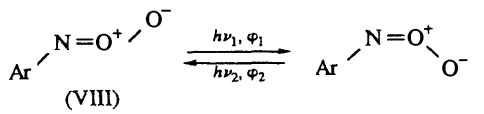
The formation of a paramagnetic adduct has also been recorded in the reaction of O_2 with 4,4′-dinitrenoazobenzene.[69] The reaction of ^{3}PhN and its *p*-nitro-, *p*-methoxy-, *p*-amino- and *p*-dimethylamino-derivatives with oxygen leads to coloured diamagnetic adducts, paramagnetic adducts not being recorded.[25,34,69] Evidently, the simultaneous formation of diamagnetic and paramagnetic adducts is more an exception than a rule.

Quantum chemical calculations by the AM1 method have shown that adducts (V–VII) can exist as two geometric isomers (*cis* and *trans*).[25]

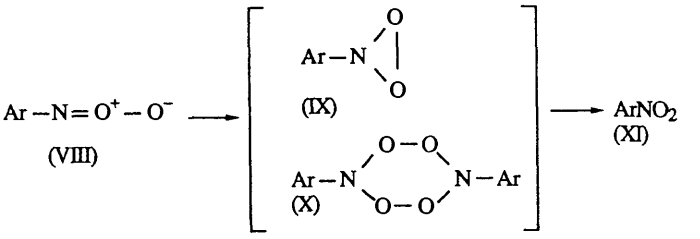


The *cis*-isomers exist principally in the singlet state (the triplet state being higher by 8–10 kcal/mol). Calculations for the *trans*-isomers point to effectively degenerate singlet and triplet states. Thus, diamagnetic and paramagnetic adducts not only have different electronic states, but also exist in isomeric forms. As a result, relaxation into the more stable adduct is not observed.[69]

Two diamagnetic adducts (λ_{max} = 495 and 588 nm), presumed to be *cis*- and *trans*-forms of (V), are produced by reaction of triplet *p*-aminophenylnitrene with O_2 at 95 K. The more stable form, absorbing at λ_{max} = 495 nm, is the sole product at 100 K. It is possible that a reversible equilibrium between the two forms is established on exposure to light ($\varphi_1 + \varphi_2 \sim 1$).[17,25]



In the thermal conversion of nitroso oxides, Brinen et al. proposed the intermediate formation of compounds (IX) or (X),[69] by analogy with carbene chemistry.[127,128]



In practice, warming compound (V) to 115 K produces a species exhibiting an absorption maximum in the region 336 nm (in methylcyclohexane) and at 318 nm (in toluene/THF). On freezing the matrix, *p*-nitro- (XII) and *p*-nitroso-aniline (XIII) are formed in comparable amounts.[17,25] The simultaneous formation of nitro and nitroso compounds would be consistent with the intermediate formation of compound (X).

Compound (V) has been detected at room temperature:

$$^3ArN + O_2 \xrightarrow{k_{16}} \underset{(V)}{ArNOO} \quad . \qquad (17)$$

$Ar = NH_2C_6H_4$.

By measuring the absorption against time, the kinetics of the decay of (V) was found to be of the second order [as would be anticipated if (X) is the initial reaction product]

$$(V) + (V) \xrightarrow{k_{17}} (X). \qquad (18)$$

In toluene, the rate constant k_{17} is (1.4 ± 0.4) × 10^9 l mol^{-1} s^{-1} and (0.72 ± 0.2) × 10^{10} l mol^{-1} s^{-1} in hexane.[34,130]

The dimeric peroxide (X) decomposes in two ways (Table 13):

$$(X) \xrightarrow{k_{18}} 2(XII), \qquad (19)$$

$$(X) \xrightarrow{k_{19}} 2(XIII) + O_2 \quad . \qquad (20)$$

Table 13. Activation parameters for the rate constants for the formation of *p*-nitro- (k_{18}) and *p*-nitroso-aniline (k_{19}).[33,34]

Solvent	k_{18} (298 K), s^{-1}	$\lg k^{\circ}_{18}$	k_{19} (298 K), s^{-1}	$\lg k^{\circ}_{19}$	$E_{18} = E_{19}$, kJ/mol
Hexane	1.9	15.8±0.8	0.8	15.4±0.8	88.5±4.6
Toluene	0.8	12.9±0.6	1.0	13.1±0.6	74.5±3.8

Thus, the mechanism of the photo-conversion of *p*-azidoaniline (XIV) in the presence of O_2 can be described as follows:[17,33,34]

Scheme 4

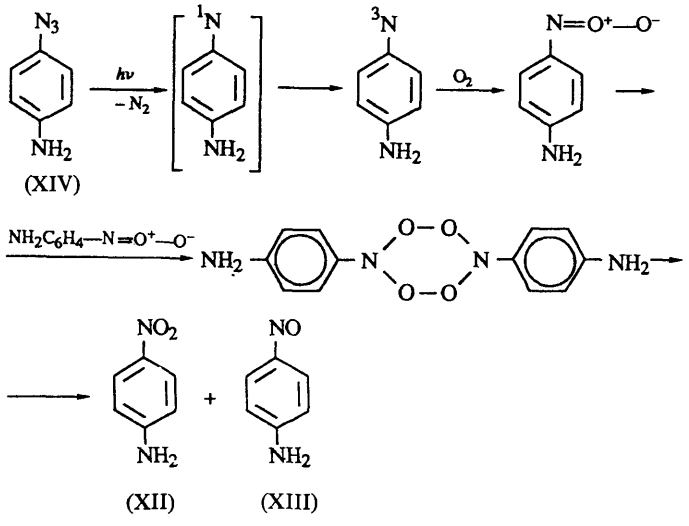


Table 14. Experimental and theoretical values for the long-wavelength maxima in the spectra of phenylnitroso oxide derivatives.[17,25]

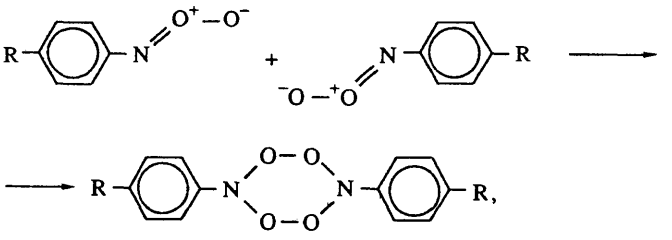
Substituent	λ_{max}^{exp} (77 K), nm	λ_{max}^{exp} (300 K), nm	λ_{max}^{theor}, nm	
			cis	*trans*
p-NH_2	495 and 588	440±5	406	430
p-NO_2	388	380±5	381	393
p-Me	400	395±5	393	415

Table 15. Values of the rate constants (k_{16}) for the reaction of triplet aromatic nitrenes (^{3}ArN) with oxygen.[17,25]

Ar	Solvent	*T*, K	$k_{16}.10^{-6}$, l.mol^{-1} s^{-1}
p-Aminophenyl	hexane	285	4.5±1.2
	toluene	—	8.0±2.0
p-Nitrophenyl	hexane	293	0.8±0.1
	ethanol	290	1.1±0.1
p-Tolyl*	acetonitrile	290	1.9±0.2
1-Pyrenyl**	benzene	—	0.9±0.1**

* The photolysis of *p*-tolyl azide was sensitised by benzophenone.
** The value of k_{16} was determined by Yamaoka et al.[70]

The formation of nitroso oxides has also been detected on low-temperature and flash photolysis of *p*-nitro- and *p*-methyl-phenyl azide (Table 14). However, intermediate species with structure (IX) and (X) were not evident. Kinetic data for the decomposition of (VII), based on absorption measurements, are in accord with a first order process, the rate constant being 0.2 s^{-1} in hexane at 20 °C. The kinetic curve for the decay of (VI) was not exponential, nor corresponded to a second order process ($\tau_{1/2} \approx 0.2$ s).[25] One may assume that the photo-conversion of *p*-nitro- and *p*-methyl-phenyl azide proceeds by a mechanism other than that described by Scheme 4, although the experimental observations are in accord with the process in outline. It is possible that the dimeric peroxide is formed by the cycloaddition of two *trans*-arylnitroso oxide molecules:



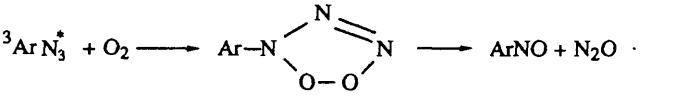
R = NO_2, Me.

The cyclodimerisation of *cis*-arylnitroso oxides would be sterically inhibited. Thus, it would appear that the adduct (V) is either formed in the *trans*-configuration or is readily converted into this form prior to dimerisation into (X) at a rate approximating to that of diffusion. If *cis*-(VI) and *cis*-(VII) are primary intermediates formed on reaction of *p*-nitro- and *p*-methyl-phenylnitrene, respectively, in the presence of oxygen, and if *cis*–*trans* isomerisation is a limiting step, then the decay of (VI) and (VII) would not follow second order kinetics.[25]

In order for reaction (17) to become dominant, a low concentration of azide and intermediate species is required. The desired conditions would also exist in polymeric matrices.[25,36,131–133] It has not been possible to detect reaction (17) on laser excitation in solution. Only the upper limit of the rate constant has been determined: $k_{16} \leqslant 10^6$ l mol^{-1} s^{-1} for 2,4,6-tribromophenylnitrene[16] and $k_{16} \leqslant 2 \times 10^5$ l mol^{-1} s^{-1} for *p*-nitrophenylnitrene.[32] The rate constants k_{16} obtained by flash photolysis are given in Table 15.[17,25,70] As can be seen, the values of k_{16} are significantly lower than that for a diffusion-controlled process and there is effectively no dependence on the nature of the aromatic nitrene. It should be noted that the rate constant for the reaction of oxygen with triplet carbenes[134–136] is significantly higher, being $(1-5) \times 10^9$ l mol^{-1} s^{-1} (1.9×10^8 l mol^{-1} s^{-1} for dimesitylcarbene[137]):

$$^3(R^1R^2C) + O_2 \rightarrow R^1R^2COO$$

A small propotion (~20%) of *p*-nitrosobenzene is formed without the involvement of triplet nitrenes, possibly by the route:[32,124]



Ar = $NO_2C_6H_4$. (21)

Recently, attempts were made to study the reactivity of PhNOO,[127] which, in the opinion of the authors, is a biradical. Irradiation of PhN_3 in the presence of diphenyl sulphide, diphenyl sulphoxide or *p*-chloronitrosobenzene results in oxidation of the additive. It is thought that oxidation takes place by interaction of the additive with PhNOO, as shown below with a nitrosoarene.

$$PhNOO + ArNO \longrightarrow Ph-\dot{N}-O-O-\underset{\underset{O\cdot}{|}}{N}-Ar \longrightarrow$$

$$\longrightarrow PhNO + ArNO_2 \qquad (22)$$

The following order of reactivity has been established

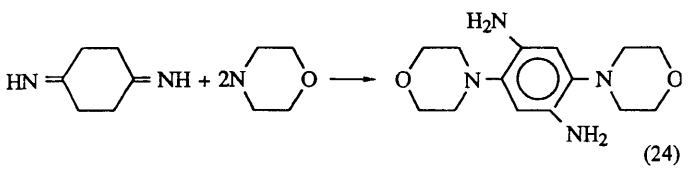
$$PhNO >> Ph_2S > Ph_2SO > PhH \quad \text{(Ref.127)}.$$

The observed increase in the yield of $PhNO_2$ on increasing the concentration of azide could be explained by the intervention of reaction (22).[29]

The photoconversion depicted in Scheme 4 proceeds only on irradiation of *p*-azidoaniline (XIV) in aprotic media. *p*-Benzoquinone diimine (XV) is formed on photolysis of (XIV) in water or in hexane containing an alcohol, amine, or a mercaptan at a concentration of 10^{-2} to 10^{-1} M. Presumably this takes place by the reaction:[25,120]

(XV) (23)

Compound (XV) readily reacts with nucleophiles, as exemplified below.[120]



(24)

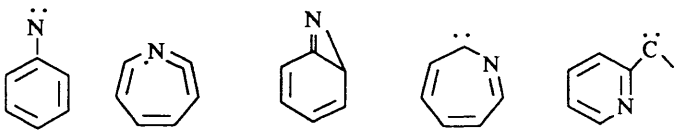
Derivatives of (XIV), e.g. nucleoside-5′-triphosphate γ-*p*-azidoanilides,[138,139] are used in the photo-affinity modification of proteins. It cannot be excluded that in such protein modification an intermediate *p*-benzoquinone diimine is implicated in a nucleophilic addition process.[140]

VI. Quantum chemical calculations on the properties of intermediates

The first quantum chemical calculations on the properties of triplet aromatic nitrenes were carried out by π-electron approximation.[44,81,141] Later, INDO calculations were made in order to interpret the ESR spectra of aromatic nitrenes.[48,50]

Information on the properties of singlet aromatic nitrenes is limited. From the photo-electron spectrum of the NH^- anion in the gas phase, a measurement was made of the splitting between the primary ($^3\Sigma^-$) state and the first excited ($^1\Delta$) state of nitrene itself (NH). This was found to be 34.6 ± 0.4 kcal/mol.[142] For a long time, it was only possible to deduce information on singlet-triplet splitting in PhN by quantum chemical calculations.[143] It was not until 1984 that experimental states of PhN in the gas phase (4.3 ± 0.4 and 8.8 ± 0.5 kcal/mol).[144,145]

Shillady et al.[143] applied the MINDO/2 method to calculate the geometry of all the possible intermediates in the photolysis and thermolysis of PhN_3:



(PhN) (A) (B) (C) (D)

The relative energies of these species were calculated by the MINDO/2 and INDO/P method (of Pople), and an assessment of the multi-configurational character of the electronic states of the intermediates was made by the INDO/P/INO method. The long-wavelength maxima in the spectrum of ^{3}PhN, as calculated by the INDO/S method, were assigned to $n_z \rightarrow \pi$ (380 nm) and $n_z \rightarrow n_y$ (330 nm) transitions,[143] although earlier it has been reported that the ^{3}PhN spectrum corresponds essentially to ππ*-type transitions. The long-wavelength transition with λ_{00} = 489 nm was not reproduced by calculation.

Table 16. Calculated values for the relative energy (E_{rel}) and absorption spectra of hypothetical intermediates from the photolysis of phenyl azide.[143]

Species	E_{rel}, kcal/mol			λ, nm (strength of the oscillator)
	MINDO/2	INDO/P	INDO/P/INO	
^{1}PhN	0	0	0	354(0.17), 307(0.03), 250(0.13)
^{3}PhN	—	-18.4	-15	380, 330, 297, 274, 222
^{1}A	6.9	—	—	—
^{1}B	-19	-68.2	-64.6	398(0.03), 313(0.02), 252(0.10)
^{3}B	—	11.3	—	382, 358, 315, 301, 284, 275
^{3}C	1.2	58.3	60.6	422(0.08), 354(0.10), 262(1.03)
^{1}D	6.3	—	—	—

It has been suggested that ^{1}PhN is formed in a configuration with seven π-electrons ($n_z^2 n_y^1 \pi^1$).[143] However, it is not known whether the singlet-triplet splitting (15–18 kcal/mol) corresponds essentially to this state or to a state with six π-electrons ($n_z^2 n_y^2$) (according to the INDO calculations of Pople et al.,[146] the latter is a lower singlet state). It has been calculated (Table 16)[143] that the bicyclic azirine (B) is a stable intermediate species, a fact which is not borne out experimentally.[12,13]

Schuster et al. calculated the heat of formation of all the considered intermediates by the MINDO method,[147] although the electronic configuration of ^{1}PhN was not specified. By comparison with other data,[17,25] it would appear that this configuration involves six π-electrons ($n_z^2 n_y^2$) (Table 17). According to these data[17,25] and the results obtained by *ab initio* 3−21G calculations,[145] the lower singlet state of ^{1}PhN is in the $n_z^2 n_y^1 \pi^1$ configuration. More detailed *ab initio* calculations on a broader basis are required in order to ascertain the exact electronic structure of singlet aromatic nitrenes.

Table 17. Results from calculations of the enthalpy of formation of intermediates (MNDO method).

Species	ΔH, kcal/mol		
	(Ref.13)	(Refs.17, 25)	MNDO+KB (2×2)
^{1}PhN	120	121 ($n_z^2 n_y^2$)	118
	—	105 ($n_z^2 n_y^1 \pi^1$)	
^{3}PhN	99	98($n_z^2 n_y^1 \pi^1$)	
^{1}A	100	—	
^{1}B	110	—	
^{3}C	103	—	

The MNDO calculations (Table 17) are roughly in accord with experimental data: the calculated singlet-triplet splitting (7 kcal/mol) is close to that measured experimentally,[144,145] and the calculated energy difference between ^{1}(PhN) and ^{1}(A) (5 kcal/mol) accords with the experimental value (5−10 kcal/mol) obtained in different solvents[17,25] (see Table 8). It follows that a didehydroazepine (^{1}A) is the most likely intermediate species formed on impulse photolysis of PhN_3, AM1, MNDO and MNDOC calculations are essentially in agreement in that acceptor (*p*-NO_2) and donor (*p*-NH_2) substituents lead to a small (1−2 kcal/mol) decrease in the singlet−triplet splitting in ArN.[17,25]

VII. Conclusions

From the material examined, it is evident that the mechanism of photolysis of azides is understood in broad outline. However, the possibility of parallel reaction pathways, involving key intermediate species (nitrenes didehydroazepines and/or azirines, etc.), adds to the overall complexity, and specific variations may simply be substrate-dependent. The precise course of the reaction may also depend on the concentration of the reactants, the temperature and presence of impurities. Thus the results obtained under different experimental conditions may differ significantly. The precise structure of the intermediate species, and their involvement in a particular pathway of azide photo-decomposition, has not been established in each instance, and more extensive kinetic data are required to obtain further information in this respect. This is particularly true for the initial processes involving singlet intermediate species. As there are no data on the rate of isomerisation of singlet aromatic nitrenes into didehydroazpines (and/or azirines), it is not possible to ascertain the effect of substitution on the formation of isomers.

Significantly more studies have been made on the reactions of triplet aromatic nitrenes, although quantitative data is still lacking. For example, the rate constant for reaction (11) has only been established under one set of conditions. Our understanding of the mechanism of azide photolysis in the presence of oxygen is limited, and contradictory results have been reported on the photo-decomposition of azides by chain propagation. In practice, when studying the reactions of aromatic azides, it is important to consider a large number of competing processes and the effect of experimental conditions on them.

References

1. *Fotokhimicheskie Protsessy v Sloyakh* (Photochemical Processes in Films) (Edited by A V El'tsov), Khimiya, Leningrad, 1978, p. 104
2. *Svetochuvstvitel'nye Polimernye Materialy* (Light-sensitive Polymeric Materials (Edited by A V El'tsov), Khimiya, Leningrad, 1985, p. 133
3. D S Breslow *Azides and Nitrenes. Reactivity and Utility* (Edited by E F V Scriven), Acad. Press, New York, 1984, pp 491−522
4. Y Bayley, J V Staros *Azides and Nitrenes. Reactivity and Utility* (Edited by E F V Scriven), Acad. Press, New York, 1984, pp 433−490
5. *Afinnaya Modifikatsiya Biopolimerov* (Affinity Modification of Bio-polymers) (Edited by D G Knorre), Nauka, Novosibirsk, 1983
6. R A Abramovitch, B A Davis *Chem. Rev.*, 1964, **64** 149
7. B Iddon, O Meth-Cohn, E F V Scriven, et al. *Angew. Chem., Int. Ed. Engl.*, 1979, **18** 900
8. *The Chemistry of the Azido Group* (Edited by S Patai), Wiley, New York, 1971, p. 256
9. P A S Smith *Nitrenes* (Edited by W Lwowski), Wiley, New York, 1970
10. P A S Smith *Azides and Nitrenes. Reactivity and Utility* (Edited by E F V Scriven), Acad. Press, New York, 1984, pp 95−204
11. T F Goryainova, Yu A Ershov, R M Livshits *Khim. Vys. Energ.*, 1975, 99
12. C J Shields, D R Chrisope, G B Schuster, et al. *J. Am. Chem. Soc.*, 1987, **109** 4723
13. Y-Z Li, J P Kirby, M W George, et al. *J. Am. Chem. Soc.*, 1988, **110** 8092
14. T Kobayashi, H Ohtani, K Suzuki, et al. *J. Phys. Chem.*, 1985, **89** 776
15. A K Schrock, G B Schuster *J. Am. Chem. Soc.*, 1984, **106** 5228
16. E Leyva, M S Platz, G Persy, et al. *J. Am. Chem. Soc.*, 1986, **108** 3783
17. N P Gritsan, E A Pritchina *J. Inf. Rec. Mater.*, 1989, **178** 391
18. G Remi *Kurs Neorganicheskoi Khimii* (A Course in Inorganic Chemistry), Mir, Moscow, 1972, Vol. 1, p. 584
19. H Okabe *Fotokhimiya Malykh Molekul* (Photochemistry of Small Molecules), Mir, Moscow, 1981, p. 337

20. R I Livingston, C N R Rao *J. Phys. Chem.*, 1960, **64** 765
21. A Mugnoli, C Mariani, M Simonetta *Acta Crystallogr.*, 1965, **19** 367
22. A Reiser, G Bowes, R J Horne *Trans. Faraday Soc.*, 1966, **62** 3162
23. V A Smirnov, S B Brichkin *Chem. Phys. Lett.*, 1982, **87** 548
24. V A Smirnov, S B Brichkin, M V Alfimov, et al. *Khim. Vys. Energ.*, 1981, **15** 526
25. E A Pritchina, Dissertations for Candidates in the Chemical Sciences, IKhKiG, Siberian Section of the Academy of Sciences of the USSR, Novosibirsk, 1989, p. 174
26. L J Leyshon, A Reiser *J. Chem. Soc., Faraday Trans. 2*, 1972, 1918
27. C J Shields, D E Falvey, G B Schuster, et al. *J. Org. Chem.*, 1988, **53** 3501
28. A Reiser, R Marley, *Trans. Faraday Soc.*, 1968, **64** 1806
29. Go C Lee, W H Waddell *J. Org. Chem.*, 1983, **48** 2897
30. R F Jenkins, W H Waddell, H W Richter *J. Am. Chem. Soc.*, 1987, **109** 1583
31. W H Waddell, Go C Lee *J. Am. Chem. Soc.*, 1982, **104** 5804
32. T-Y Liang, G B Schuster *J. Am. Chem. Soc.*, 1987, **109** 7803
33. E A Pritchina, N P Gritsan, N M Bazhin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1749
34. E A Pritchina, N P Gritsan *J. Photochem. Photobiol. A: Chemistry*, 1988, **43** 165
35. I Horner, A Christmann, A Gross *Chem. Ber.*, 1963, **96** 399
36. A Reiser, F W Willets, G C Terry, et al. *Trans. Faraday Soc.*, 1968, **64** 3265
37. N B Feilchenfeld, W H Waddell *Chem. Phys. Lett.*, 1984, **106** 297
38. Go C Lee, W H Waddell *J. Am. Chem. Soc.*, 1984, **106** 715
39. J P Constantino, H W Richter, Go C Lee, et al. *J. Am. Chem. Soc.*, 1985, **107** 1744
40. M S Platz *Azides and Nitrenes. Reactivity and Utility* (Edited by E F V Scriven), Acad. Press, New York, 1984, pp 359–393
41. A Reiser, L J Leyshon *J. Am. Chem. Soc.*, 1971, **93** 4051
42. N Sumitani, S Nagakura, K Yoshihara *Bull. Chem. Soc. Jpn.*, 1976, **49** 2995
43. G Smolinsky, E Wasserman, W A Yager *J. Am. Chem. Soc.*, 1962, **84** 3220
44. G Smolinsky, L C Snyder, E Wasserman *Rev. Mod. Phys.*, 1963, **35** 576
45. E Wasserman, L C Snyder, W A Yager *J. Chem. Phys.*, 1964, **41** 1763
46. E Wasserman, G Smolinsky, W A Yager *J. Am. Chem. Soc.*, 1964, **86** 3166
47. E Wasserman *Prog. Phys. Org. Chem.*, 1971, **8** 319
48. J H Hall, J M Fargher, M R Gisler *J. Am. Chem. Soc.*, 1978, **100** 2029
49. R M Moriarty, M Rahman, G J King *J. Am. Chem. Soc.*, 1966, **88** 842
50. J A Hebden, C A McDowell *J. Magn. Reson.*, 1971, **5** 115
51. F D Lewis, W H Saunders *J. Am. Chem. Soc.*, 1968, **90** 7033
52. J S Swenton, T J Ikeler, B H Williams *J. Am. Chem. Soc.*, 1970, **92** 3103
53. A K Schrock, G B Schuster *J. Am. Chem. Soc.*, 1984, **106** 5234
54. F D Lewis, J C Dalton *J. Am. Chem. Soc.*, 1969, **91** 5260
55. M Tsuda, O Oikawa, K Nagayama *Photogr. Sci. Eng.*, 1983, **27** 118
56. D Rehm, A Weller *Ber. Bunsenges. Phys. Chem.*, 1969, **73** 834
57. J C Scaiano, G G Wubbels *J. Am. Chem. Soc.*, 1981, **103** 640
58. S R Leone *Adv. Chem. Phys.*, 1982, **50** 255
59. P Brumer, M Shapiro *Adv. Chem. Phys.*, 1985, **60** 371
60. A Freedman, S C Yang, M Kawasaki, et al. *J. Chem. Phys.*, 1980, **72** 1028
61. J Park, C-F Yu, R Bersohn *Chem. Phys.*, 1989, **134** 421
62. D E Shemansky *J. Chem. Phys.*, 1969, **51** 689
63. D W Cornell, R S Berry, W Lwowski *J. Am. Chem. Soc.*, 1965, **87** 3626
64. V Ya Pochinok, V A Smirnov, S B Brichkin, et al. *Ukr. Khim. Zh. (Russ. Ed.)*, 1984, **50** 296
65. P F Kondratenko, E V Shrubovich *Fundamental'nye Osnovy Opticheskoi Pamyati i Sredy* (The Fundamental Basis of Optical Memory and Media), 1988, Vol. 19, p. 30
66. V G Plotnikov, A A Ovchinnikov *Usp. Khim.*, 1978, **47**(3) 444 [English translation in *Russ. Chem. Rev.*, 1978(3)]
67. S Mc-Glynn, T A Adzumi, M Kinosita *Molekulyarnaya Spektroskopiya Tripletnogo Sostoyaniya* (Molecular Spectroscopy of the Triplet State), Mir, Moscow, 1981, p. 349
68. V J Kuck, E Wasserman, W A Yager *J. Phys. Chem.*, 1972, **76** 3570
69. J C Brinen, B Singh *J. Am. Chem. Soc.*, 1971, **93** 6623
70. T Yamaoka, H Kashiwagi, S Nagakura *Bull. Chem. Soc. Jpn.*, 1972, **45** 361
71. M S Platz, G Carrol, F Pierrat, et al. *Tetrahedron*, 1982, **38** 777
72. R Alvarado, J-Ph Crivet, C Igier, et al. *Trans. Faraday Soc.*, 1977, **73** 844
73. T Autrey, G B Schuster *J. Am. Chem. Soc.*, 1987, **109** 5814
74. M E Sigman, T Autrey, G B Schuster *J. Am. Chem. Soc.*, 1988, **110** 4297
75. M Inagaki, T Shingaki, T Nagai *Chem. Lett.*, 1981, 1419
76. M Inagaki, T Shingaki, T Nagai *Chem. Lett.*, 1982, 9
77. I Woelfle, B Sauerwein, T Autrey, et al. *Photochem. Photobiol.*, 1988, **47** 1988
78. T Melvin, G B Schuster *Photochem. Photobiol.*, 1990, **51** 155
79. A Reiser, V Fraser *Nature (London)*, 1965, **208** 682
80. A Reiser, G C Terry, F W Willets *Nature (London)*, 1966, **211** 410
81. H Kashiwagi, S Iwata, T Yamaoka, et al. *Bull. Chem. Soc. Jpn.*, 1973, **46** 417
82. W H Waddell, N B Feilchenteld *J. Am. Chem. Soc.*, 1983, **105** 5499
83. O L Chapman, J-P Le Roux *J. Am. Chem. Soc.*, 1978, **100** 285
84. T Donnelly, I R Dunkin, D S D Norwood, et al. *J. Chem. Soc., Perkin Trans. 2*, 1985, 307
85. W von E Doering, R A Odum *Tetrahedron*, 1966, **22** 81
86. J S Splitter, M Calvin *Tetrahedron Lett.*, 1968, 1445
87. R J Sundberg, S R Suter, M Brenner *J. Am. Chem. Soc.*, 1972, **94** 513
88. M A Berwick *J. Am. Chem. Soc.*, 1971, **93** 5780
89. S E Carroll, B Nay, E F V Scriven, et al. *Tetrahedron Lett.*, 1977, 3175
90. R Purvis, R K Smalley, W A Strachan, et al. *J. Chem. Soc., Perkins Trans. 1*, 1978, 19
91. T Takeuchi, K Koyama *J. Chem. Soc., Perkin Trans. 1*, 1982, 1269
92. I R Dunkin, P C P Thomson *J. Chem. Soc., Chem. Commun.*, 1982, 1192
93. I R Dunkin, T Donnelly, T S Lockhart *Tetrahedron Lett.*, 1985, **26** 359
94. O L Chapman, R S Sheridan, J-P Le Roux *J. Am. Chem. Soc.*, 1978, **100** 6245

95. E Leyva, M S Platz *Tetrahedron Lett.*, 1985, **26** 2147
96. E Leyva, M J Young, M S Platz *J. Am. Chem. Soc.*, 1986, **108** 8307
97. S B Brichkin, V A Smirnov, M V Alfimov *J. Photochem.*, 1980, **12** 25
98. J S Hayes, R S Sheridan *J. Am. Chem. Soc.*, 1990, **112** 5879
99. A Reiser, L Leyshon *J. Am. Chem. Soc.*, 1970, **92** 7487
100. P A Lehman, R S Berry *J. Am. Chem. Soc.*, 1973, **95** 8614
101. R J Sundberg, D W Gillespie, B A DeGraff *J. Am. Chem. Soc.*, 1975, **97** 6193
102. B A DeGraff, D W Gillespie, R J Sundberg *J. Am. Chem. Soc.*, 1973, **95** 7491
103. R J Sundberg, R W Heintzelman *J. Org. Chem.*, 1974, **39** 1974
104. P E Nielsen, O Buchardt *Photochem. Photobiol.*, 1982, **35** 317
105. N B Feilchenfeld, W H Waddell *Chem. Phys. Lett.*, 1983, **98** 190
106. T-Y Liang, G B Schuster *J. Am. Chem. Soc.*, 1986, **108** 546
107. A Miura, T Kobayashi *J. Photochem. Photobiol. A: Chemistry*, 1990, **53** 223
108. S B Brichkin, V A Smirnov, M V Alfimov, et al. *Khim. Vys. Energ.*, 1980, **14** 23
109. S E Hilton, E F V Scriven, H Suschitzky *J. Chem. Soc., Chem. Commun.*, 1974, 853
110. J Rigaudy, C Igier, J Barcelo *Tetrahedron Lett.*, 1975, 3845
111. J Rigaudy, C Igier, J Barcelo *Tetrahedron Lett.*, 1979, 1837
112. I R Dunkin, P C P Thomson *J. Chem. Soc., Chem. Commun.*, 1980, 499
113. E Leyva, M S Platz *Tetrahedron Lett.*, 1987, **28** 11
114. J H Hall, J W Hill, J M Fargher *J. Am. Chem. Soc.*, 1968, **90** 5313
115. R E Banks, G R Sparkts *J. Chem. Soc., Perkin Trans. 1*, 1972, 2964
116. R A Odum, G Wolf *J. Chem. Soc., Chem. Commun.*, 1973, 360
117. R A Odum, A M Aaronson *J. Am. Chem. Soc.*, 1969, **91** 5680
118. T-Y Liang, G B Schuster *Tetrahedron Lett.*, 1986, **27** 3325
119. T de Boer, J I G Cadogan, H M William, et al. *J. Chem. Soc., Perkin Trans. 2*, 1975, 554
120. T S Gall, N P Gritsan, S D Myzina, et al. *Dokl. Akad. Nauk SSSR*, 1983, **273** 883
121. R J Sundberg, M Brenner, S R Suter, et al. *Tetrahedron Lett.*, 1970, 2715
122. J M Lindley, I M McRoblie, O Meth-Cohn, et al. *J. Chem. Soc., Perkin Trans. 1*, 1977, 219
123. R A Abramovitch, C J Azogu *J. Chem. Soc., Chem. Commun.*, 1971, 134
124. R A Abramovitch, S R Challand *J. Chem. Soc., Chem. Commun.*, 1972, 964
125. A B Bulacinski, B Nay, E F V Scriven, et al. *Chem. Ind. (London)*, 1975, 746
126. E A Kuklina (Pritchina) *Materialy XII Vsesoyuz. Nauch. Studencheskoi Konferentsii* (Material from the 12th All-Union Scientific Student Conference), Novosibirsk State University, 1984, p. 25
127. Y Sawaki, S Ishikawa, H Iwamura *J. Am. Chem. Soc.*, 1987, **109** 584
128. P D Bartlett, T G Traylor *J. Am. Chem. Soc.*, 1962, **84** 3408
129. J I G Cadogan, D H Hey, W A Sanderson *J. Chem. Soc.*, 1960, 4897
130. E A Pritchina, N P Gritsan *Kinet. Katal.*, 1987, **82** 1044
131. V M Treushnikov, N V Zelentsova, A V Oleinik *Zh. Nauchn. Prikl. Fotogr. Kinematogr.*, 1984, **29** 226
132. V M Treushnikov, N V Zelentsova, A V Oleinik *Zh. Nauchn. Prikl. Fotogr. Kinematogr.*, 1987, **32** 308
133. V M Treushnikov, N V Zelentsova, A V Oleinik *Zh. Nauchn. Prikl. Fotogr. Kinematogr.*, 1988, **33** 146
134. N H Werstiuk, H L Casal, J C Scaiano *Can. J. Chem.*, 1984, **62** 2391
135. H L Casal, M Tanner, N H Werstiuk, et al. *J. Am. Chem. Soc.*, 1985, **107** 4616
136. R L Barcus, L M Hadel, L J Johnston, et al. 1986, **108** 3928
137. A S Nazran, D Griller *J. Am. Chem. Soc.*, 1984, **106** 543
138. M A Grachev, D G Knorre, O I Lavrik *Soviet Scientific Reviews, Sec. D* (Edited by V P Skulachev), Harwood Acad., New York, 1981, Vol. 2, p. 107
139. V N Buneva, D G Knore, N V Kudryasheva *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1982, 122
140. A G Badashkeyeva, T S Gall, E V Efimova, et al. *FEBS Lett.*, 1983, **155** 263
141. J A R Cooper, J B Farmer, C L Gardner *J. Chem. Soc.*, 1965, **62** 54
142. P C Engelking, W C Lineberger *J. Chem. Phys.*, 1976, **65** 4323
143. D D Shillady, C Trindle *Theoret. Chim. Acta*, 1976, **43** 137
144. P S Drzaic, J I Brauman *J. Phys. Chem.*, 1984, **88** 5285
145. P S Drzaic, J I Brauman *J. Am. Chem. Soc.*, 1984, **106** 3443
146. J A Pople, D L Beverige *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970
147. M J S Dewar, W Thiel *J. Am. Chem. Soc.*, 1977, **99** 4899

Translated from *Uspekhi Khimii* **61** 940–977 (1992) U.D.C. 542.91

Polyfluoroalkanesulphenyl chlorides

A Yu Sizov, A K Kolomiets, A V Fokin
A N Nesmeyanov Institute of Heteroorganic Compounds, Russian Academy of Sciences, Moscow

ABSTRACT. **Data appearing since 1975 are correlated for the methods of synthesis of polyfluoroalkanesulphenyl chlorides, their reactions with O-, S-, N-, P- and C-nucleophiles, with unsaturated aromatic and heteroaromatic compounds, for their behaviour in oxidation and heterocyclisation reactions and in free radical conversions.**

Contents

I Introduction 517
II. Methods of Preparation 517
III. Reactivity 520

I. Introduction

The first information on polyfluoroalkanesulphenyl chlorides (PFASC) appeared in the fifties.[1,2] Certain unusual properties of these compounds served as a spur towards a wider study of the chemistry of the fluorine-containing sulphenyl chlorides. By 1975 more than 190 publications had appeared on the synthesis and reactivity of PFASC and have been correlated in a detailed review.[3]

Theoretical interest in the chemistry of these compounds has grown markedly in recent years. As functionally substituted aliphatic compounds of two-coordinate sulphur the PFASC and their numerous conversion products are an interesting subject for studying the dependence of reactivity on intramolecular *pd* interactions. In several unfluorinated analogues these are particularly strongly displayed in C–C–S triads and determine the high reactivity of these compounds towards heterocyclisation and numerous rearrangements through the episulphonium state.[4,5] The appearance of the abundant 2*p* electrons of fluorine atoms at positions 3, 4 and 5 to the sulphur atom does not affect these properties appreciably.

However in the last two decades most attention has been paid to the investigation of the applied chemistry of PFASC. The high electron-accepting properties of polyfluoroalkylthio groups and particularly of their oxidation products,[6] imparting to the molecule a reduced light sensitivity and combustibility, have stimulated syntheses of numerous compounds desirable in practice and materials derived from these compounds. Opportunities for using PFASC as effective precursors of biologically active compounds have been more widely investigated.

The main types of compound studied from this point of view are given below in Tables 1 and 2. They reflect the main trend in the development of the chemistry of biologically active fluorine-containing compounds, viz. a continuation of the study of the highly reactive fluoroalkanesulphenamides, on the basis of which the fungitoxic preparations Euparen and Euparen-M were designed previously and are in use. A second direction has also developed based on the modification, using polyfluoroalkylthio groups, of known natural and synthetic biologically active compounds, their analogues and precursors. The opportunities in this direction are caused by the relatively low stability of the S–R_F bond, which is inclined to ready biodegradation with the elimination of fluoride ion, the appearance of which in the cytosol of cells aids normalisation of cellular hormone metabolism disturbed in numerous pathological states.[7] Information already available in this area enables consideration of various PFASC as efficient synthons for the synthesis of target preparations for medicine and agriculture.

The most important data on the chemistry and application of PFASC appearing during 1975–1991 are correlated in this review. Mainly, attention is paid to a consideration of the features of their methods of formation and reactivity and also to the opportunities for use in syntheses of biologically active compounds.

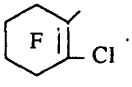
II. Methods of preparation

In the search for methods of obtaining PFASC the usual reactions for the unfluorinated analogues have been studied, such as the chlorination of disulphides, sulphides with labile leaving groups, thiols, thiocarbonyl compounds and thiiranes, the hydrochlorination of sulphenamides, reactions of sulphur chlorides with unsaturated compounds, the functionalisation of compounds with an S–Cl bond and also certain methods specific to fluorine chemistry. The features of the general methods of synthesising PFASC are most frequently displayed under the more forcing conditions of highly selective conversions and in side reactions which do not occur in the chemistry of the unfluorinated analogues.

1. Chlorination of disulphides

Symmetrical bispolyfluoroalkyl disulphides are usually converted unequivocally into PFASC on chlorination.[8–14]

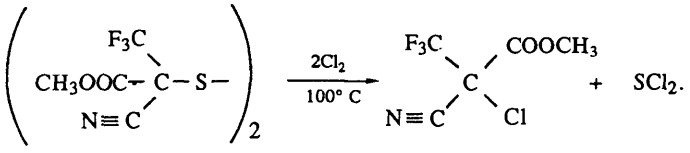
$$R_FSSR_F \xrightarrow{Cl_2} 2R_FSCl,$$

R_F = $ClCH_2-CH(CF_3)$, $CF_3CHClCH_2$, $CF_3OCFClCF_2$, $ClCF_2CF_2$, Cl_2CFCF_2, $CF_3(CF_2)_2$, $CF_3(CF_2)_6$, $(CF_3)_2CFO(CF_2)_2$, $(CF_3)_2CF$, $(CF_3)_3C$, $ClCF_2-C(CF_3)_2$, $CH_3OOC-C(CF_3)_2$,  .

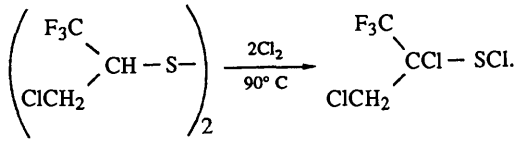
The reaction conditions depend appreciably on the nature of the polyfluoroalkyl group. The introduction of a CF_3 group into the α and β positions of the alkyl group does not show a marked effect on the conditions of chlorolysis of the S–S bond. Thus 2-chloro-1-trifluoromethylethanesulphenyl chloride was obtained in high yield from the corresponding disulphide at 20 °C or on mild cooling.

Disulphides with a CF_2 group on the sulphur atom are chlorinated at 90–110 °C. Replacement of one or two fluorine atoms of the CF_2 group by trifluoromethyl or a methoxycarbonyl group leads to a further reduction of the nucleophilicity of the sulphur atom and an increase in the chlorolysis temperature to 100–130 °C. The chlorolysis of bis(2-chloroperfluoro-1-hexenyl) disulphide occurs at 150 °C. In these reactions the nucleophilicity of the polyfluoroalkyl disulphides is controlled mainly by the efficient three-centre 2*p*3*d* interactions of the fluorine and sulphur atoms and also by the electron-withdrawing effects of the substituents at the α-carbon atom. Chlorolysis of the S–S bond of low reactivity disulphides is facilitated on UV irradiation.[12] The bispolyfluoroalkyl polysulphides undergo chlorolysis into PFASC under the same conditions as the corresponding disulphides.

In sulphides with strongly electron-accepting groups the R_F–S bond as well as the S–S bond may undergo chlorolysis:[13]



When a CH bond is present in the α position to sulphur it is readily chlorinated at increased temperature.[15]



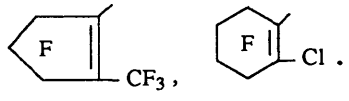
2. Chlorination of sulphides and other polyfluoroalkylthio derivatives

The conditions of forming PFASC from polyfluoroalkyl sulphides are determined mainly by the nature of the readily leaving alkyl group. However the structure of the polyfluoroalkyl group also has some effect.

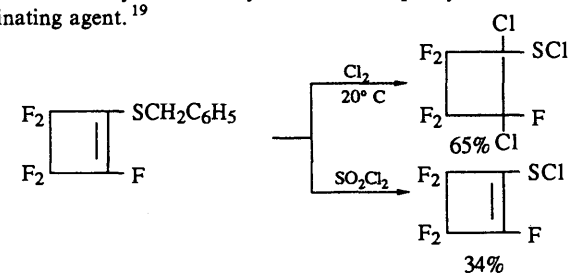
Various polyfluoroalkyl and polyfluoroalkenyl benzyl sulphides are chlorinated to PFASC at 20 °C in polyfluoroalkanes or without a solvent[16–22]

$$R_FSCH_2C_6H_5 \xrightarrow[20^\circ C]{Cl_2} R_FSCl + C_6H_5CH_2Cl,$$

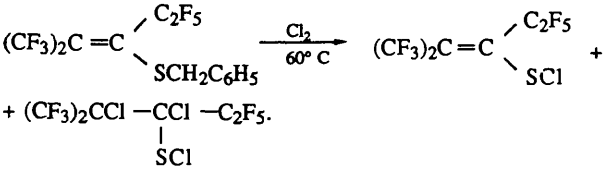
$R_F = CHF_2$, $(CF_3)_2CHCF_2$, CF_3CFCl, $(CF_3)_2CF$, $CHFClCF_2$, $(CF_3)_2C{=}CF$, $(CF_3)_2C{=}C{-}C_2F_5$, $((CF_3)_2CF)_2C{=}C{-}CF_3$,



In some cases chlorination of a multiple bond occurs simultaneously. This is successfully excluded by the use of sulphuryl chloride as the chlorinating agent.[19]

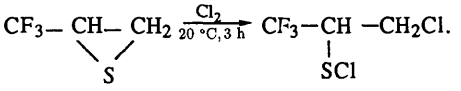


In the case of polyfluoroalkenyl benzyl sulphides the reaction may by accompanied by a chlorotropic conversion of the resulting PFASC. This leads to a mixture of compounds.[22]

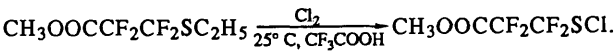


Chlorination of benzyl 2,2,2-trifluoroethyl sulphide occurs initially at the C–H bond of the trifluoroethyl group and fission of the benzyl group occurs after this.[23]

Chlorolysis of cyclic sulphides, for example trifluoromethylthiirane, is a reaction of this type[24]



The ethyl group may act as the leaving group on chlorination in trifluoroacetic acid, which enables β-methoxycarbonyltetrafluoroethanesulphenyl chloride to be obtained.[25]



As with the unfluorinated analogues the t-butyl group is eliminated more readily than benzyl. In this case the PFASC are formed in the cold even on chlorination with sulphuryl chloride.[26]

$$R_FSC(CH_3)_3 \xrightarrow[10^\circ C]{SO_2Cl_2} R_FSCl + (CH_3)_3CCl,$$

$R_F = CH_3OOC{-}\underset{\displaystyle CF_3}{\underset{|}{CH}}{-}CF_2$, $CH_3OOC{-}\underset{\displaystyle CF_3}{\underset{|}{C}}{=}CF$

Chlorinating agents split S–P [26] and S–N [27] bonds even more readily.

$$R_FSP(OC_2H_5)_2 \xrightarrow{SO_2Cl_2} R_FSCl,$$

$R_F = (CF_3)_2CHCF_2$, $(CF_3)_2CHC(O)$;

$$CF_3SN{=}S{=}S \xrightarrow[-30^\circ C,\ CCl_4]{Cl_2} CF_3SCl.$$

Polyfluoroalkanesulphenamides are converted into PFASC on treatment with dry HCl.[28]

$$R_FSN(C_2H_5)_2 \xrightarrow{HCl} \underset{60\text{—}70\%}{R_FSCl},$$

$R_F = (CF_3)_3C$, $CH_3OOC{-}C(CF_3)_2$.

3. Chlorination of thiols and thiocarbonyl compounds

Stable polyfluoroalkenethiols are readily chlorinated to give PFASC at 20 °C.[21,29] However 2-chlorooctafluoro-1-cyclohexenesulphenyl chloride was obtained by this method only at 150 °C,[14]

which indicates the extremely strong *pd* atomic interactions in the four-centre Cl–C=C–S system.

$$R_FSH + Cl_2 \longrightarrow R_FSCl,$$
$$R_F = (CF_3)_2C{=}\ C{-}\ C_2F_5,\ ((CF_3)_2CF)_2C{=}\ C{-}\ CF_3,$$

Chlorolysis of 1,1-diphenyltrifluoroethanethiol occurs under mild conditions with sulphuryl chloride.[30]

$$CF_3{-}\ C(C_6H_5)_2SH \xrightarrow{SO_2Cl_2} CF_3\ {-}C(C_6H_5)_2SCl.$$
96%

Many PFASC which are impossible to synthesise by other methods have been obtained by the reaction of highly reactive thiocarbonyl compounds with chlorine and chlorine fluoride under mild conditions.[11,22,31–34]

$$\begin{matrix} X \\ \diagdown \\ C=S \\ \diagup \\ Y \end{matrix} \xrightarrow[-80\text{ to }90\ ^\circ C]{Cl_2} XYCCl-SCl,$$

$X = CF_3$, $Y = F$, Cl, CF_3; $X = CF_3$, $Y = Br$; $X = Y = F$;
$X = C_2F_5$, $Y = (CF_3)_2CH$, $(CF_3)_2CCl$;

$$\begin{matrix} X \\ \diagdown \\ C=S \\ \diagup \\ Y \end{matrix} \xrightarrow[-100^\circ C]{ClF} XYCF-SCl,$$

$X = Y = CF_3$; $X = Y = Br$; $X = CF_3$, $Y = F$, Br; $X = S = C = N$, $Y = F$.

4. Addition of sulphur chlorides to unsaturated compounds

The thermal reactions of sulphur chlorides with polyfluoroalkenes has been studied widely in the search for methods of synthesising precursors of PFASC such as the bis(2-chloropolyfluoroalkyl) disulphides.[35] Trifluoroethylene, tetrafluoroethylene, chlorotrifluoroethylene, perfluoromethyl vinyl ether and 2H-pentafluoropropene participate in these reactions. Symmetrical and unsymmetrical dichlorodifluoroethylenes, hexafluoropropene and octafluoromethylpropene do not react. The electrophilic addition of SCl_2 on thermolysis always gives a complex mixture of compounds including PFASC, polyfluoroalkylpolythiosulphenyl chlorides, sulphides, polysulphides and products of alkene chlorination. The addition of S_2Cl_2 with the predominant formation of disulphides occurs only under forcing conditions (140–155 °C) with a large excess of polyfluoroalkene, which has made several PFASC available for investigation.

$$\begin{matrix} R \\ \diagdown \\ C= \\ \diagup \\ X \end{matrix} CF_2 \xrightarrow{S_2Cl_2} \left(\begin{matrix} R \\ \diagdown \\ CCl \\ \diagup \\ X \end{matrix} -CF_2 \right)_2 S_2 \xrightarrow{Cl_2} \begin{matrix} R \\ \diagdown \\ CCl-CF_2SCl, \\ \diagup \\ X \end{matrix}$$

R = H, F, Cl, CF_3, CF_3O; X = H, F.

The preparative value of these reactions is markedly extended by carrying out the process in the presence of catalysts. 1,2-Dichlorodifluoroethylene is converted into 1,2-dichlorotrifluoroethanesulphenyl chloride in the system $SF_4-HF-S_2Cl_2$ under relatively mild conditions.[36] It is considered that ionisation of S_2Cl_2 in the presence of SF_4 and HF facilitates the electrophilic addition of sulphur monochloride cation at the multiple bond and the presence of fluoride ion and the chlorine formed in the reaction mixture enables the unequivocal formation of the sulphenyl chloride.

$$S_2Cl_2 \xrightarrow{HF,\ SF_4} Cl^- + {}^+SSCl,$$
$$SF_4 + 4Cl^- \xrightarrow[-4F]{} SCl_4 \longrightarrow SCl_2 + Cl_2,$$
$$CFCl{=}CFCl \xrightarrow{{}^+SSCl} \left[{}^+CFClCFClSSCl \xrightarrow{F^-} \right.$$
$$\left. \longrightarrow CF_2ClCFClSSCl \right] \xrightarrow{Cl_2} CF_2ClCFClSCl.$$

Chlorotrifluoroethylene reacts similarly with S_2Cl_2 under these conditions, however the reaction products proved to be the two possible regioisomers.

$$CF_2{=}\ CFCl \xrightarrow{SF_4-HF-S_2Cl_2} CF_3CFClSCl + CF_2ClCF_2SCl.$$

Hexafluoropropene forms a combined addition product with sulphur dichloride and fluorosulphonic acid (1:3) with elimination of HCl at 40–60 °C.[37,38]

$$CF_3CF{=}\ CF_2 \xrightarrow[-HCl]{SCl_2,\ HSO_3F} CF_3-\underset{\displaystyle SCl}{\underset{|}{CF}}-CF_2OSO_2F.$$
75%

A mixture of chlorosulphonic acid and SCl_2 gives a similar product in 34% yield. In combined reactions of this type S_2Cl_2 gives a mixture of compounds containing thiosulphenyl chlorides and trisulphides in addition to sulphenyl chlorides.

Under conditions of the specific solvation of the S–Cl bond (acetonitrile, benzonitrile, $POCl_3$ and SO_2) sulphur mono- and dichlorides add to hexafluorodimethyl ketene with the formation of sulphenyl and thiosulphenyl chlorides.[39]

$$(CF_3)_2C{=}C{=}O + S_nCl_2 \longrightarrow (CF_3)_2C \begin{matrix} \diagup\ C(O)Cl \\ \diagdown\ S_nCl \end{matrix}.$$
$n = 1, 2.$ 90%

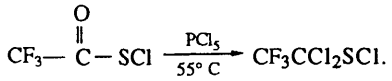
These reactions are effected particularly readily (at negative temperatures) in acetonitrile.

5. Functionalisation of compounds with an S–Cl bond

The C–H bond in the α position to a sulphur atom is readily chlorinated. This enables 1,2-dichloro-1-trifluoromethylethanesulphenyl chloride, which is inaccessible by other methods, to be obtained.[15]

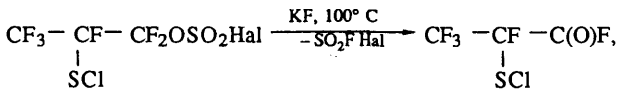
$$\begin{matrix} F_3C \\ \diagdown \\ CH-SCl \\ \diagup \\ ClCH_2 \end{matrix} \xrightarrow[90^\circ C]{Cl_2} \begin{matrix} F_3C \\ \diagdown \\ CCl-SCl. \\ \diagup \\ ClCH_2 \end{matrix}$$
86%

Trifluoroacetylsulphenyl chloride is converted into 1,1-dichlorotrifluoroethanesulphenyl chloride on reaction with PCl_5.[40]



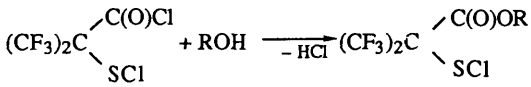
75%

The sulphenyl chloride formed on combined addition of SCl_2 and HSO_3F or HSO_3Cl to hexafluoropropene is converted on heating with KF into the acid fluoride of α-chlorosulphenyltetrafluoropropionic acid.[38]



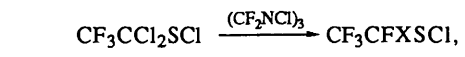
Hal = F, Cl. 74%

The acid chloride of α-chlorosulphenylhexafluoroisobutyric acid reacts under mild conditions with saturated and unsaturated alcohols forming esters in the absence of HCl acceptors.[41] The S–Cl bond is not affected by this.



R = CH_3, CH_2=$CHCH_2$.

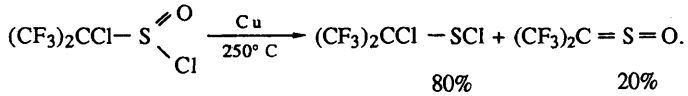
Chloro- and chlorofluoroalkanesulphenyl chlorides react by replacement of chlorine by fluorine exclusively at the C–Cl bond in the position α to the sulphur atom. In these reactions, which were widely studied for trichloromethanesulphenyl chloride previously,[3] HF, FeF_3, HF/CrF_3 and NH_4F have also been studied as fluorinating agents.[42–45] Hexafluorotrichloro-sym-triazine proved to be a new fluorinating agent in principle. Its application enables selective replacement by fluorine of one or two chlorine atoms in 1,1-dichlorotrifluoroethanesulphenyl chloride.[40]



X = Cl, F.

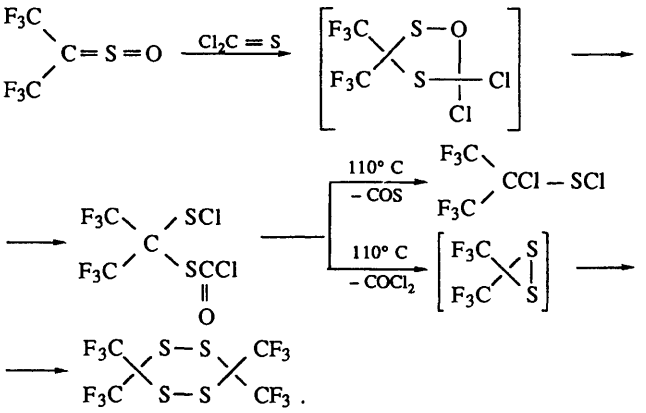
6. Other preparative routes

On heating α-chlorohexafluoroisopropanesulphinyl chloride with activated copper under forcing conditions it undergoes deoxygenation with the formation of a sulphenyl chloride.[46] Only a small portion of the starting material is converted into the dechlorination product bis(trifluoromethyl)methylene sulphoxide.



80% 20%

The (2 + 3) cycloaddition of thiophosgene to bis(trifluoromethyl)methylene sulphoxide leads to α-chloroformylthiohexafluoroisopropanesulphenyl chloride, seemingly through the intermediate dithioxolane.[46] On heating to 110 °C the sulphenyl chloride is decomposed with the elimination of carbonyl sulphide or phosgene with the formation of the corresponding α-chlorohexafluoroisopropanesulphenyl chloride and 3,3,6,6-tetrakis(trifluoromethyl)-1,2,4,5-tetrathiane.



III. Reactivity

The reactivity of PFASC has been studied in the majority of conversions typical of aliphatic sulphenyl chlorides. The polyfluoroalkylthiolation of various nucleophilic reagents, aromatic and heteroaromatic compounds has been widely clarified as has the reaction of PFASC with unsaturated compounds. The information obtained enables PFASC to be considered to be compounds with high reactivity, though appreciably more moderate than their unfluorinated analogues.

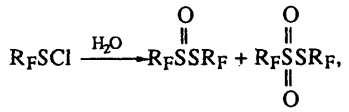
1. Reactions with nucleophilic reagents

The reaction of PFASC with nucleophilic reagents takes place according to the following equation

$$Nu(H) + R_FSCl \rightarrow NuSR_F + Cl^- + (H^+).$$

It is assumed that these reactions occur by an S_N2 mechanism in which the entering and leaving groups are at the vertices of a trigonal bipyramid.[47]

Reaction with O-nucleophiles. The hydrolysis of PFASC was considered in detail in the review[3] using CF_3SCl as example. In addition it was shown that these compounds are stable to water, unlike their unfluorinated analogues. Only on prolonged shaking with water were the final hydrolysis products, sulphides and sulphonic acids, obtained in some cases. The hydrolysis of the chlorofluoromethanesulphenyl chlorides was successfully stopped at the stage of forming thiosulphinates and/or thiosulphonates.[48]



R_F = $CFCl_2$, CF_2Cl.

1,1-Dichlorotrifluoroethanesulphenyl chloride is partially converted after 48 h at 45 °C into chloro(trifluoromethyl)methylene sulphoxide.[23,49]

$$CF_3CCl_2SCl \xrightarrow[45^\circ C]{H_2O} \begin{matrix} CF_3 \\ \diagdown \\ C=S=O \\ \diagup \\ Cl \end{matrix} \quad 28\%$$

α-Chlorohexafluoroisopropanesulphenyl chloride is unchanged under these conditions.[46]

The PFASC are as stable to alcohols as to water. The stable esters of polyfluoroalkanesulphenic acids are obtained under relatively mild conditions in the presence of acceptors of HCl [$N(C_2H_5)_3$, Py] [50,51] and without acceptors only in certain cases on heating.[26]

$$R_FSCl + ROH \rightarrow R_FSOR,$$

$R_F = CF_3$, $R = C_2H_5$, $CH_3OC_6H_4CH_2$, $CF_3SNHCH_2CH(C_6H_5)$;

$R_F = (CF_3)_2CHCF_2$,

$R = C_2H_5$.

The PFASC react more readily with alkoxides and phenoxides of the alkali metals and particularly of mercury.[30,52] Under these conditions the acylsulphenyl chlorides give desulphurisation products.

$$CF_3 - C(C_6H_5)_2SCl + ROH \xrightarrow[20\ ^\circ C, 3\ h]{NaH/THF} CF_3 - C(C_6H_5)_2SOR,$$

$R = (CH_3)_3CCH_2$, $C_6H_5CH_2O(CH_2)_2$, $4\text{-}O_2NC_6H_4$,

$CH_3(CH_2OCH_2)_3CH_2$.

$$(CF_3)_3COHgCl \xrightarrow[0\ ^\circ C,\ 24\ h]{CF_3SCl} (CF_3)_3COSCF_3$$

$$(CF_3)_3COHgCl \xrightarrow[0\ ^\circ C,\ 24\ h]{CF_3CSCl} (CF_3)_3COSC(=O)CF_3 \xrightarrow{-S} (CF_3)_3COC(=O)CF_3$$

On reacting PFASC with allyl alcohol in the presence of pyridine, equilibrium mixtures are formed of sulphuric acid esters and products of their [2,3]-sigmatropic rearrangement with a significant preponderance of the latter.[53] On heating or on increasing the electron-donating properties of the polyfluoroalkyl group the content of sulphenate in the mixture is increased.

$$R_FSCl + HOCH_2CH=CH_2 \xrightarrow[CH_2Cl_2]{Py} R_FSOCH_2CH=$$

$$= CH_2 \rightleftharpoons R_FSC(=O)CH_2CH=CH_2,$$

$R_F = CCl_2F$, $CClF_2$, CF_3, $(CF_3)_2CH$, $(CF_3)_2CCl$.

The PFASC form mixed anhydrides with salts of carboxylic acids which differ from the unfluorinated analogues in increased stability.[54,55] Their yield was increased with an increase in the number of fluorine atoms at the α-carbon atom.

$$R_FSCl + MOC(O)R \rightarrow R_FSOC(O)R,$$

$R_F = CCl_2F$, $CClF_2$, CF_3; $R = CH_3$, C_2H_5, CF_3, C_2F_5; $M = Na$, Ag.

The mixed anhydrides obtained were more reactive than PFASC in their activity in reactions of electrophilic addition and substitution.[55]

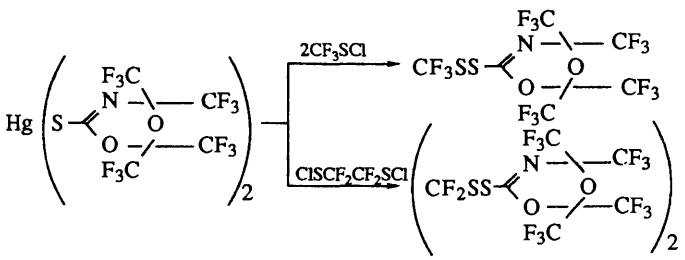
Reactions with S-nucleophiles. Thiolates and thiols react with PFASC in the presence of acceptors of HCl giving unsymmetrical disulphides.[22,24,26,32,56–63] Strong bases aid the symmetrisation of these compounds which may be the reason for the sharp reduction in the yield of the desired products.

$$R_FSCl + RSH \xrightarrow[-HCl]{\ddot{B}} R_FSSR \xrightarrow[RSH]{\ddot{B}} R_FSSR_F + R_2S_2,$$

$R_F = CCl_2F$, CF_3, $FC(O)$, $ClCH_2 - CH(CF_3)$, $(CF_3)_2CHCF_2$, $CF_3 - CCl(CH_2Cl)$, $(CF_3)_2C=C-C_2F_5$, $CF_3C(O)$;

$R = H$, CH_3, $C_6H_5CH_2$, $HOOCCH_2$, CF_3, $C_6H_5NH-C(S)$.

$$2CF_3SCl + \begin{matrix} NaS \\ \diagdown \\ C=S \\ \diagup \\ NaS \end{matrix} \longrightarrow \begin{matrix} CF_3SS \\ \diagdown \\ C=S, \\ \diagup \\ CF_3SS \end{matrix}$$



Dialkyl disulphides also react analogously. Thus CF_3SCl reacts under mild conditions with dimethylsulphide with the formation of an unsymmetrical disulphide.[64]

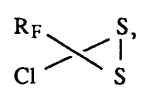
$$CF_3SCl + CH_3SSCH_3 \xrightarrow[-50\ to\ 25\ ^\circ C]{} CF_3SSCH_3 + CH_3SCl.$$

The disulphides formed in reactions of α,α-dichloropolyfluoroalkanesulphenyl chlorides with thioacetic acid are readily split by morpholine with the formation of morpholides of chlorofluorothioacetic acids.[65]

$$R_FCCl_2SCl + \underset{+HSCCH_3}{\overset{O}{\parallel}} \xrightarrow[60^\circ C,\ CCl_4]{} R_FCCl_2SSCCH_3 \xrightarrow{HN\langle O\rangle} R_FC(=S)-N\langle O\rangle,$$

$R_F = CFCl_2$, CF_2Cl.

Initially, decomposition of the disulphide to a dithiirane is proposed



the desulphurisation of which leads to the thioacid chloride $R_FC(S)Cl$ giving the corresponding morpholide with morpholine.

Reaction with N-nucleophiles. The reaction of PFASC with N-nucleophiles with the formation of polyfluoroalkanesulphenamides has been widely studied. Ammonia,[15,30,66] primary[30,51,67–69] and secondary[10,15,19,30,70–74] amines, primary and secondary amides of

carboxylic acids[75–78] and sulphonic acid amides[79] participate in these reactions.

$$R_FSCl + HN\!\!\begin{array}{l}\diagup\\\diagdown\end{array} \xrightarrow[-HCl]{} R_FSN\!\!\begin{array}{l}\diagup\\\diagdown\end{array}\ .$$

The reaction is usually effected in the presence of HCl acceptors such as trimethyl-, triethylamine, pyridine or an excess of the reacting amine. In certain cases better results are obtained when reacting PFASC with metal amides.

When reacting ammonia and primary amines with an excess of PFASC a second or third polyfluoroalkylthio group is introduced at the nitrogen atom.[3] Tetrafluoroethane-1,2-disulphenyl chloride reacts with primary amines giving 1,3,2-dithiazolidines.[69]

$$ClSCF_2CF_2SCl + H_2NR \longrightarrow \begin{array}{l} CF_2 - S \\ | \quad\quad \diagdown \\ CF_2 - S \end{array} \!\!> N - R$$

The polyfluoroalkanesulphenamides are markedly more stable than their unfluorinated analogues. Their thermal and hydrolytic stability is increased with an increase in the electron-accepting properties of the polyfluoroalkyl group and is reduced with an increase in the basicity of the amine. Many of the sulphenamides obtained possess high biological activity. Highly active compounds are found among them which are of interest in agriculture and medicine. Data on the structure and biological activity of the sulphenamides obtained from N-nucleophiles and PFASC are given in Tables 1 and 3.

N-Silylated compounds are sulphenylated by PFASC with elimination of chlorotrimethylsilane. Stable fluorocarbonylated azides and thionylimines are obtained in this way.[59]

$$FC(=O)-SCl + (CH_3)_3SiX \xrightarrow[-(CH_3)_3SiCl]{} FC(=O)-SX,$$

$X = N_3, \quad -N{=}S{=}O.$

Trifluoromethylthioazide obtained in a similar way is converted even at 20 °C into tetrakis(trifluoromethylthiazyl).[127]

$$CF_3SCl + (CH_3)_3SiN_3 \xrightarrow[-(CH_3)_3SiCl]{-50 \text{ to } -30\ ^\circ C} CF_3SN_3 \xrightarrow[-N_2]{20\ ^\circ C} (CF_3SN)_4\,.$$

Sulphodiimides silylated at nitrogen form crystalline 1,3,5-trithia-2,4-diazepines in high yield with 1,2-bis(chlorosulphenyl)-tetrafluoroethane.[128]

$$ClSCF_2CF_2SCl + \begin{array}{l}(CH_3)_3SiN \\ (CH_3)_3SiN\end{array}\!\!>S\!<\!\begin{array}{l}R\\R\end{array} \xrightarrow[-78 \text{ to } 20\ ^\circ C]{CH_2Cl_2} \begin{array}{l} CF_2-S-N \\ | \quad\quad \diagdown \\ CF_2-S-N \end{array}\!\!>S\!<\!\begin{array}{l}R\\R\end{array}$$

$R = CH_3, C_2H_5.$

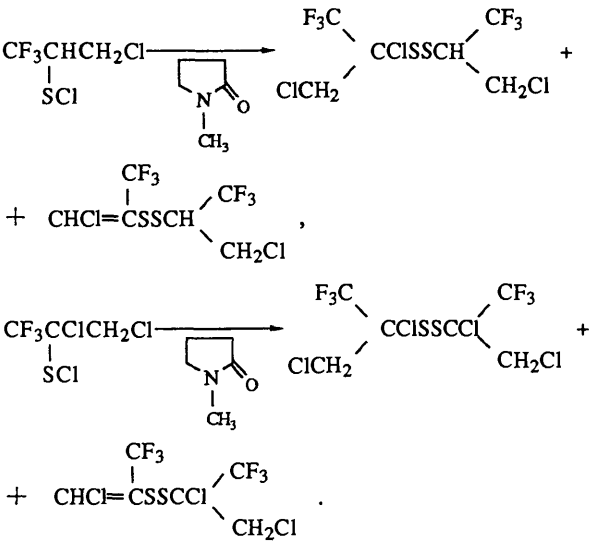
On the other hand hexamethyldisilazane is thiolated by CF_3SCl at the N–H bond. A second molecule of hexamethyldisilazane acts as HCl acceptor in this reaction.[28,51]

Tertiary amines convert PFASC into disulphides.[129] Disulphides are frequently byproducts in reactions where tertiary amines are used as HCl acceptors for this reason.

$$R_FSCl + R_3N \rightarrow R_FSSR_F + [R_3N \cdot Cl_2],$$

$R_F = CF_3, CF_2Cl, CFCl_2.$

2-Chloro-(1-trifluoromethyl)ethanesulphenyl chloride and 1,2-dichloro-(1-trifluoromethyl)ethanesulphenyl chloride are converted in *N*-methylpyrrolidone into the thiocarbonyl compound $CF_3C(S)CH_2Cl$ and the thiirene $CF_3-C=CH$ respectively, which give a mixture of unsymmetrical disulphides with the initial sulphenyl chlorides.[15]



Reactions with P-nucleophiles. The reaction of PFASC with P-nucleophiles has been widely studied in the search for new insecticides. The reaction of trialkyl and diaryl alkyl phosphites with trichloro-, chlorodifluoro-, and dichlorofluoro-, and trifluoromethanesulphenyl chlorides[130,133] occurs under milder conditions than for the unfluorinated alkanesulphenyl chlorides. The main reaction products are the corresponding trihalomethyl thiophosphates. In addition products of the 'anomalous' breakdown of the intermediate phosphorane, viz. trihalomethyl alkyl sulphides, were formed with some contamination by other compounds.

$$(RO)_3P + CCl_{3-n}F_nSCl \rightarrow (RO)_2P(O)SCCl_{3-n}F_n + CCl_{3-n}F_nSR +$$
$$+ (RO)_2P(O)Cl + RCl,$$

$n = 0$ to 3; R = Alk, Ar.

The trihalomethanesulphenyl chlorides react analogously with dialkyl or sodium dialkyl phosphites. Conditions have successfully been found[133] under which diisopropyl and di(trimethylsilyl) phosphites are converted quantitatively into the corresponding trihalomethyl thiophosphates.

$$CCl_{3-n}F_nSCl + (RO)_2P(O)H \rightarrow (RO)_2P(O)SCCl_{3-n}F_n,$$

$n = 1$ to 3; $R = iso\text{-}C_3H_7, (CH_3)_3Si$.

Table 1. Biological activities of sulphenamides obtained by reacting PFASC with primary and secondary amines ($R_FS-NR^1R^2$).

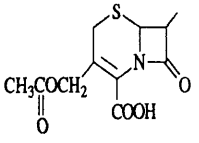
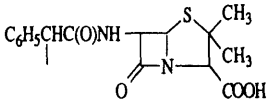
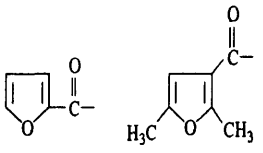
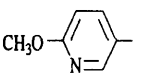
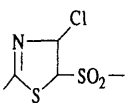
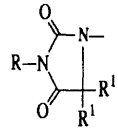
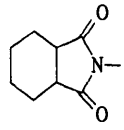
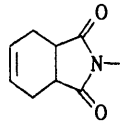
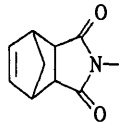
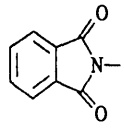
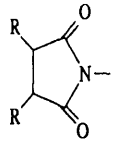
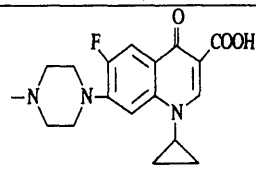
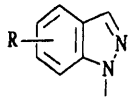
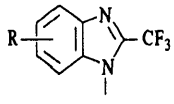
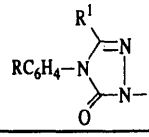
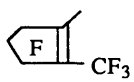
R_F	R^1	R^2	Activity	Ref.
$CFCl_2$, CF_3CCl_2, CF_2ClCCl_2, $CFCl_2CFCl$, $CF_2ClCFCl$, $CFCl_2CCl_2$, CCl_3CF_2	RSO_2—, R = Alk, Ar, $N(CH_3)_2$	Alk, All, $IC{\equiv}CCH_2$, Ar	Herbicides, insecticides, microbiocides, fungicides, antihelminthic agents	[80—88]
$CFCl_2$	R_2N—C(O)C_6H_4—, R = H, Alk, Ar	CF_3	Fungicides, microbiocides	[89—91]
CF_3		H	Antibacterial activity	[92]
CF_3		H	Antibacterial acitivity	[51]
$CFCl_2$, $CFCl_2CCl_2$, $CFCl_2CFCl$	R—C_6H_4—C(O)— R = H, Hal, CF_3, CH_3O	C_6H_5,п-F—C_6H_4	Fungicides, acaricides, antimosquito agents	[93—98]
$CFCl_2CCl_2$, $CFCl_2CFCl$		C_6H_5	Fungicides, acaricides	[99, 100]
$CFCl_2$	X(O)C— X = H, F	Ar	Fungicides, antimicrobial activity	[101—103]
$CFCl_2$	Ar—NH—C(O)—	Ar	Fungicides	[102]
$CFCl_2$	RX—C(O)[illegible]C(O)— X = O, S, N; R = Alk, Ar	Alk, All	Fungicides	[67, 68, 104, 105]
$CFCl_2$, CF_2Cl, CF_3	$(RO)_2P(X)$— R = Alk, Ar X = O, S	Alk	Insecticides	[106, 107]
$CFCl_2CCl_2$	R—N=C(—SC_2H_5)—	Alk, Ar	Herbicides, lepidoptericidal activity	[108]
$CFCl_2CCl_2$			Fungicides	[109]
$CFCl_2$		H, Alk, C_6H_5	Fungicides	[110]
$CFCl_2$, $CFCl_2CCl_2$	$PhCH_2C(O)$	CH_2CN	Fungicides	[111]

Table 2. Biological activity of sulphenamides obtained by reacting PFASC with secondary cyclic amines (R_FS-NR_2).

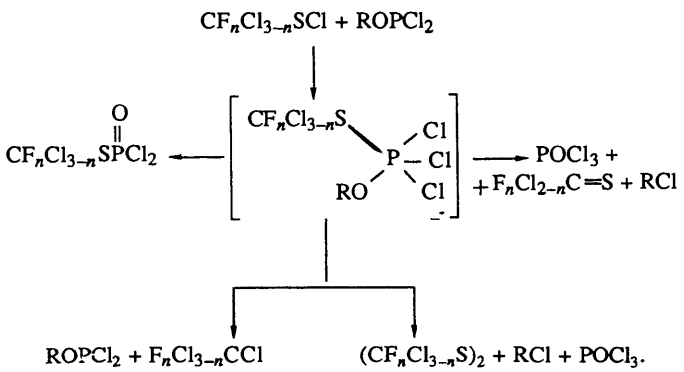
R_F	R_2N-	Activity	Ref.
$CFCl_2$	 R = Alk, Ar, SAlk, R^1 = H, CH_3	Antimicrobial, herbicides, fungicides, insecticides	[112—115]
CF_2ClCCl_2, $CF_2ClCFCl$		Herbicides, insecticides	[84]
$CFCl_2$, $CFCl_2CCl_2$		Antitick action, fungicide	[101, 116]
$CFCl_2$		Antimicrobial activity	[117]
$CFCl_2$, $CFCl_2CCl_2$		Herbicides, insecticides	[83, 84, 118, 119]
$CFCl_2$, $CFCl_2CCl_2$	 R = Alk, Ar	Microbiocides, fungicides	[120, 121]
$CFCl_2$		Antibacterial activity	[122]
CF_3, $CFCl_2$	 R = H, OAlk, SAlk	Plant protection agent	[123]
$CFCl_2$	 R = H, Cl, CF_3, SCF_3	Herbicides	[124]
$CFCl_2$ R = H, Cl, F, Alk; R^1 = H, Alk		Fungicides	[125, 126]

Sulphenyl chlorides with highly electrophilic perfluoroalkenyl groups react with trialkyl phosphites with the exclusive formation of perfluoroalkenyl alkyl sulphides.[19]

$$R_FSCl + P(OC_2H_5)_3 \xrightarrow{-78^\circ C} [(C_2H_5O)_3PCl]^+(SR_F)^- \longrightarrow R_FSC_2H_5,$$

$R_F = (CF_3)_2C{=}CF$,  .

The reaction of trihalomethanesulphenyl chlorides with alkyl dichlorophosphites at −30 to 20 °C leads to trihalomethylthio dichlorophosphates in about 50% yield.[134,135] In addition the products were contaminated by many byproducts the relative quantities of which depend appreciably on the number of fluorine atoms in the trihalomethyl group.



Mono-, di- and trithiophosphites with trihalomethyl groups are cleaved by trihalomethanesulphenyl chlorides to a mixture of symmetrical and unsymmetrical disulphides.[135]

$$(R_FS)_xPCl_{3-x} + R'_FSCl \longrightarrow R_FSSR_F + R_FSSR'_F + R'_FSSR'_F + PCl_3$$

$x = 1$ to 3; R_F, $R'_F = CF_nCl_{3-n}$, $n = 1$ to 3.

In contrast, methylthio dichlorophosphite behaves in these reactions as a CH acid.[13]

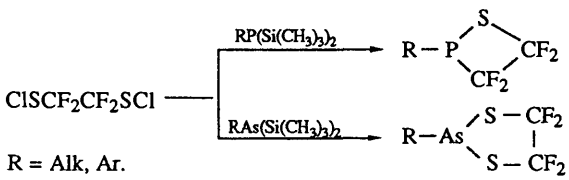
$$CF_3SCl + CH_3SPCl_2 \rightarrow CF_3SCH_2SPCl_2.$$
34%

The trihalomethanesulphenyl chlorides react with white phosphorus under mild conditions (−80 °C) forming mainly dialkyldithiochlorophosphites with contamination by other substances.[135]

$$R_FSCl + P_4 \rightarrow (R_FS)_xPCl_{3-x} + R_FSSR_F + F_mCl_{2-m}C{=}S,$$

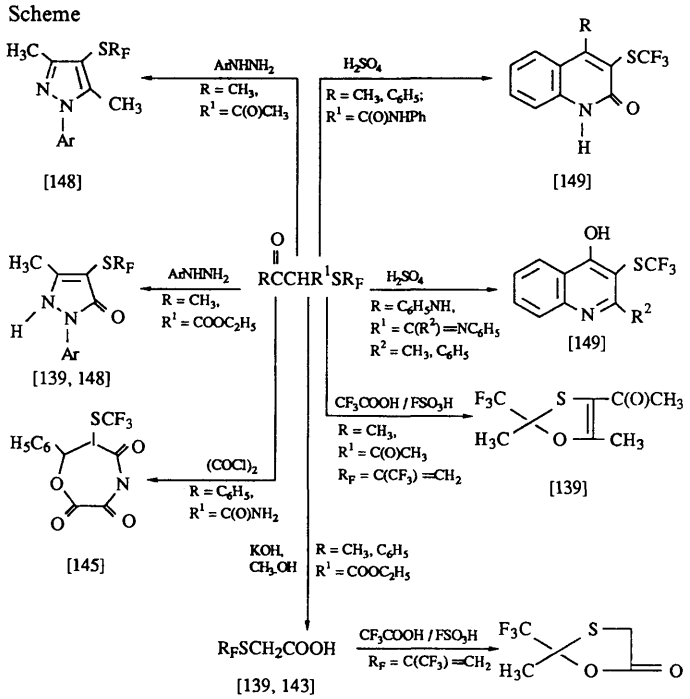
$R_F = CF_nCl_{3-n}$, $n = 1$ to 3, $x = 1$ to 3; $m = 1.2$.

The reaction of 1,2-bis(chlorosulphenyl)tetrafluoroethane with bis(trimethylsilyl) phosphonites and with bis(trimethylsilyl) arsenites leads to thiophosphetanes and dithiarsolanes respectively.[136]



Reactions with C-nucleophiles. Reactions of this type arouse increased interest from the point of view of synthesising numerous polyfluoroalkylthiolated biologically active substances and their precursors. PFASC display a more moderate activity than their unfluorinated analogues when reacting with various C-nucleophiles.

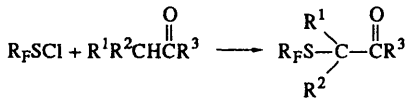
Scheme



Enolising carbonyl compounds, including aldehydes, ketones, α- and β-diketones and various β-ketocarboxylic acid derivatives, are *C*-polyfluoroalkylthiolated most readily and unequivocally in the majority of cases.[16,26,137,147] Actual examples of reactions of this type are given in Table 3. Carbonyl compounds modified by PFASC are widely involved in syntheses of biologically active compounds (see Scheme) and include pyrazoles and pyrazolones,[139,148] oxazepines,[145] quinolinones[149] and 1,3-oxathioles.[139] These are used in the synthesis of cephalosporin antibiotics, polyfluoroalkylthiocarboxylic acids[139,143,150] and 1,3-oxathiolanones.[139]

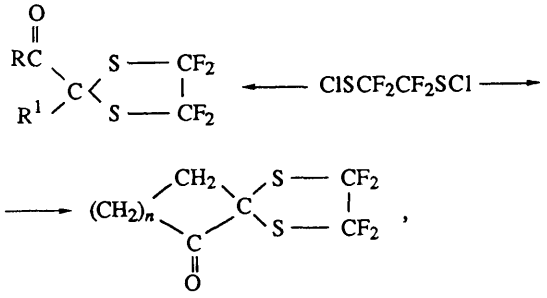
Only products of monosubstitution are formed in the majority of reactions of PFASC with carbonyl compounds,[143,147] however the formation of products of bispolyfluoroalkylthiolation was recorded in the case of acetone and benzoylacetamide.[137,139,145]

Table 3. Reactions of PFASC with carbonium compounds



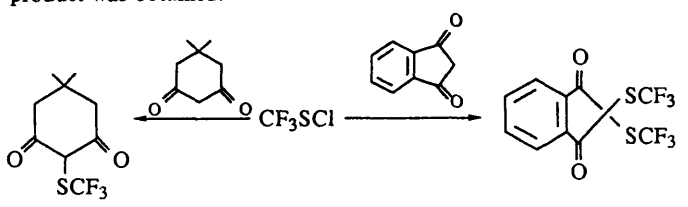
R_F	R^1	R^2	R^3	Ref.
CF_3, $CFCl_2$	CH_3	CH_3	H	[137]
CF_3, $ClCH_2CH(CF_3)$, $CH_3OOC-C(CF_3)=$	H	H	CH_3	[26, 137, 139]
CF_3	CH_3	CH_3	CH_3	[137, 138]
CF_3, CF_2H	H	H	$(CH_3)_3C$	[16]
$ClCH_2CH(CF_3)$	H	H	C_6H_5	[139]
CF_3	H	CH_2CH_2Cl	X–C_6H_5	[140, 141]
$ClSCF_2CF_2$	H	H	$CH_3C(O)$	[142]
CF_3, $ClCH_2CH(CF_3)$	H	$COOC_2H_5$	CH_3	[139, 143]
$ClCH_2CH(CF_3)$	H	$CH_3C(O)$	CH_3	[139]
$ClCH_2CH(CF_3)$	CH_3	$COOC_2H_5$	CH_3	[139]
CF_3	$CH_2C(O)CH_2CH_2$	$COOC_2H_5$	CH_3	[144]
CF_3	H	$C(O)NHC_6H_5$	CH_3	[143]
CF_3	H	$C(O)NHC_6H_5$	C_6H_5	[143]
CF_3	H	$C(O)NHC_6H_5$	C_6H_5	[143]
CF_3	H	$C(O)NH_2$	C_6H_5	[145]
CF_3	H	$C(S)NHC_6H_4Br$	CH_3	[145]
CF_3	H	R–C=N–C_6H_5 R = CH_3, C_6H_5	C_6H_5NH	[143]
CF_3	H	(R–C=N–CH_2–)$_2$ R = CH_3, C_6H_5	CH_3, C_6H_5	[146]

1,2-Bis(chlorosulphenyl)tetrafluoroethane forms only heterocyclic disubstitution products with acyclic and cyclic carbonyl compounds.[142,151]

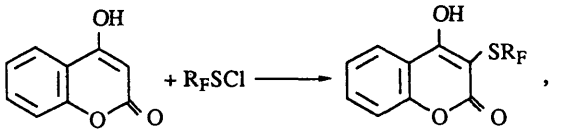


R = CH_3, $(CH_3)_3C$; R^1 = H, $C(O)CH_3$; n = 1. 2.

Monosubstitution products of 1,3-cyclohexadiones are formed with CF_3SCl even with an excess of sulphenyl chloride but in the analogous reaction with indane-1,3-dione only the disubstituted product was obtained.[147]

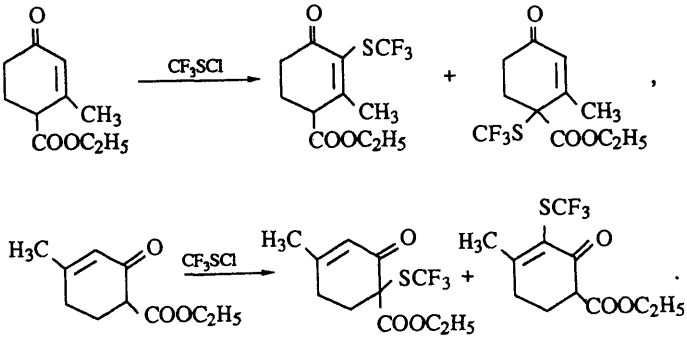


The effect of the PFASC structure on the conditions for thiolating carbonyl compounds has not yet been studied. Only in the example of 4-hydroxycoumarin was it established that the formation of 3-polyfluoroalkylthiolated derivatives was hampered by an increase in the electron-accepting properties of the polyfluoroalkyl group.[52]

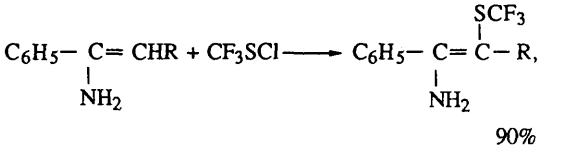


R_F = $ClCH_2-CH(CF_3)$, CCl_2FCF_2, $CH_3OOC-C(CF_3)_2$.

The polyfluoroalkylation reaction is usually effected regiospecifically at the α position to the C=O group. Moreover cyclohexenenonecarboxylic acids, having two CH-acid centres, give a mixture of two products with a predominance of the thiolation product at the more reactive centre.[144]

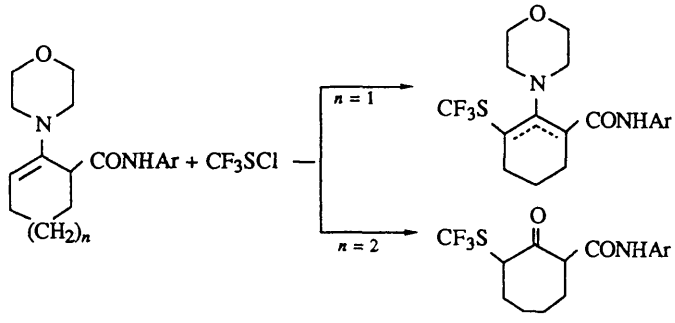


Enamines react with PFASC like the enolised ketones giving monosubstitution products.[145]



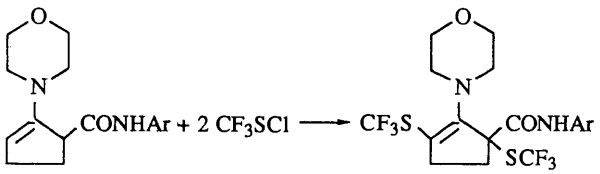
R = $C(O)NH_2$, CN.

Enamines based on derivatives of cyclohexanone- and cycloheptanone-2-carboxylic acids are thiolated in the presence of pyridine only at the unsubstituted 2 position of the ring.[153]



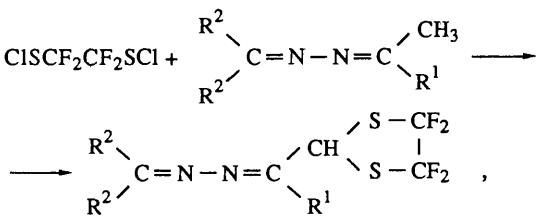
Ar = C_6H_5, 4-ClC_6H_4.

In contrast, the more strained derivatives of cyclopentanone-2-carboxylic acid are converted by an excess of CF_3SCl into 2,5-dithiolation products.[153]

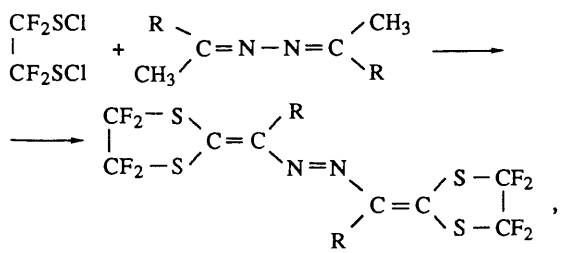


$Ar = C_6H_5$, 4-ClC_6H_4.

1,2-Bis(chlorosulphenyl)tetrafluoroethane readily thiolates azines containing methyl groups. The reaction is accompanied by the evolution of HCl and leads either to dithiolanylazines or to a *trans*-diazene.[154]

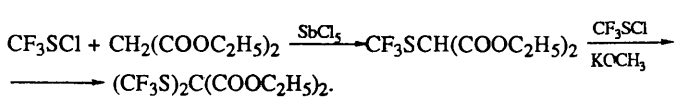


$R^1 = CH_3$, C_6H_5; $R^2 = CF_3$, C_6H_5;

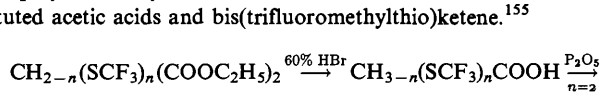


$R = CH_3$, C_2H_5, C_6H_5.

In contrast to ketones, malonic ester reacts with trifluoro- and chlorodifluoromethanesulphenyl chlorides only on heating above 100 °C giving mono- and disubstituted products.[148] Mild trifluoromethylthiolation of malonic ester occurs only on electrophilic catalysis. The monothiolation product reacts further with CF_3SCl in the presence of base.[155]

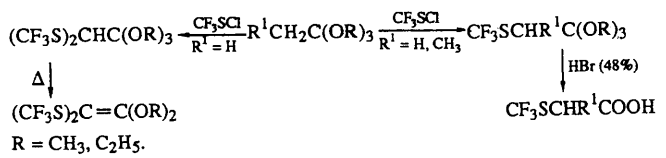


The polyfluoroalkylthiomalonates obtained are converted into substituted acetic acids and bis(trifluoromethylthio)ketene.[155]



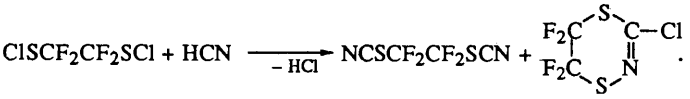
n = 1, 2.

Under mild conditions (−5 °C) orthoesters of carboxylic acids form products of mono- and in certain cases ditrifluoromethylthiolation which proved to be good precursors for a series of valuable products.[156]

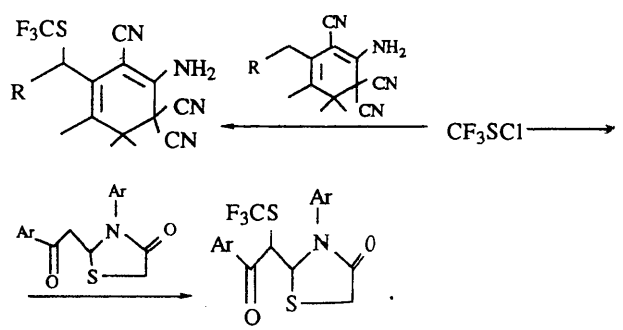


$R = CH_3$, C_2H_5.

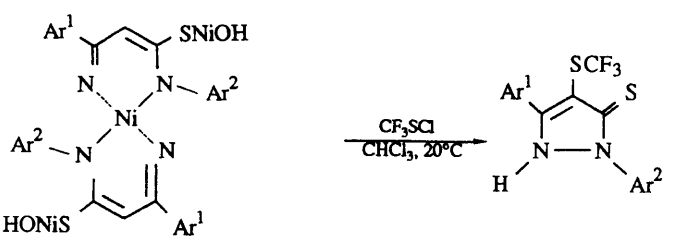
1,2-Dithiocyanotetrafluoroethane, with a 1,4,2-dithiazene as contaminant (4%), is readily formed in the reaction of 1,2-bis-(chlorosulphenyl)tetrafluoroethane with HCN.[157]



Trifluoromethylthiolation occurs fairly readily at the CH-acid centre activated by the cyclohexadiene[158] or thiazolidine[159] rings.



In some cases the trifluoromethylthiolation of compounds is accompanied by heterocyclisation. For example the nickel complex of β-aminothiocinnamic acid anilide is converted into a substituted 3-pyrazoline-5-thione.[160]



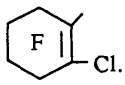
Ar^1, $Ar^2 = C_6H_5$, ClC_6H_4, $CH_3C_6H_4$.

The anilines of the *N*-benzoylamide of benzoylthioacetic acid are converted on trifluoromethylthiolation into 1,3-oxazoline-4-thione and the CF_3S group is lost on heterocyclisation.[145]

Organometallic compounds react readily with PFASC. This enables sulphenylation of lithium alkyl compounds to be carried out with fluorocarbonylsulphenyl chloride,[59] and of various lithium-acetylenes with 1,2-bis(chlorosulphenyl)tetrafluoroethane.[161] The

reaction of perfluoroalkenesulphenyl chlorides with KCN is effected unambiguously under mild conditions.[162] Stable alkenyl thiocyanates are formed by this which indicates the stabilising effects of the *pd* interactions in the F–C–S triad and in the F–C–C–S four-centre systems.

$$R_FSCl + KCN \longrightarrow R_FSCN,$$

$R_F = (CF_3)_2C{=}CF,\ (CF_3)_2C{=}C{-}C_2F_5,$ 

The trifluoromethylthiolation of sodium derivatives of nitromalonic ester is effected less unequivocally,[163] and also the reaction of trihalomethylsulphenyl chlorides with salts of such strong CH-acids as a tetraalkyl methylenediphosphonate.[164]

2. Reactions with aromatic and heteroaromatic compounds

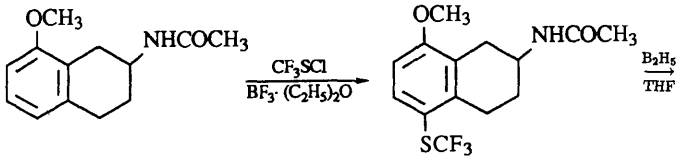
In the last decade interest in polyfluoroalkylthiolated aromatic and heteroaromatic compounds has grown in connection with the prospect of biologically active compounds with valuable properties. The number of studies on the direct thiolation of various types of aromatic and heteroaromatic compounds with PFASC has increased for this reason. Presently this method competes in many cases with the previously widely studied indirect routes of forming polyfluoroalkylthio groups in an aromatic matrix.[6]

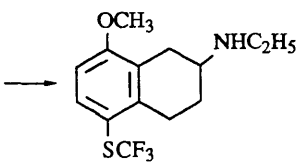
Benzene is thiolated by CF_3SCl on heating (100 °C) in the presence of BF_3 or at 20 °C in the presence of catalytic quantities of CF_3SO_3H.[165]

$$C_6H_6 + CF_3SCl \xrightarrow[[CF_3SO_3H]]{20\ ^\circ C,\ 5\ h} C_6H_5SCF_3 + HCl.$$

Toluene reacts similarly giving a mixture of *ortho* and *para* substitution products but chloro- and bromobenzene in the presence of HF form mixtures of all the possible isomers only at 200 °C.

Trifluoromethanesulphenyl chloride reacts mainly as a chlorinating agent with trifluoromethyl phenyl sulphide in the presence of CF_3SO_3H.[165] A methoxy group in the ring facilitates thiolation and was used in the synthesis of trifluoromethylthiolated compounds with antidepressant activity.[166]



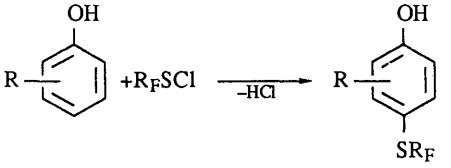


Di- and trimethoxybenzenes are distinguished by an increased ability to polyfluoroalkylthiolate. Both 1,3-di- and 1,3,5-trimethoxybenzenes react without a catalyst.[167,168] It is convenient to use magnesium and mercury derivatives for the thiolation of aromatic compounds with electron-accepting groups, PFASC do not display a marked chlorinating action with these compounds.[168]

$$4\text{-}XC_6H_4HgCl + CF_3SCl \rightarrow 4\text{-}XC_6H_4SCF_3 + 4\text{-}XC_6H_4Cl + C_6H_5X,$$

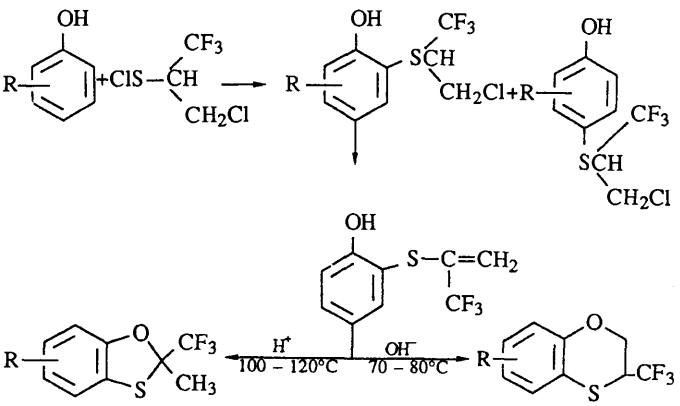
$X = CH_3O,\ CH_3,\ H,\ Cl,\ NO_2.$

Phenol and its derivatives containing electron-donating substituents in the aromatic ring react with PFASC in the absence of catalyst. Reactions are carried out in the presence of pyridine to bind the evolved HCl in the case of the volatile CF_3SCl. Otherwise Lewis acids are used as catalysts to increase the thiolation rate.[3,41,72,167,168,170] Under these conditions *ortho* and *meta* substituted phenols are usually thiolated at the *para* position.



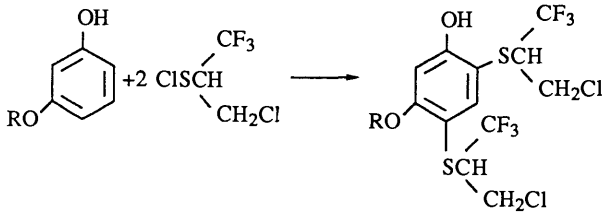
R = H, Alk, Cl, F, OH, OCH_3; $R_F = CF_3,\ C_7F_{15},\ ClCF_2CF_2,$
$Cl_2CFCF_2,\ CH_3OOC{-}C(CF_3)_2,\ AllOOC{-}C(CF_3)_2$

Only particularly reactive PFASC such as $ClCH_2{-}CH(CF_3)SCl$ form *ortho* and *para* substitution products with phenols. The selectivity of the reaction increases in the presence of solvent, the nature of which determines the direction of thiolation to a significant degree.[167] To separate the *ortho*-thiolated phenols it is possible to use their tendency to cyclise.



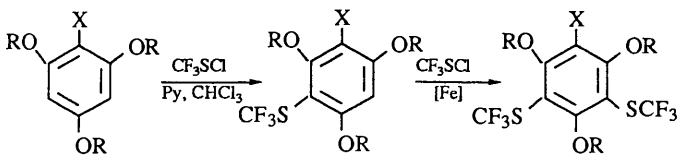
In the absence of a catalyst *para* substituted phenols usually form *ortho* substitution products on heating.[41] Monosubstituted phenols in general are characterised by a marked reduction in the ability to be thiolated by PFASC in the series *meta* > *ortho* ≫ *para* and electron-donating substituents are arranged in the usual series CH_3O > CH_3 > F ≫ Cl in inactivating ability. *m*-Methoxyphenol proved to be the most reactive of the studied phenols of this series and gave a mixture of *ortho* and *para* substitution products. Even disubstitution products are formed with an excess of sulphenyl chloride.[167] Dihydroxybenzenes are arranged in the same series as monosubstituted phenols in their reactivity towards PFASC.

Resorcinol is the most reactive and also forms a dithiolation product at 20 °C.



R = H, CH_3 .

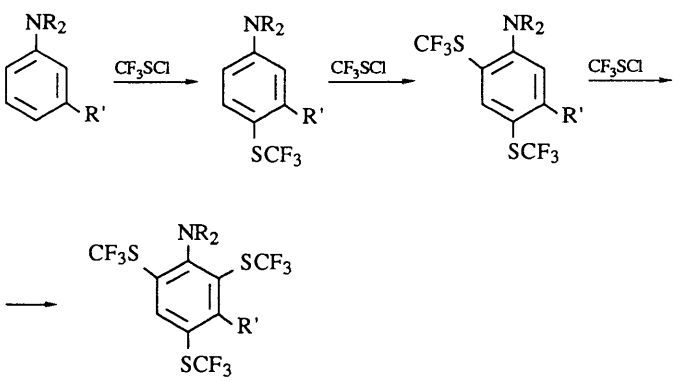
Phenols with electron-withdrawing substituents do not react with PFASC. The only exceptions are derivatives of resorcinol and phloroglucinol which, depending on the conditions, form substitution products with one or two molecules of CF_3SCl.[168]



R = H, CH_3; X = $CH_3(O)C$, CH_3OOC, C(O)H.

The conditions of the reactions under consideration are also determined in many cases by the nature of the PFASC. The polyfluoroalkylthiolation of phenols is appreciably suppressed by an increase in the electron-accepting properties of the polyfluoroalkyl group and the steric effects at the S—Cl group.[41,167]

The *N,N*-dialkylanilines are appreciably more reactive towards CF_3SCl and form *para* substitution products and 2,4-di- and 2,4,6-trisubstitution products when activating OH and CH_3O groups are present.[72]

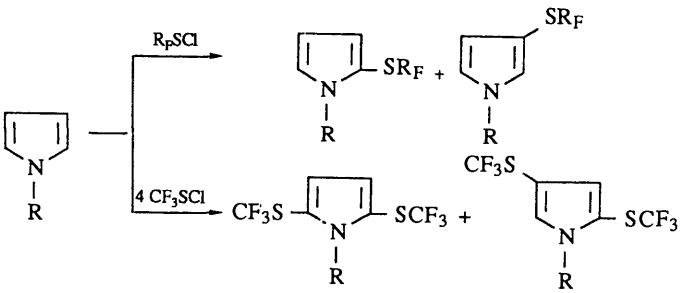


R = CH_3, C_2H_5; R' = H, OH, OCH_2CF_3.

Only *meta*-hydroxy and *meta*-alkoxy derivatives of primary and secondary arylamines give *C*-trifluoromethylthiolation products.[72]

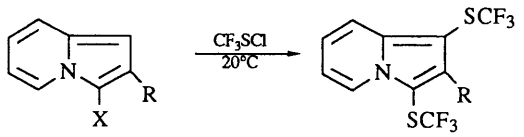
Of the heteroaromatic compounds only compounds with high π-donor properties react with PFASC in the absence of a catalyst.

Pyrrole and *N*-methylpyrrole readily form 2- and 2,5-substitution products in the presence of HCl acceptors. Contamination of 3(4)-substitution compounds as side products has been recorded.[171,172]



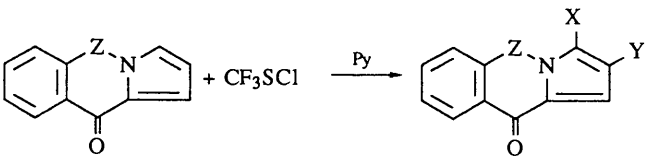
R = H, CH_3; R_F = CF_3, CF_2Cl, $CFCl_2$, CF_3SCFCl, F(O)C, C_7F_{15}.

Indole gives a C(3) thiolation product with CF_3SCl under these conditions.[172] Donating substituents in the pyrrole ring facilitate and accepting substituents hinder thiolation directing it to the 3(4) position.[172] Indolizines react particularly readily with CF_3SCl forming 1,3-disubstituted derivatives even in the case of indolizines acetylated at the 1 position.[173]



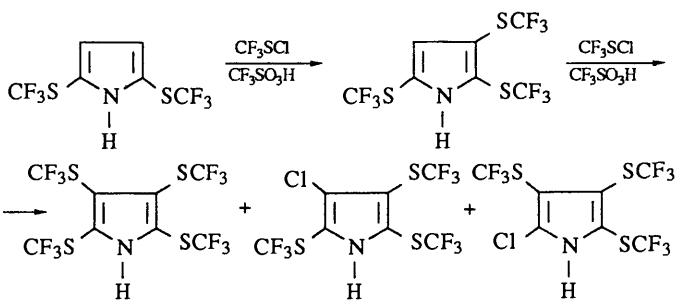
X = H, $C(O)CH_3$; R = H, CH_3, C_6H_5.

The polyfluoroalkylthiolated derivatives of pyrroles possess high biological activity.[174,175] The pyrrolo[2,1-*b*][3]benzazepines with CF_3S substituents in the pyrrole ring are of particular interest, possessing myorelaxant and tranquilising action.[176,177]

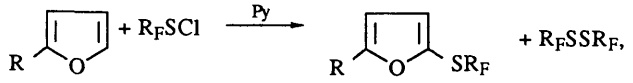


Z = —CH=CH—, X = SCF_3, Y = H; Z = $—CH_2—CH_2$;
X = SCF_3, Y = H; X = H, Y = SCF_3.

The exhaustive trifluoromethylthiolation of the pyrrole ring is of theoretical interest. In the presence of CF_3SO_3H this is accompanied by chlorinating effects of CF_3SCl and 1,2-migration of a trifluoromethylthio group.[178]

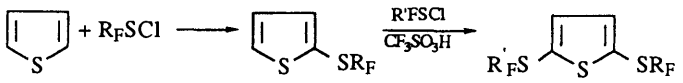


Furan and sylvane (α-methylfuran) react with significantly more difficulty with trihalomethanesulphenyl chlorides in the presence of pyridine. The products are 2- and 5-trihalomethylthio derivatives of furan (sylvane) together with disulphides and polymeric compounds.[171,179] The use of Lewis acids as catalysts or $(C_2H_5)_3N$ as an HCl acceptor proved to be ineffective.



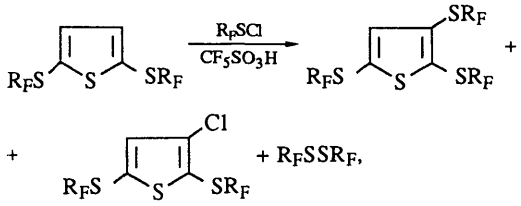
R = H, CH_3; R_F = CF_3, CF_2Cl, $CFCl_2$.

Thiophene reacts with even more difficulty. Monothiolation occurs only on catalysis by $SnCl_4$,[180] in the presence of pyridine under pressure[171] or in CF_3COOH.[181] Disubstitution products were successfully obtained on catalysis by perfluoroalkanesulphonic acids.[180,182]



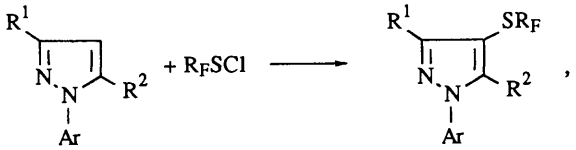
R_F, R_F = CF_3, CF_2Cl, $CFCl_2$.

On further thiolation of thiophene the chlorinating action of R_FSCl is shown.[165]



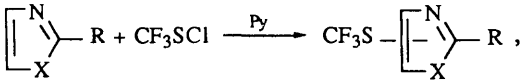
R_F = CF_3, CF_2Cl.

Selophene reacts with CF_3SCl like thiophene.[179] Five-membered heteroaromatic compounds with two heteroatoms react with PFASC only in the presence of electron-supplying substituents. Thus *N*-arylpyrazoles with an OH or NH_2 group in the 5 position are thiolated by trihalomethanesulphenyl chlorides at the C(4) atom. The compounds obtained and also their sulphoxides and sulphones display high insecticidal, acaricidal and nematocidal activity.[183–189]



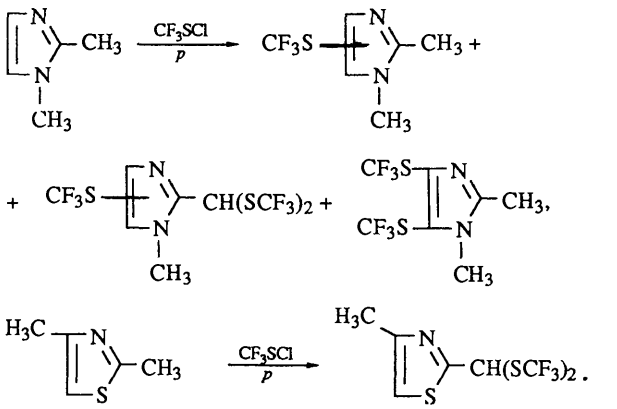
R_F = CF_3, CF_2Cl, $CFCl_2$; R^1 = H, Alk; R^2 = OH, NH_2.

Imidazoles and thiazoles activated by substituents display similar properties. The course of thiolation in this case has not been established precisely.[171,190]

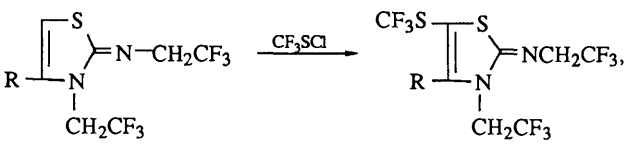


X = S, R = $NHSO_2CH_3$, $NHSO_2CF_3$, $NHCOCH_3$,
X = NCH_3, R = SCH_3, SCH_2CF_3.

The trifluoromethylthiolation of the 1,2-dimethylimidazole ring under pressure is accompanied by the side thiolation of the CH_3 group in the 2 position but in the analogous reaction of 2,4-dimethylimidazole the thiolation of the 2-CH_3 group is the sole course of the reaction.

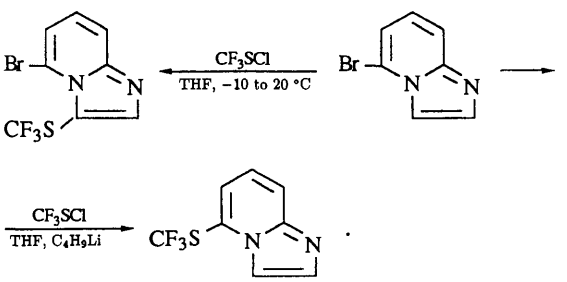


On the other hand derivatives of 2-aminothiazole are readily trifluoromethylthiolated at the C(5) atom.[171]



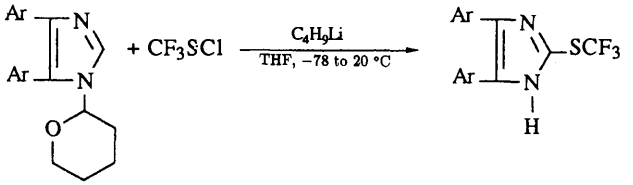
R = H, CH_3.

The reaction of CF_3SCl with 5-bromoimidazo[1,2-a]pyridine under mild conditions is effected in the imidazole ring after generation of a carbanionic centre with butyllithium in the pyridine ring.[191,192]

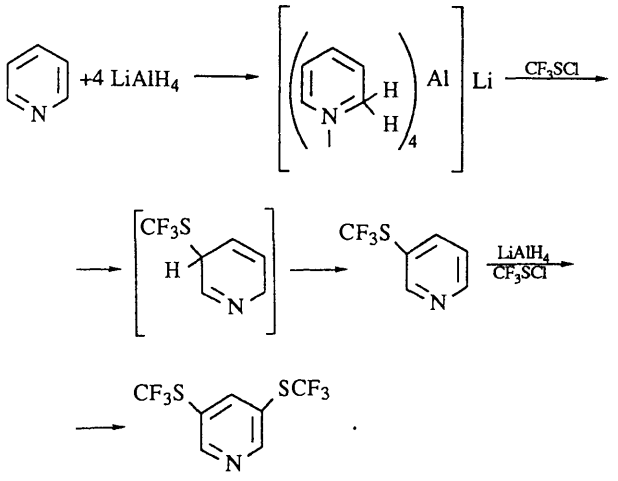


The compounds obtained possess a hypotensive action.

Butyllithium is widely used to generate anions of aromatic[193] and heterocyclic[186,194] compounds which are reactive towards PFASC. A series of active blood pressure regulators was obtained by this route among the 2-trifluoromethylthio-4,5-diarylimidazoles.[194]

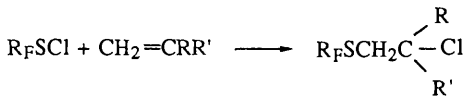


The trifluoromethylthiolation of pyridine was successfully effected only after reducing it to a dihydropyridine derivative.[179,195] The main reaction product is that of 3 substitution together with contamination by the 3,5-bisthiolated compound.



3. Reactions with unsaturated compounds

Features of the electrophilic properties of PFASC are most clearly displayed in their reactions with alkenes.[10,13,36,39,142,196–203] Only 2-chloro-1-trifluoromethylethanesulphenyl chloride reacts with ethylene and its homologues at 20 °C. With the appearance of fluorine atoms or CF_3 and other electron-withdrawing groups in the α position to the S–Cl bond the reaction temperature is abruptly increased (to 100–150 °C). Under relatively mild conditions such compounds add to ethylene only in polar solvents such as CH_3CN. Sterically hindered PFASC generally do not react in the absence of CH_3CN.[10,13,196,198] The addition of PFASC to a terminal ethylene occurs exclusively according to the Markownikov rule with the formation of products under thermodynamic reaction control.



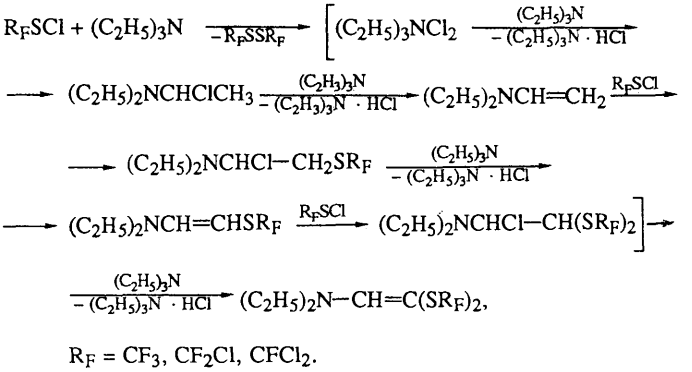
R, R' = H, Alk, Cl, OC_4H_9, $OC(O)CH_3$; R_F = $ClCH_2CH(CF_3)$, $ClCF_2CF_2$, Cl_2CFCF_2, $CH_3OOC-C(CF_3)_2$.

The formation of both regioisomers was observed only on carrying out the reaction in the presence of CF_3COOH which increases the reaction rate markedly.[197]

R = C_4H_9, $BrCH_2$, Br; R_F = CF_3, CF_2Cl, $CFCl_2$.

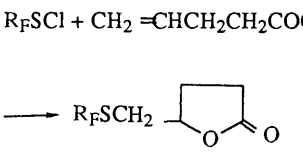
An important feature of the products formed under kinetic control is their stability on storage and fractionation which indicates the significant difficulties in this case of forming an episulphonium ion.

Of the functionally substituted ethylenes only vinyl alkyl ethers and vinyl acetate react readily with PFASC.[198] Seemingly enamines react even more readily as is indicated by the results of the mild reaction or perhalomethanesulphenyl chlorides with triethylamine.[129]



R_F = CF_3, CF_2Cl, $CFCl_2$.

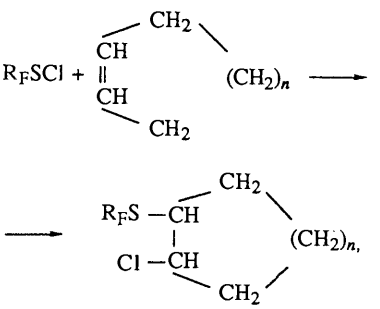
γ,δ-Unsaturated acids and their esters react under unusually mild conditions (−30 to 0 °C) with PFASC forming lactones.[200]



R_F = $ClCH_2-CH(CF_3)$, $ClCF_2CF_2$.

On the other hand β,γ-unsaturated acids and their esters react with PFASC as with other ethylenic compounds giving a mixture of regioisomers.[200] Evidently nucleophilic cooperation in the transition state by the carboxyl or carbalkoxyl groups favours a mild reaction of these compounds with the β,γ-unsaturated acids and their esters.

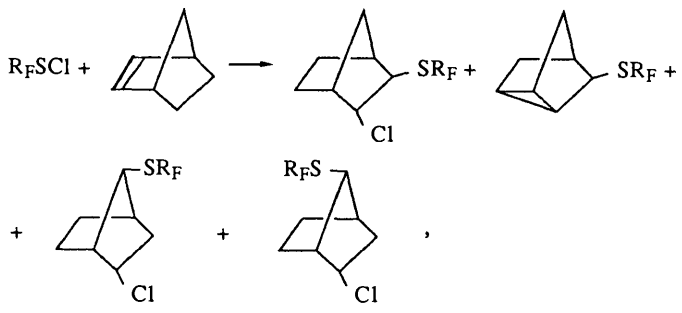
The PFASC, like their unhalogenated analogues, react more readily with strained cycloalkenes than with ethylene homologues. Thus cyclopentene and cycloheptene, differing in the higher strain and lower steric hindrance at the multiple bond, are more reactive in these reactions.[10,13,36,39,196,197]



R_F = CF_3, CF_2Cl, $CFCl_2$, Cl_2CFCF_2, $CF_3OCFClCF_2$, $ClSCF_2CF_2$, $CF_2ClCFCl$, $(CF_3)_3C$, $CH_3OOC-C(CF_3)_2$, $Cl(O)C-C(CF_3)_2$; n = 1, 2, 3.

The addition is effected *trans*-stereospecifically, including when CF_3COOH is present.[197]

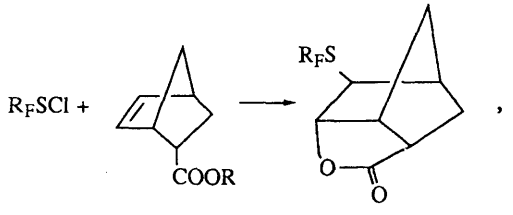
The more strained norbornene molecule reacts vigorously with chlorofluoro-containing methanesulphenyl chlorides in the absence of solvent giving products of *trans*-addition and Wagner–Meerwein rearrangement.[201]



$R_F = CF_3$, CF_2Cl, $CFCl_2$.

Trifluoromethanesulphenyl chloride is particularly reactive in this reaction and forms all four products even at −40 °C. This indicates an episulphonium mechanism for the reaction. The CF_3 group is capable of transforming the primary episulphonium ion into a norbornyl carbonium ion to a greater extent than a $ClCF_2$ or a Cl_2CF group.

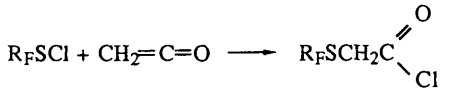
In contrast to norbornene, norbornene-5-carboxylic acid and its esters are lactonised unequivocally like acyclic γ,δ-unsaturated acids.[199]



R = H, CH_3; $R_F = ClCH_2-CH(CF_3)$, $ClCF_2CF_2$, Cl_2CFCF_2, $ClCH_2CCl(CF_3)$, $CH_3OOC-C(CF_3)_2$.

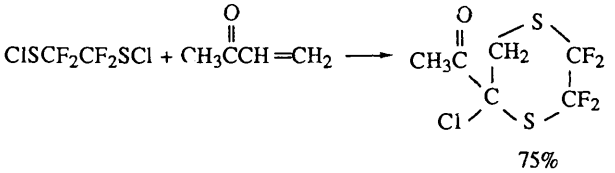
Under more forcing conditions the regioisomeric *trans*-addition products are formed in addition to the lactones. The acid chloride and nitrile of this acid react under more forcing conditions and give only a mixture of the products of *endo* and *exo* addition.

Under mild conditions at −20 to 20 °C PFASC add to ketene giving acid chloride of *S*-polyfluoralkylthioglycolic acid although this is more difficult than with the unfluorinated sulphenyl chlorides.[202,203]



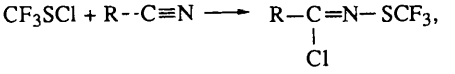
$R_F = CF_3$, $ClCH_2-CH(CF_3)$, $ClCF_2CF_2$, Cl_2CFCF_2.

1,2-Bis(chlorosulphenyl)tetrafluoroethane reacts with methyl vinyl ketone at 20 °C.[142] The primary addition product cyclises into a 1,4-dithiane with elimination of HCl.



75%

Highly electrophilic unsaturated compounds usually do not react with PFASC. However hexafluorodimethylketene forms an adduct with the highly reactive 2-chloro-1-trifluoromethylethanesulphenyl chloride in acetonitrile.[39] Under forcing conditions (150 °C) fluoro-olefins are predominantly chlorinated by PFASC. Addition products are also isolated in 20% yield.[39,196] On heating, in the presence of catalysts or on UV irradiation trifluoromethanesulphenyl chloride adds at the C≡N bond activated by electron-withdrawing substituents.[204–206]



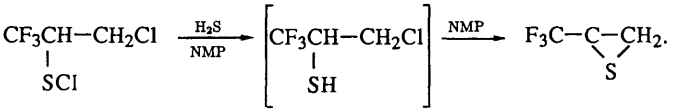
R = CF_3, Cl, $F_2S{=}N$, $F_2S(O){=}N$.

Products of combined trifluoromethylthiolation and fluorination of the C≡N bond were obtained on carrying out this reaction with ClCN, CF_3CN and CCl_3CN in the presence of HgF_2, i.e. $CF_3N(SCF_3)_2$, $CF_3CF{=}NSCF_3$ and $CCl_3CF{=}NSCF_3$ respectively.[207]

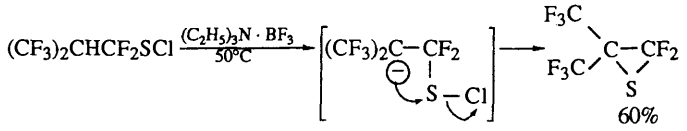
The above information enables it to be assumed that PFASC, like their unfluorinated analogues, react with unsaturated compounds by an Ad_E2 mechanism through an episulphonium transition state. The features of these reactions are determined by the reduction in the energy of formation and stability of the transition states connected with the efficient intramolecular $2p3d$-interactions of the F and S atoms, particularly in the F–C–S triad, and also the high electron-withdrawing ability of the polyfluoroalkyl groups.

4. Cyclisation reactions

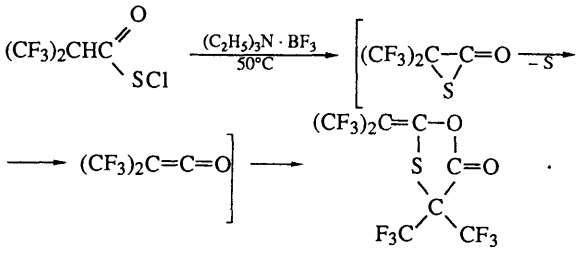
The ability of PFASC to form rings is linked primarily with anionotropic conversions in three-centre C–C–S systems. Thus 2-chloro-1-trifluoromethylethanesulphenyl chloride reacts with H_2S in *N*-methylpyrrolidone (NMP) with the formation of trifluoromethylthiirane. 2-Chloro-1-trifluoromethylethanethiol is an intermediate reaction products.[24]



2-Hydrooctafluoroisobutanesulphenyl chloride is smoothly dehydrochlorinated on heating with the $(C_2H_5)_3N.BF_3$ complex with the formation of perfluoroisobutene episulphide.[26]

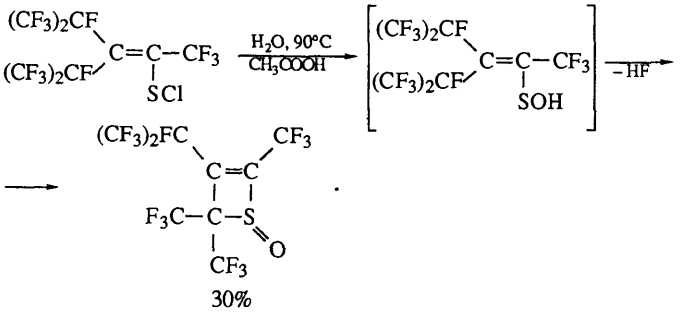


2-Hydrohexafluoroisobutyrylsulphenyl chloride also reacts in this way. However the intermediate thiiranone is desulphurised under the reaction conditions and the resulting bis(trifluoromethyl)ketene undergoes a (3 + 2) cycloaddition with the thiiranone.[26]



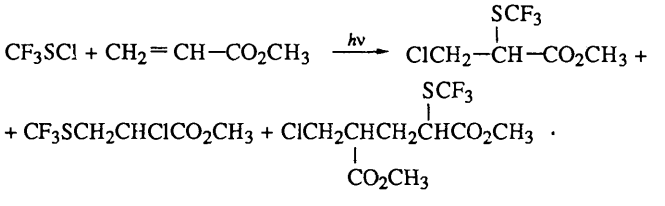
This reaction scheme was confirmed by the positive effect of bis(trifluoromethyl)ketene on the yield of final product.

Mild formation of a thietene ring, which is unusual for sulphur compounds, was observed on acid hydrolysis of the α,β-unsaturated sulphenyl chloride perfluoro-3-isopropyl-4-methyl-2-pentene-2-sulphenyl chloride. In the authors' opinion[137] an unstable sulphenic acid is the intermediate product.



5. Free radical reactions

PFASC undergo free radical conversions on UV or X irradiation and on catalysis by azo compounds. The addition of PFASC to olefins, including fluorine-containing olefins, initiated by UV light leads to both possible isomers and several byproducts.[3] For example CF_3SCl adds to methyl acrylate with the formation of a mixture of three main products,[203] from which CF_3S-containing acrylates are obtained by dehydrochlorination.



Irradiation with UV light initiates a reaction between PFASC and hydrocarbons. Depending on the structure of the sulphenyl chloride and the hydrocarbon the reaction leads to the predominant formation of four types of organic compound.[11,208–210]

$$R_FSCl + RH \rightarrow R_FSH + R_FSR + R_FSSR_F + RCl + HCl.$$

The mechanism of their formation is as follows:

$$R_FSCl \longrightarrow R_FS^{\cdot} + Cl^{\cdot}, \quad (1)$$

$$Cl^{\cdot} + RH \longrightarrow R^{\cdot} + HCl, \quad (2)$$

$$R_FS^{\cdot} + RH \longrightarrow R^{\cdot} + R_FSH, \quad (3)$$

$$R_FSCl + R_FSH \longrightarrow R_FSSR_F + HCl, \quad (4)$$

$$R^{\cdot} + R_FSCl \longrightarrow RCl + R_FS^{\cdot}, \quad (5)$$

$$R^{\cdot} + R_FSCl \longrightarrow R_FSR + Cl^{\cdot}, \quad (6)$$

$$R^{\cdot} + R_FSSR_F \longrightarrow R_FSR + R_FS^{\cdot}. \quad (7)$$

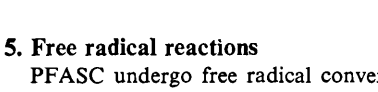
The chief factors determining the composition of the product mixture in these reactions are steric effects at the reaction centres of the sulphenyl chloride and the hydrocarbon. In a series of R_FSCl where R_F was $CF_3 < HCF_2CF_2 < n\text{-}C_3H_7 < (CF_3)_2CF < (CF_3)_3C$ and also in the series $CF_3 < ClCF_2 < Cl_2CF$ the yield of sulphide is significantly reduced. Sulphide was not detected in the reaction mixture in the case of perfluoro-t-butanesulphenyl chloride and stage (4) of the process did not occur for steric reasons. Consequently perfluoro-t-butanethiol and a chlorohydrocarbon are formed exclusively in the free radical reaction of $(CF_3)_3CSCl$ with hydrocarbons. Similarly the ratio of sulphide to chlorohydrocarbon is reduced in the series benzyl < butyl < sec-butyl < cyclohexyl with increasing bulk of the alkyl groups.

6. Oxidation reactions

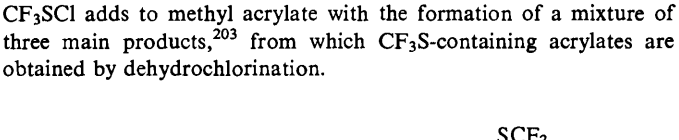
The possibility of obtaining polyfluoroalkanesulphonyl chlorides by the oxidation of PFASC with chlorine in water or hydrochloric acid has been shown in several cases.[12,14,25,196]

$$R_FSCl \xrightarrow[H_2O]{Cl_2} R_FSO_2Cl,$$

$R_F = (CF_3)_2CFOCF_2CF_2$, $CH_3OOCCF_2CF_2$,



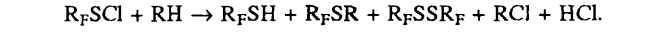
Perfluoroalkyl hypochlorites react with CF_3SCl giving either sulphuranes of S(IV) fluorides.[211]



The PFASC are oxidised by peracids under controlled conditions to polyfluoroalkanesulphinyl chlorides.[23,30,46]

$R_F = CF_3CCl_2$, $CF_3{-}C(C_6H_5)_2$, $(CF_3)_2CCl$.

On oxidising $ClSCF_2CF_2SCl$ with 30% hydrogen peroxide di-(2-chlorosulphonyltetrafluoroethyl) disulphide is formed in addition to oxidation to the sulphonyl chloride.[212]



Various fluorinating agents (ClF_3, AgF_2, BrF_3/HgF_2) convert PFASC to a mixture of different products including organic fluorides of tetra- and hexavalent sulphur,[213,214] such as

$$ClCF_2SCl \xrightarrow[60-70°C]{AgF_2} ClCF_2SF_3 + CF_3SF_3 + CF_3SF_5.$$

The information discussed above show that the chemistry of PFASC and of their unfluorinated analogues are mainly similar. In addition, important features of the fluorine-containing sulphenyl chlorides may also be noted. They are more difficult to form, they possess higher stability and markedly less reactivity and their reactions usually occur by thermodynamically controlled routes. The R_FS group of perfluoroalkanesulphenyl chlorides has a clearly expressed 'pseudo-halogen' character as the PFASC display chlorinating properties and the perfluoroalkanethiol group frequently acts as a leaving group in rearrangements and heterocyclisations.

All these features are undoubtedly linked with the effective intramolecular $2p3d$-interactions of the F and S atoms which leave an imprint on the properties of the products of the numerous conversions of PFASC. The stabilising effects of these interactions determine the unusually high static and kinetic stability of the new type of compound, viz. the α-polyfluoroalkenesulphenyl chlorides.

From a practical point of view the PFASC are more convenient reagents for organic synthesis than the functionally unsubstituted alkanesulphenyl chlorides. They store well and are not afraid of moisture. Their reactions are sensitive to solvent effects which enables processes to be controlled reliably. In spite of the somewhat reduced reactivity the PFASC possess a wide spectrum of properties and are efficient precursors of fluorine-containing compounds of numerous types.

Up to the present completely halogenated fluorine-containing methane- and ethanesulphenyl chlorides have been predominantly studied to obtain fluorine-containing analogues of first and second generation pesticides in the synthesis of biologically active compounds for agriculture. The corresponding derivatives of hormonal preparations are practically uninvestigated. In medicine only trifluoromethylthiolated derivatives of neuroregulators of hormone metabolism have been investigated. However the result of even these few investigations indicate that the time has now arrived for an intensive development of the chemistry of PFASC as potential precursors of biologically active compounds for various purposes.

References

1. R N Haszeldine, J M Kidd *J. Chem. Soc.*, 1953, 3219
2. I L Knunyants, A V Fokin *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1955, 705
3. A Haas, U Niemann *Adv. Inorg. Chem. Radiochem.*, 1976, **18** 143
4. A V Fokin, A F Kolomiets *Khimiya Tiiranov* (Chemistry of Thiiranes), Nauka, Moscow, 1978
5. A V Fokin, M A Allakhverdiev, A F Kolomiets *Usp. Khim.*, 1990, **59**(4) 705 [English translation in *Russ. Chem. Rev.*, 1990(4)]
6. L M Yagupol'skii *Aromaticheskie i Geterotsiklicheskie Soedineniya s Ftorsoderzhashchimi Zametstitelyami* (Aromatic and Heterocyclic Compounds with Fluorine-containing Substituents), Nauk. Dumka, Kiev, 1988
7. A F Kolomiets, A V Fokin *VI Vsesoyuz. Konf. po Khimii Ftororganicheskikh Soedinenii* (VIth All-Union Conference on the Chemistry of Organofluorine Compounds), Novosibirsk, 1990, Abstracts, p. 16
8. R A Bekker, V Ya Popokova, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1688
9. G F Il'in, S N Shkurak, A F Kolomiets, G A Sokol'skii *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1983, **28** 235
10. A V Fokin, S N Shkurak, A F Kolomiets, F M Mukhametshin *Zh. Org. Khim.*, 1985, **21** 1835
11. J F Harris *J. Org. Chem.*, 1979, **44** 563
12. US P. 3 821 290; *Chem. Abs.*, 1974, **81** 104 751
13. A Yu Sizov, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1186
14. R A Bekker, V Ya Popokova, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2175
15. V Ya Popkova, R A Bekker, E I Mysov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2740
16. US P. 3 932 508; *Chem. Abs.*, 1976, **84** 121 158
17. R A Bekker, V Ya Popokova, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1692
18. T Nguyen, M Rubinstein, C Wakselman *J. Org. Chem.*, 1981, **46** 1938
19. R A Bekker, V Ya Popokova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1123
20. R A Bekker, V Ya Popkova, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1692
21. V Ya Popkova, V F Snegirev, M Yu Antipin, Yu T Struchkov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1123
22. V Ya Popkova, M V Galakhov, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 116
23. H Fritz, W Sundermeyer *Chem. Ber.*, 1989, **122** 1757
24. R A Bekker, V Ya Popkova, L A Rosov, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2558
25. Japanese Application 55-160008; *Chem. Abs.*, 1981, **94** 176 061
26. R A Bekker, L A Rozov, V Ya Popkova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2575
27. A Haas, R Walz *Chem. Ber.*, 1985, **118** 3248
28. Yu V Zeifman, L T Lantseva, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2640
29. R A Bekker, V Ya Popkova, V F Snegirev, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2167
30. T Netscher, H Prinzbach *Synthesis*, 1987, 683
31. A Haas, B Koch, N Welcman *Chem. Ztg.*, 1974, **98** 511
32. G Diderrich, A Haas *Chem. Ber.*, 1976, **109** 3432
33. A Haas, B Koch, N Welcman *Z. Anorg. Allg. Chem.*, 1976, **427** 114
34. R A Bekker, B Ya Popkova, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 2347
35. A V Fokin, A F Kolomiets *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1820
36. N N Muratov, N M Mokhamed, B V Kunshenko, et al. *Zh. Org. Khim.*, 1986, **22** 964
37. A V Fokin, A I Rapkin, V I Matveenko *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2652
38. A V Fokin, A I Rapkina, V I Matveenko, O V Verenikin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2367
39. S N Shkurak, V V Ezhov, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 1371
40. R L Kirochmeier, G M Sprenger, J M Shreeve *Inorg. Nucl. Chem. Lett.*, 1975, **11** 699

41. A Yu Sizov, A K Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1619
42. G B Fazekas, G A Takacs *J. Photochem.*, 1981, **16** 249
43. GDR P. 274819; *Chem. Abs.*, 1990, **113** 58491
44. GDR P. 274820; *Chem. Abs.*, 1990, **113** 114647
45. GDR P. 274821; *Chem. Abs.*, 1990, **113** 58492
46. A Elsäser, W Sundmeyer *Chem. Ber.*, 1985, **118** 4553
47. D H R Barton, W Ollis (Editors) *Comprehensive Organic Chemistry* (Translated into Russian), Khimiya, Moscow, 1983, Vol. 5, p. 426
48. A Haas, W Wanzke, N Welcman *J. Fluorine Chem.*, 1983, **23** 471
49. H Fritz, W Sundermeyer *Tetrahedron Lett.*, 1985, **26** 5505
50. S Braverman, H Manor *Phosphorus Sulfur*, 1976, **2** 215
51. A Haas, D Kortmann *J. Fluorine Chem.*,1978, **11** 337
52. S D Morse, K A Laurence, H Sprenger, J M Shreeve *J. Fluorine Chem.*, 1978, **11** 327
53. J Holoch, W Sundermeyer *Chem. Ber.*, 1986, **119** 269
54. S-L Yu, J M Shreeve *J. Fluorine Chem.*, 1975, **6** 259
55. A Haas, M Lieb, Yu Zhang *J. Fluorine Chem.*, 1985, **29** 297
56. W Combler, F Seel *Z. Naturforsch.*, 1975, **30b** 169
57. C A Burton, J M Shreeve *Inorg. Nucl. Chem. Lett.*, 1976, **12** 373
58. US P. 4058609; *Chem. Abs.*, 1978, **88** 89688
59. C O Della Vedova, A Haas *J. Fluorine Chem.*, 1989, **45** 75
60. G Stajer, J Reisch, A E Szabo *Acta Chim. Acad. Sci. Hung.*, 1980, **105** 99
61. V Ya Popkova, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 209
62. V Ya Popkova, B L Tumanskii, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1160
63. H W Roesky, V W Pogatzi, K S Dhathathreyan, et al. *Chem. Ber.*, 1986, **119** 2687
64. W Gombler, R Budenz *J. Fluorine Chem.*, 1976, **7** 115
65. A Senning, H C Hansen, M F Abdel-Megeed, et al. *Tetrahedron*, 1986, **42** 739
66. W Bludssus, R Mews, O Glemser, G G Alange *Isr. J. Chem.*, 1978, **17** 137
67. FRG Application 3049448; *Chem. Abs.*, 1982, **97** 215545
68. FRG Application 3146231; *Chem. Abs.*, 1983, **99** 194637
69. H W Roesky *J. Fluorine Chem.*, 1987, **35** 24
70. W P Trompen, J Geevera *Recl. Trav. Chim. Pays-Bas*, 1976, **95** 106
71. T Kitazume, J M Shreeve *J. Fluorine Chem.*, 1976, **8** 437
72. T S Croft *Phosphorus Sulfur*, 1976, **2** 133
73. E Kuhle, E Klaule, *Kem-Kemi*, 1974, **1** 99
74. O D Gupta, W A Kamil, J M Shreeve *Inorg. Chem.*, 1985, **24** 2126
75. I V Koval', A I Tarasenko, M M Kremlev, N R Molchanov *Zh. Org. Khim.*, 1981, **17** 533
76. H E Borowski, A Haas *Chem. Ber.*, 1982, **115** 523
77. D Kost, H Egozy *J. Org. Chem.*, 1989, **54** 4909
78. FRG Application 3142857; *Chem. Abs.*, 1983, **99** 53749
79. E Behrend, A Haas *J. Fluorine Chem.*, 1974, **4** 99
80. Roumanian P. 54635; *Chem. Abs.*, 1973, **79** 16594
81. FRG Application 1800836; *Chem. Abs.*, 1969, **71** 21885
82. US P. 4193933; *Chem. Abs.*, 1969, **71** 21885
83. FRG Application 2336290; *Chem. Abs.*, 1975, **82** 172912
84. FRG Application 2652451; *Chem. Abs.*, 1977, **87** 134723
85. Australian P. 517016; *Chem. Abs.*, 1982, **97** 23461
86. FRG Application 3137061; *Chem. Abs.*, 1983, **99** 22110
87. FRG Application 3313718; *Chem. Abs.*, 1985, **102** 113030
88. FRG Application 353162; *Chem. Abs.*, 1987, **106** 196040
89. FRG Application 2064596; *Chem. Abs.*, 1975, **83** 96076
90. FRG Application 2512814; *Chem. Abs.*, 1977, **86** 12693
91. FRG Application 3033863; *Chem. Abs.*, 1982, **97** 55501
92. US P. 3907788; *Chem. Abs.*, 1976, **85** 108654
93. FRG Application 2611902; *Chem. Abs.*, 1978, **88** 120819
94. Austrian P. 343097; *Chem. Abs.*, 1978, **89** 167534
95. US P. 4115582; *Chem. Abs.*, 1978, **89** 179719
96. US P. 4097512; *Chem. Abs.*, 1978, **89** 181541
97. US P. 4357346; *Chem. Abs.*, 1982, **96** 180998
98. US P. 4390549; *Chem. Abs.*, 1983, **99** 212292
99. US P. 4199594; *Chem. Abs.*, 1980, **93** 71535
100. FRG Application 2703023; *Chem. Abs.*, 1978, **89** 163386
101. FRG Application 2838750; *Chem. Abs.*, 1980, **93** 114119
102. FRG Application 3032327; *Chem. Abs.*, 1982, **96** 199346
103. FRG Application 3151445; *Chem. Abs.*, 1983, **99** 104997
104. FRG Application 3049440; *Chem. Abs.*, 1982, **97** 162622
105. FRG Application 3049439; *Chem. Abs.*, 1982, **97** 215593
106. FRG Application 3110595; *Chem. Abs.*, 1983, **98** 143640
107. FRG Application 3712937; *Chem. Abs.*, 1989, **111** 134474
108. US P. 4357351; *Chem. Abs.*, 1983, **99** 21964
109. US P. 4766135; *Chem. Abs.*, 1988, **108** 94404
110. FRG Application 3805058; *Chem. Abs.*, 1990, **112** 55849
111. US P. 4785019; *Chem. Abs.*, 1989, **111** 7078
112. FRG Application 2722035; *Chem. Abs.*, 1978, **89** 197541
113. US P. 4198423; *Chem. Abs.*, 1980, **83** 71784
114. FRG Application 3222523; *Chem. Abs.*, 1984, **100** 103349
115. FRG Application 3305203; *Chem. Abs.*, 1984, **101** 211146
116. US P. 3840555; *Chem. Abs.*, 1975, **82** 108654
117. FRG Application 3131250; *Chem. Abs.*, 1983, **99** 22314
118. Japanese Application 55-087707; *Chem. Abs.*, 1980, **93** 144709
119. Japanese Application 57-055943; *Chem. Abs.*, 1982, **97** 110840
120. FRG Application 3415532; *Chem. Abs.*, 1986, **104** 64210
121. US P. 4602029; *Chem. Abs.*, 1987, **106** 98089
122. FRG Application 3306771; *Chem. Abs.*, 1985, **102** 6542
123. FRG Application 3505905; *Chem. Abs.*, 1987, **106** 84598
124. W B Wright, A S Tomcufcik, P S Chan, et al. *J. Med. Chem.*, 1987, **30** 2277
125. FRG Application 3015090; *Chem. Abs.*, 1982, **96** 20108
126. FRG Application 3133405; *Chem. Abs.*, 1983, **99** 22472
127. D Bielefeldt, A Haas *Chem. Ber.*, 1983, **116** 1257
128. H W Roesky, N Benmohamed, K Keller, et al. *Z. Naturforsch., B*, 1987, **42** 1249
129. M R C Gerstenberger, A Haas *J. Fluorine Chem.*, 1983, **22** 81
130. US P. 2811543; *Chem. Abs.*, 1958, **52** 4922
131. US P. 632757; *Chem. Abs.*, 1964, **61** 9402
132. Y O El Nigumi, H J Emeléus *J. Inorg. Nucl. Chem.*, 1970, **32** 3213
133. G M Blackburn, T W Maciej *J. Chem. Soc., Perkin Trans. 1*, 1985, 1419
134. A Haas, W Kortmann *Z. Anorg. Allg. Chem.*, 1983, **501** 79
135. A Haas, D Winkler *Z. Anorg. Allg. Chem.*, 1980, **468** 68
136. H W Roesky, U Otten *J. Fluorine Chem.*, 1990, **46** 433
137. US P. 3937738; *Chem. Abs.*, 1976, **84** 150119
138. FRG Application 3119391; *Chem. Abs.*, 1983, **98** 166894
139. A Yu Sizov, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 676
140. FRG Application 3732388; *Chem. Abs.*, 1989, **111** 174099
141. FRG Application 3811302; *Chem. Abs.*, 1990, **112** 178989

142. H W Roesky, N Benmohamed *Z. Anorg. Allg. Chem.*, 1987, **545** 143
143. A Kolasa *J. Fluorine Chem.*, 1987, **36** 29
144. A Haas, W Zankowska-Jasinska, B Zaleska *J. Fluorine Chem.*, 1984, **24** 363
145. W Zankowska-Jasinska *J. Fluorine Chem.*, 1983, **38** 85
146. M Jamrozik *J. Fluorine Chem.*, 1986, **31** 293
147. V I Popov, A Haas, M Lieb *J. Fluorine Chem.*, 1990, **47** 131
148. M Bauer, A Hass, H Muth *J. Fluorine Chem.*, 1980, **16** 129
149. A Kolasa *J. Fluorine Chem.*, 1988, **38** 257
150. R M DeMarinis, J R E Hoover, G L Dunn, et al. *J. Antibiot.*, 1975, **28** 463
151. H W Roesky, N Benmohamed *Chem. Ztg.*, 1986, **110** 417
152. A U Sizov, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.* (in the Press)
153. K Bogdanowiez-Szwed, B Kawatek, M Lieb *J. Fluorine Chem.*, 1987, **35** 317
154. H W Roesky, U Otten, R Herbst, et al. *Z. Naturforsch., B*, 1989, **44** 543
155. A Haas, M Lieb, H-W Praas *J. Fluorine Chem.*, 1989, **44** 329
156. W L Mendelson, J-H Liu, B L Killmer, S H Levinson *J. Org. Chem.*, 1983, **48** 298
157. H W Roesky, N Benmohamed, J Schimkowiak, et al. *Z. Anorg. Allg. Chem.*, 1987, **544** 209
158. M J Mokzosz *J. Fluorine Chem.*, 1986, **34** 201
159. B Zaleska, W Winnik *J. Pract. Chem.*, 1989, **331** 55
160. B Zaleska, M Kurdziel *Synth. Commun.*, 1988, **18** 1863
161. U Otten, H W Roesky *Z. Anorg. Allg. Chem.*, 1988, **560** 55
162. V Ya Popkova, V A Nikanorov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2148
163. T I Cherkasova, V M Khutoretskii, L V Okhlobystina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1125
164. G M Blackburn, T W Maciej *J. Chem. Soc., Perkin Trans. 1*, 1985, 1935
165. A Haas, V Hellwig *J. Fluorine Chem.*, 1975, **6** 521
166. US P. 4 320 148; *Chem. Abs.*, 1982, **97** 23 487
167. A Yu Sizov, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 832
168. T S Croft *Phosphorus Sulfur*, 1976, **2** 129
169. V I Popov, N V Kondratenko, A Haas *Ukr. Khim. Zh.*, 1983, **49** 861
170. A Yu Sizov, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1625
171. T S Croft, J J McBrady *J. Heterocycl. Chem.*, 1975, **12** 845
172. A Haas, U Niemann *Chem. Ber.*, 1977, **110** 67
173. J Mirek, A Haas *J. Fluorine Chem.*, 1981, **23** 67
174. S Dorn, P Eggenberg, M R C Gerstenberger, et al. *Helv. Chim. Acta*, 1979, **62** 1442
175. US P. 4 267 184; *Chem. Abs.*, 1981, **95** 61 982
176. US P. 4 075 225; *Chem. Abs.*, 1978, **88** 190 617
177. US P. 4 112 112; *Chem. Abs.*, 1979, **91** 91 624
178. M R C Gerstenberger, A Haas, F Liebig *J. Fluorine Chem.*, 1982, **19** 461
179. M R C Gerstenberger, A Haas *J. Fluorine Chem.*, 1983, **23** 525
180. A Haas, V Hellwig *Chem. Ber.*, 1976, **109** 2475
181. US P. 4 302 461; *Chem. Abs.*, 1982, **96** 104 081
182. M R C Gerstenberger, A Haas, H Pauling, *Helv. Chim. Acta*, 1982, **65** 490
183. FRG Application 3 602 728; *Chem. Abs.*, 1987, **106** 171 144
184. FRG Application 3 529 829; *Chem. Abs.*, 1987, **106** 156 465
185. FRG Application 3 600 287; *Chem. Abs.*, 1988, **108** 6015
186. FRG Application 3 617 554; *Chem. Abs.*, 1988, **108** 73 807
187. FRG Application 3 606 476; *Chem. Abs.*, 1988, **108** 6005
188. FRG Application 3 727 260; *Chem. Abs.*, 1989, **111** 57 726
189. Europ. P. 303 118; *Chem. Abs.*, 1989, **111** 39 362
190. D M Mulvey, H Jones *J. Heterocycl. Chem.*, 1975, **12** 597
191. FRG Application 2 820 938; *Chem. Abs.*, 1979, **90** 87 458
192. Europ. P. 6614; *Chem. Abs.*, 1980, **93** 114 518
193. Japanese P. 62 158256; *Chem. Abs.*, 1988, **108** 131 604
194. US P. 4 190 666; *Chem. Abs.*, 1980, **93** 8178
195. A Haas, U Niemann *J. Fluorine Chem.*, 1978, **11** 509
196. A V Fokin, A F Kolomiets, S N Shkurik, et al. *Zh. Org. Khim.*, 1985, **21** 2337
197. A Haas, M Lieb, Yu Zhang *J. Fluorine Chem.*, 1983, **30** 203
198. N V Kondrashov, A F Kolomiets, G A Sokol'skii *Zh. Org. Khim.*, 1986, **22** 521
199. A Yu Sizov, V V Linev, N V Kondrashev, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 150
200. A Yu Sizov, A F Kolomiets, A V Fokin *VI Vsesoyuz. Konf. po Khimii Ftororganicheskikh Soedinenii* (VIth All-Union Conference on the Chemistry of Organofluorine Compounds), Novosibirsk, 1990, Abstracts, p. 165
201. A Haas, M Lieb, Yu Zhang *J. Fluorine Chem.*, 1985, **29** 311
202. N V Kondrashov, G A Sokol'skii, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2358
203. J F Harris *J. Org. Chem.*, 1972, **37** 1340
204. C A Burton, J M Shreeve *Inorg. Chem.*, 1977, **16** 1408
205. E Kuhle, H Hagemann, L Oehlmann *Angew. Chem.*, 1975, **87** 707
206. H-U Höfs, R Mews, M Noltemeyer, et al. *Z. Naturforsch., B*, 1983, **38** 454
207. M Geisel, R Mews *Chem. Ber.*, 1987, **120** 1675
208. US P. 3 808 249; *Chem. Abs.*, 1974, **81** 25 797
209. FRG Application 2 415 670; *Chem. Abs.*, 1975, **82** 44 672
210. J F Harris *J. Org. Chem.*, 1981, **46** 268
211. Q-C Mir, K A Laurence, R W Shreeve, et al. *J. Am. Chem. Soc.*, 1979, **101** 5949
212. H W Roesky, A Thiel *Chem. Ber.*, 1984, **117** 1980
213. G H Sprenger, A J Cowley *J. Fluorine Chem.*, 1976, **7** 333
214. W Gombler *J. Fluorine Chem.*, 1977, **9** 233

Translated from *Uspekhi Khimii* **61** 978–1001 (1992) U.D.C. 542.957:547.257.1

Organic derivatives of manganese(II) in organic synthesis

A N Kasatkin, O Yu Tsypyshev, T Yu Romanova, G A Tolstikov
Institute of Organic Chemistry, Urals Division, Russian Academy of Sciences, Ufa

ABSTRACT. Literature data on the use of organic compounds of Mn(II) as reagents for organic synthesis have been correlated. Methods of obtaining and using them in acyl-, alkenyl- and allyldemetallation reactions and in 1,2- and 1,4-additions to carbonyl substrates are considered. The reactions of manganese derivatives containing Mn–Si and Mn–Sn bonds are discussed.

The bibliography contains 99 references.

Contents

I. Introduction 537
II. Preparation, stability and structure of organic compounds of Mn(II) 537
III. Reactions of organic compounds of Mn(II) 538
IV. Reactions of manganese derivatives containing Mn–Si and Mn–Sn bonds 546
V. Conclusion 547

I Introduction

The synthesis of organic derivatives of Mn(II) with a metal–carbon bond was achieved for the first time in 1937 by Gilman and collaborators.[1] It was found that on reacting MnI_2 with 1 or 2 equiv. PhMgI red-brown solutions of the complexes PhMnI and Ph_2Mn were formed. In spite of the intensive development in recent years of the chemistry of organomanganese compounds containing carbonyl ligands,[2,3] during the period from 1937 to 1976 only a few studies were published which were devoted to the preparation and properties of derivatives of the type of RMnI, R_2Mn and R_3MnLi (R = Alk, Ar).[4–10] The main reason for this is the extremely low stability of such complexes which exist (with rare exceptions) only as solutions in ether or THF, frequently at low temperatures and for a limited time. After 1976 progress became focussed, thanks to the work of Normant and collaborators,[11–13] on the use of organic Mn(II) derivatives as efficient reagents for forming new carbon–carbon bonds. Methods have been developed for obtaining the various alkyl-, alkenyl-, aryl- and alkynylmanganese halides, the corresponding di-organo derivatives and the lithium and magnesium triorganomanganates, without isolating them in the free state. In spite of the absence of detailed information on the structure of the reagents (the formulae RMnX, R_2Mn, R_3MnLi and R_3MnMgX reflect only the ratio of the starting materials) their application has in many cases proved to be extremely successful.[14]

The main applications of Mn(II) derivatives with a Mn–C bond and also with Mn–Si and Mn–Sn bonds in synthetic organic chemistry are considered below.

II. Preparation, stability and structure of organic compounds of Mn(II)

The most general method of obtaining organic compounds of Mn(II) in ether is the reaction of RLi or RMgX with MnI_2 at 0–20 °C (R = n-alkyl, alkenyl, aryl, alkynyl) or at −30 to −50 °C (R = sec-, t-alkyl).[14,15] Complexes of the type of RMnI or R_3MnLi are obtained depending on the ratio of RLi (or RMgX) and MnI_2. It must be noted that in ether the treatment of MnI_2 with 3 equiv. RMgX does not lead to the formation of the corresponding triorganomanganate R_3MnMgX. The synthesis of the di-organo derivatives R_2Mn was in all cases carried out at temperatures below −30 °C.

$$RM + MnI_2 \xrightarrow{Et_2O} RMnI + MI,$$
$$2\,RM + MnI_2 \xrightarrow{Et_2O} R_2Mn + 2\,MI,$$
$$3\,RLi + MnI_2 \xrightarrow{Et_2O} R_3MnLi + 2\,LiI,$$
M = Li, MgCl, MgBr, MgI.

The reagents are suspensions or homogeneous red-brown solutions but occasionally, when R = CH_2=CH or Ar, they are green. They are extremely sensitive to oxygen and moisture of the air.

The use of the more readily available $MnCl_2$ and $MnBr_2$ in place of MnI_2 is less efficient due to their low solubility in Et_2O.[14] The synthesis of organic compounds of Mn(II) from $MnBr_2$ in ether is successful if the practically insoluble dibromide is replaced by the soluble complex Li_2MnBr_4, prepared by treating $MnBr_2$ with an ether solution of LiBr (the latter was obtained from metallic lithium and Br_2 in Et_2O).[16] It is also possible to use previously prepared complexes of Grignard reagents with LiBr or ether solutions of organolithium compounds containing lithium halides.

$$MnBr_2 \xrightarrow[Et_2O]{LiBr} Li_2MnBr_4 \xrightarrow[Et_2O]{RMgX} RMnBr,$$
$$RMgX \xrightarrow[Et_2O]{LiBr} \text{«RMgX}\cdot\text{LiBr»} \xrightarrow[Et_2O]{MnBr_2} RMnBr,$$
$$RX \xrightarrow[Et_2O]{Li} RLi;\ RLi \xrightarrow[Et_2O]{MnBr_2} RMnBr,$$
X= Cl, Br.

It is best to use the readily available $MnCl_2$ or its soluble complex Li_2MnCl_4 in combination with 1–3 equiv. RLi or RMgX (R is alkyl, alkenyl, aryl, alkynyl) to synthesise organic derivatives of Mn(II) in THF.[14] The reaction is effected at 20 °C and in the majority of cases leads to the formation of homogeneous yellow or

brown solutions of derivatives of RMnCl, R_2Mn or R_3MnM (M = Li, MgX). All three types of complex may be synthesised using Grignard reagents in THF (in contrast to Et_2O).

$$MnCl_2 + 2LiCl \xrightarrow{THF} Li_2MnCl_4,$$

$$RM + MnCl_2(Li_2MnCl_4) \xrightarrow{THF} RMnCl + MCl(+2LiCl),$$

$$2RM + MnCl_2(Li_2MnCl_4) \xrightarrow{THF} R_2Mn + 2MCl(+2LiCl),$$

$$3RM + MnCl_2(Li_2MnCl_4) \xrightarrow{THF} R_3MnM + 2MCl(+2LiCl),$$

M = Li, MgCl, MgBr, MgI.

The stability of organomanganese compounds is determined by the type of complex, the nature of the organic fragment and the solvent. The tri-organomanganates R_3MnM (M = Li, MgX) possess the greatest stability. The thermal stabilities of the RMnX complex and particularly of R_2Mn are markedly less.[14] The decomposition point of Bu_3MnLi in ether is above 35 °C and of BuMnI and Bu_2Mn it is 20 and −30 °C.

The stability of Mn(II) derivatives with a Mn−C bond depends chiefly on the ease of β-elimination determined by the presence of alkyl β-hydrogen atoms.[9,10,14,17] It was found that the stabilities of the complexes RMnX and R_2Mn increase in the folowing series of R: t-alkyl < sec-alkyl < n-alkyl < methyl, alkenyl, aryl.[14] The decomposition points of the compounds RMnI in Et_2O are

R	t-Bu	iso-Pr	n-Bu	Me, Ph, $Me_2C=CH$
T, °C	−35	−30	20	>35

The formation of hydride intermediates during decomposition of the manganese reagents was confirmed by the isolation of hydrogenation products of unsaturated hydrocarbons introduced into the reaction mixture.[10,18]

On changing from ether to THF a marked increase was observed in the stability of organic Mn(II) compounds which is seemingly associated with stronger coordination.[14,15] The complexes t-BuMnCl, iso-PrMnCl, n-BuMnCl and PhMnCl do not undergo marked decomposition in THF even at 66 °C. A similar effect may also be caused by certain other donor ligands. Thus the addition of 5 equiv. DMF to a solution of iso-PrMnI in Et_2O raises the decomposition temperature of the complex from −30 to 35 °C.

Allyl derivatives of manganese of the type RMnCl may be obtained by the reaction of allyl Grignard reagents with Li_2MnCl_4 in THF at −78 °C.[19] The allylmanganese halides are significantly less stable than the alkyl, alkenyl, aryl and alkynyl σ-complexes considered above. Their decomposition with the formation of a mixture of regioisomeric 1,5-dienes occurs even at −78 °C.

$$R^1CH=C(R^2)CH_2MgX + Li_2MnCl_4 \xrightarrow{THF}$$

$$\longrightarrow R^1CH=C(R^2)CH_2MnCl + Mg(X)Cl + 2LiCl$$

R^1, R^2 = H, Alk; X = Cl, Br.

The direct synthesis of allyl compounds of Mn(II) from metallic manganese and allyl halides is described in section III.3.

Only a few examples are known of the isolation of organic Mn(II) derivatives in the free state. The existence of molecular associates (dimer, trimer and polymers) has been proved for $(Me_2PhCCH_2)_2Mn$, $(Me_3SiCH_2)_2Mn$ and $(Me_3CCH_2)_2Mn$ by X-ray structural analysis.[20] Intermolecular interaction is effected by bridging bonds between the Mn atoms and CH_2 groups and is confirmed by a shift of the appropriate absorption bands in the IR spectrum. The elemental analysis of the isolated Me_2Mn and Ph_2Mn shows that they exist as associates with Mg salts.[20] On attempting to isolate Me_3MnLi a compound was obtained the composition of which corresponded to the formula $Li_2MnMe_4.0.5Et_2O$.[20]

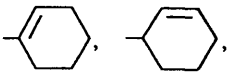
III. Reactions of organic compounds of Mn(II)

1. Alkenyl- and allyldemetallation

The first attempts to use organic compounds of Mn(II) in cross-coupling reactions generally did not give positive results. In contrast to the lithium dialkylcuprates[21,22] the alkyl derivatives of manganese of type R_3MnLi and R_2Mn gave cross-coupling products in less than 10% yield on reaction with alkyl halides.[23] Reaction with alkenyl and allyl halides (bromides and iodides) occurred relatively smoothly only in the case of the most stable Me_3MnLi.

$$Me_3MnLi + RX \xrightarrow[0°C]{Et_2O} R{-}Me$$

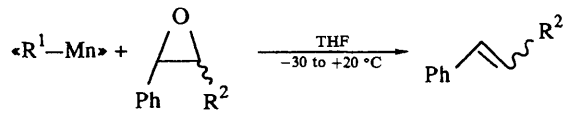
65—82%

R =  , (E)-PhCH=CH,

(E)-(n-C_7H_{15})CH=CH; X = Br, I.

The main side reactions were reduction of the substrates RX to 'dimeric' products R_2 and the formation of dehalogenation products RH (when β-hydrogen atoms are present in the reagent).

The complexes MeMnCl and Bu_3MnLi may be used for deoxygenating epoxides.[24] The reaction occurs selectively under mild conditions and leads to the *trans*-olefin using either *cis*- or *trans*-oxiranes.

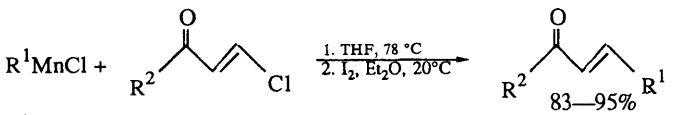


R^1	R^2	Yield of olefin, %
Me	H	63
Bu	*E*-Ph	66 (*E*:*Z* = 100:0)
Bu	*Z*-Ph	59 (*E*:*Z* = 90:10)

Further study of the cross-coupling reaction involving organomanganese compounds led to the development of efficient methods of synthesis of alkenyl- and allyl-demetallation products.

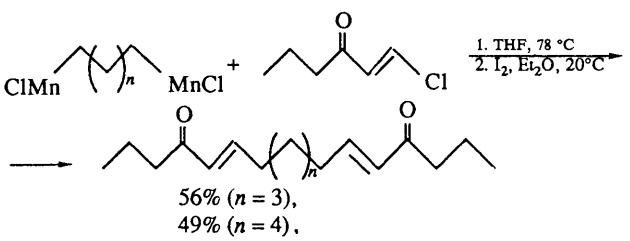
The alkyl derivatives of manganese RMnCl react with β-chlorovinyl ketones forming the corresponding β-alkyl substituted α,β-unsaturated ketones in good yield as a mixture of *trans* and *cis* isomers. The *cis* isomeric enones are readily isomerised in the presence of trace amounts of I_2.[25,26] Under the same conditions the dimanganese derivatives give unsaturated diketones as the main

product. It must be noted that replacement of halogen by alkyl using organocuprate complexes proceeds smoothly only in the case of the cyclic β-chloro-α,β-enones.[27,28]



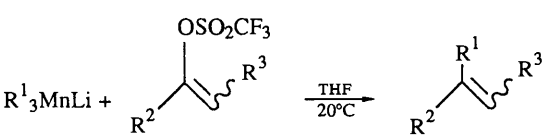
R^1 = Me, Bu, iso-Bu, sec-Bu, cyclo-C_6H_{11};

R^2 = Pr, Ph;

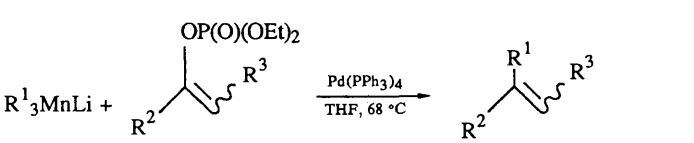


56% (n = 3),
49% (n = 4).

The formation of alkenyldemetallation products is observed in reactions of Ph_3MnLi and trialkylmanganates with enol phosphates and enol triflates.[29] the enol phosphates, unlike the enol triflates, react only in the presence of a palladium catalyst [10 mol% $Pd(PPh_3)_4$]. On changing from Me_3MnLi and Ph_3MnLi to Bu_3MnLi the yield of cross-coupling products was reduced due to the reduction side reactions.

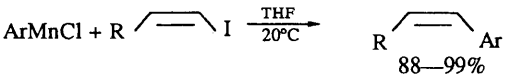


R^1 = Me, Bu, Ph;
R^2 = n-$C_{10}H_{21}$, R^3 = H; R^2, R^3 = n-C_5H_{11};

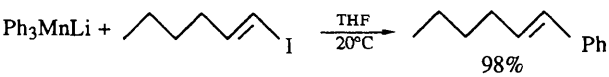


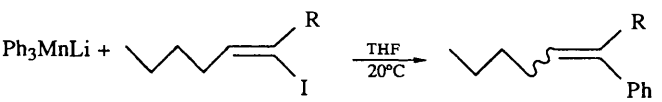
R^1 = Me, Bu, Ph; R^2 = n-C_5H_{11}, R^3 = Bu; R^2–R^3 = –$(CH_2)_{10}$– .

The cross-coupling of aryl manganese compounds with alkenyl iodides is a convenient and efficient method of synthesis of various substituted styrenes.[30] It was found that the reaction of reagents of the type of ArMnCl and Ar_3MnLi with substrates containing a 1,2-disubstituted double bond is accompanied by the complete retention of its geometry. In the case of the less reactive trisubstituted iodides a high yield of alkenyldemetallation products was achieved only when using the "ate" complexes Ar_3MnLi. The reactions lead to the formation of a mixture of stereoisomers.



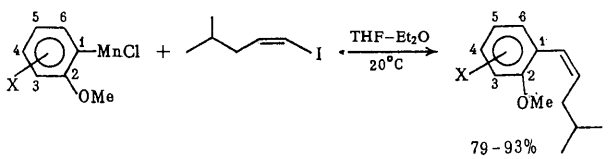
Ar = Ph, p-MeC_6H_4, p-$MeOC_6H_4$, p-ClC_6H_4,
p-BrC_6H_4, α-napthyl; R = Bu, iso-Bu.



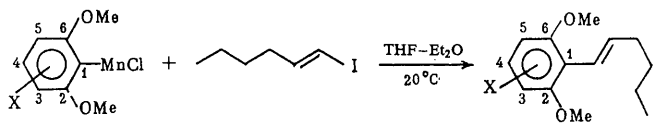


68% (R = Bu, E:Z = 38:62)
58% (R = $SiMe_3$, E:Z = 88:12)

Aryl *ortho*-*o*-substituted σ-complexes of manganese as well as p-$MeOC_6H_4MnCl$ undergo cross-coupling with alkenyl iodides.[31] Since the corresponding lithium reagents may readily be obtained by the *ortho* lithiation of ethers of di- and trihydroxybenzenes,[32] the combination of the stages of lithiation, transmetallation and cross-coupling is a convenient method for introducing an alkenyl fragment into aromatic polyhydroxy compounds.



X = 3-OMe, 5-OMe, 6-OMe



88% (X = 3-OMe),
60% (X = 4-OMe)

It must be noted that the cross-coupling of aryl manganese compounds with alkenyl iodides, unlike the analogues reactions with derivatives of Li,[33] Mg,[34] Zn,[35] Al [36]and several other metals, proceeds without a catalyst (Pd or Ni complex). The corresponding organocopper reagents react with alkenyl iodides without a catalyst but under far more forcing conditions.[37]

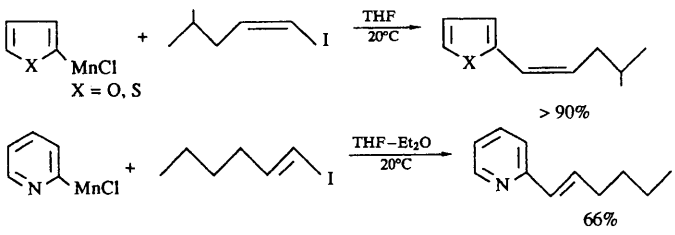
The mechanism of alkenyldemetallation seemingly includes an oxidative addition step (*a*) [the intermediate (I) containing tetravalent manganese is formed] and a reductive elimination step (*b*).[30,38]

$$Ph_3MnLi + RI \xrightarrow{(a)} \underset{(I)}{Ph_3MnR} + LiI,$$

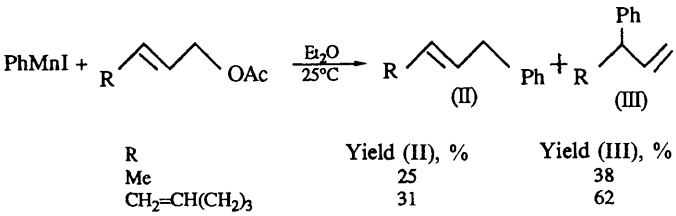
$$Ph_3MnR \xrightarrow{(b)} PhR + Ph_2Mn.$$

The fact that in several cases the yield of cross-coupling product continues to grow after complete disappearance of the initial alkenyl substrate supports this scheme. A possible explanation is that step (a) proceeds at a higher rate than step (b). Furthermore the formation of dehalogenation products RH [by hydrolysis of complex (I)], the yield of which falls depending on the accumulation of compounds RPh, becomes understandable.[30]

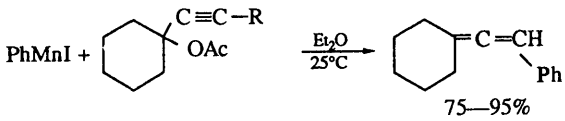
The organomanganese derivatives of furan, thiophene, pyridine and *N*-methylindole react with alkenyl iodides to give the corresponding α-alkenyl substituted O-, S- and N-containing heterocycles in high yield with complete retention of the configuration at the double bond.[39]



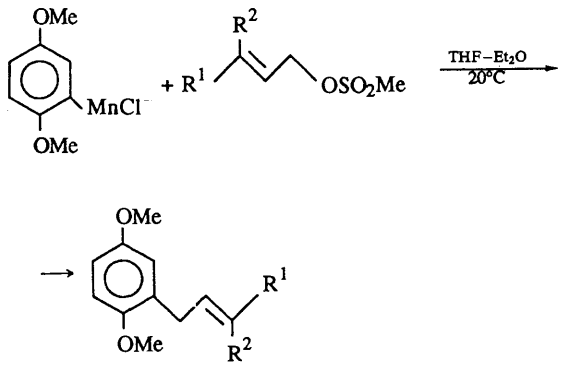
The reaction of PhMnI with allyl and propargyl acetates leads to substituted allylbenzenes and phenylallenes.[40] Unlike phenylmanganese iodide, the 2,5-dimethoxyphenyl derivative does not react with allyl acetates.[31] The synthesis of the practically important *O,O*-dimethylhydroquinones containing an allyl fragment may be effected by replacing the acetates by the corresponding mesylates.[31] The reactions take place with high regiospecificity (products of cross-coupling contain a dimethoxyphenyl group at the least substituted carbon atom of the allylic system) and are accompanied by the retention of the geometry of both *trans* and *cis* double bonds.



R	Yield (II), %	Yield (III), %
Me	25	38
CH_2=$CH(CH_2)_3$	31	62

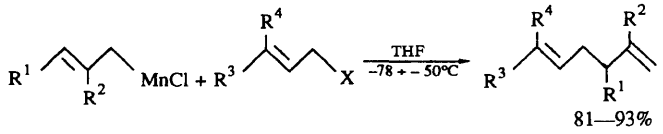


R = H, Ph, n-C_5H_{11}.



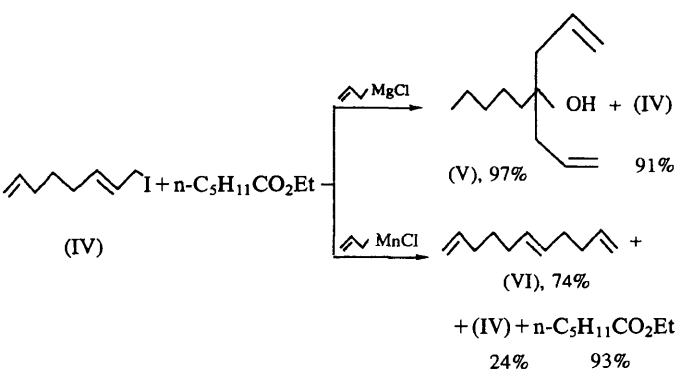
R^1 = CH_2=$CH(CH_2)_3$, R^2 = H; R^1 = H, R^2 = Bu;
R^1 = Me_2C=$CH(CH_2)_2$, R^2 = Me.

Allyl compounds of manganese of the type RMnCl may also be used in cross-coupling reactions. Their reaction with allyl bromides and iodides is effected under mild conditions and is an efficient method for synthesising 1,5-dienes.[19] The formation of allyldemetallation products occurs with the participation of the α-carbon atom of the substrate and the γ-carbon atom of the reagent with high stereoselectivity.

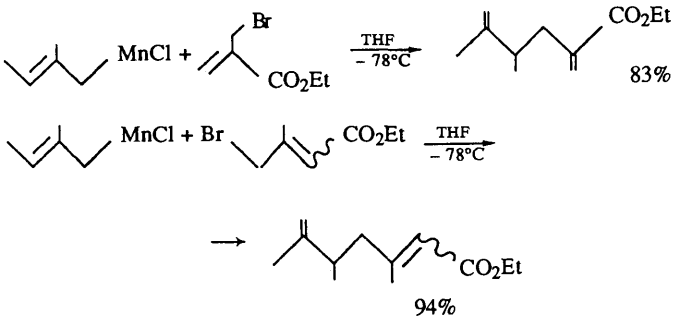


R^1, R^2 = H; R^1 = Me, R^2 = Me, Bu; R^3 = Ph, *E*-MeCH=CH, CH_2=$CH(CH_2)_3$, R^4 = H; R^3 = Me_2C=$CH(CH_2)_2$, R^4 = Me; X = Br, I.

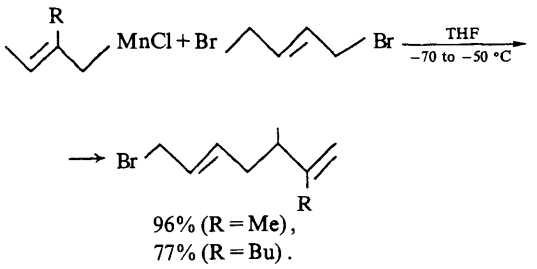
Allyl derivatives of magnesium, like the manganese derivatives, react with allyl halides giving 1,5-dienes,[41] however in contrast to the latter several functional groups are affected.[19] Treatment of an equimolar mixture of the iodide (IV) and ethyl caproate with 2 equiv. CH_2=$CHCH_2MgCl$ leads to the tertiary alcohol (V). The initial iodide is practically unreacted. Reaction of the same mixture with 2 equiv. CH_2=$CHCH_2MnCl$, on the other hand, leads to the formation of the hydrocarbon (VI) and the ester is completely unaffected. A similar result was observed in the reaction of CH_2=$CHCH_2M$ (M = MgCl, MnCl) with an equimolar mixture of the iodide (IV) and BuCN.



The inert nature of the organomanganese compounds in relation to ester groups enables cross-coupling reactions to be effected with esters of α,β-unsaturated carboxylic acids (2-methylacrylic, 3,3-dimethylacylic, tiglic, angelic) containing an allylic halogen atom which cannot be achieved using Grignard reagents.[42] In the case of alkyl 3-bromocrotonates the main course of the reaction is the formation of cyclopropanes (see section III.3).



The use of allyl complexes of manganese enables a selective monoallylation of allylic 1,4-dibromides to be effected while magnesium derivatives give chiefly diallylation products.[43]



96% (R = Me),
77% (R = Bu).

Comparatively little has been published on work devoted to the use of Mn(II) compounds as catalysts in cross-coupling reactions. It was shown that reaction of Grignard reagents RMgX (R = Ph, $PhCH_2$, $CH_2=CHCH_2$, $MeCH=CHCH_2$; X = Cl, Br) with enol triflates in the presence of 10 mol% Li_2MnCl_4 leads to the alkenyldemetallation product in 74–92% yield. On changing to MeMgI, EtMgBr and $CH_2=CHMgBr$ the yield was reduced to 6–35%.[29] Under approximately the same conditions iso-PrMgBr reacts with alkenyl and aryl halides to give mainly products of reduction.[44]

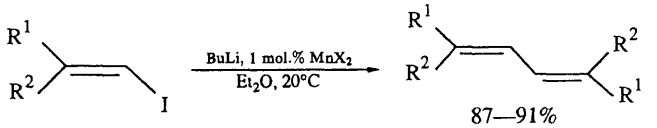
$$RX + \text{iso-PrMgBr} \xrightarrow[\text{THF, 25 to 45 °C}]{\text{1 mol.\% } MnX_2} RH \quad 65-93\%$$

R = (*E*) and (*Z*)-Bu(Et)C=CH, $Bu_2C=CH$, (*Z*)-(n-C_7H_{15})CH=CH

$CH_2=C$(n-C_8H_{17}), 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$, 2,4,6-$Me_3C_6H_2$,

α-napthyl; X = Br, I.

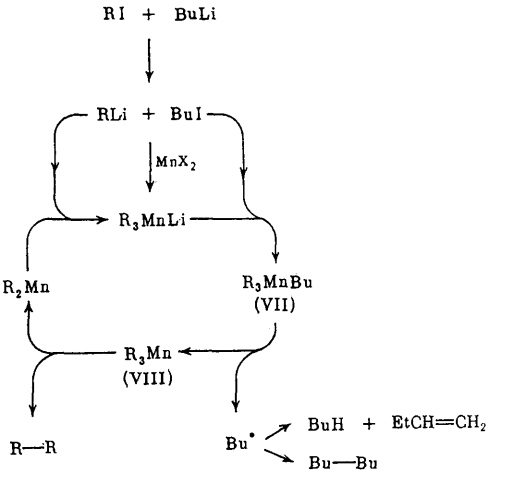
Manganese halides (1 mol% $MnCl_2$ or $MnBr_2$) efficiently catalyse the reductive 'dimerisation' of alkenyl iodides to symmetrical 1,3-dienes on treatment of the iodides with 1 equiv. n-butyllithium.[45] Both double bonds in the reaction product have the same geometry as in the substrate.



87—91%

R^1 = H, R^2 = n-C_7H_{15}; R^1 = Me, Bu, R^2 = Et; R^1 = Et, R^2 = Bu.

The mechanism proposed for the 'dimerisation' is the formation *in situ* (by metal–halogen exchange) of a lithium alkenyl derivative and butyl iodide. The successive reaction of the catalyst with the lithium reagent and BuI leads to the mixed tetraorgano-derivative (VII) containing quadrivalent manganese which is converted into the trialkenyl complex (VIII) by expulsion of a butyl radical. Decomposition of the intermediate (VIII) gives a conjugated diene and a dialkenylmanganese which continues the catalytic cycle.



2. Acyldemetallation

The acyldemetallation of organic Mn(II) derivatives is one of the most efficient and well characterised routes for using these reagents in synthesis. In comparison with organic compounds of cadmium, zinc and aluminium, which are traditionally used to obtain unsymmetrical ketones from acid chlorides or anhydrides of carboxylic acids,[46–49] the manganese reagents generally give a higher yield of ketone particularly in the case of substrates containing other reactive functional groups in place of the acid chloride (or anhydride).[14] The preferential use of the latter must be attributed to the accessibility, cheapness and lack of toxicity of the initial manganese halides, the ease of preparing reagents of various types from them, and also the possibility of carrying out the reactions at temperatures close to ambient in a relatively short time. Frequently the use of organocopper complexes gives better results,[21,50,51] however the smooth acyldemetallation of many of them occurs only at low temperatures (−78 °C) and with a large excess of reagent (unlike the manganese reagents).

The reaction of alkyl-, aryl-, alkenyl- and alkynylmanganese halides, obtained by treating MnI_2 (in ether) or Li_2MnCl_4 (in THF) with organolithium or organomagnesium compounds, with carboxylic acid chlorides leads to the formation of alkyl, aryl, alkenyl and alkynyl ketones respectively in high yield.[11,12,14,52]

$$R^1MnX + R^2COCl \xrightarrow[-10 \text{ to } +20\ ^\circ C]{Et_2O \text{ or THF}} R^1COR^2$$

R^1 = Me, Bu, n-C_7H_{15}, Ph, (*Z*)-BuCH=CH, (*Z*)-Et(Me)C=CH,

$Me_2C=CH$, $BuC\equiv C$;

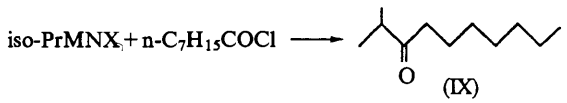
R^2 = Et, Bu, n-C_7H_{15}, iso-Pr, t-Bu, Ph, $Me_2C=CH$; X = Cl, I.

Reactions involving alkenyl derivatives of manganese are accompanied by complete retention of the double bond geometry. On changing from complexes RMnI (R = Alk) to the di-organo

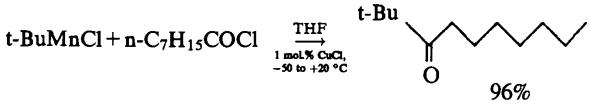
derivatives R_2Mn and the trialkylmanganates R_3MnLi the yield of ketone is reduced by 5–10%. In the case of R_2Mn two and in the case of R_3MnLi three alkyl fragments are transferred. The introduction of α,β-unsaturated acid chlorides into the reaction is only possible when two β-alkyl substituents are present in the latter. β-Monosubstituted α,β-unsaturated acid chlorides polymerise in the presence of the manganese reagents.

The initial use of Et_2O almost exclusively as solvent (in combination with MnI_2) and not THF [11,12,14] was associated with the possible opening of the tetrahydrofuran ring by an acid chloride in the presence of a Lewis acid, viz. the manganese dihalide, formed in addition to the ketone.[53] It was found subsequently that this process does not take place under the usual acyldemetallation conditions.[52]

Replacement of ether by THF enables the cheaper and more available $MnCl_2$ or its soluble complex Li_2MnCl_4 (see section II) to be used instead of MnI_2 to prepare organomanganese compounds. There are other advantages. The higher stability of the thermally unstable secondary and tertiary alkyl derivatives of manganese in an ether–THF mixture, in comparison with pure Et_2O, leads to an increase in the yield of acyldemetallation products.[14] The yield becomes practically quantitative on carrying out the reaction in THF in the presence of 1 mol% CuCl.[52]

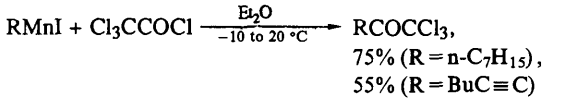


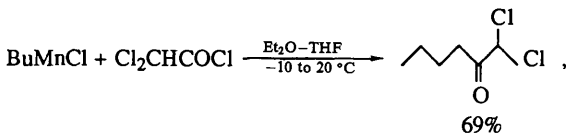
X	Solvent	T, °C	Yield of ketone (IX), %
I	Et_2O	−35	65
I	Et_2O–THF	−35	78
Cl	THF (1 mol.% CuCl)	−30 to +20	93

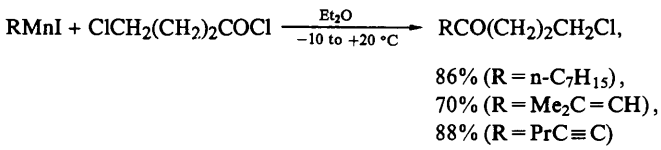


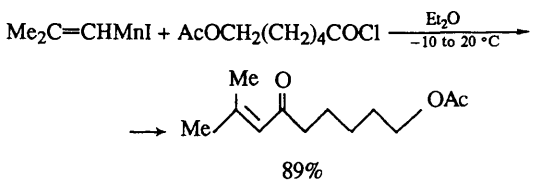
It turned out that on using THF (but no Et_2O) the addition of catalytic amounts of CuCl markedly increased the yield of ketone in reactions involving MeMnCl and also σ-complexes of manganese RMnCl (R is aryl, alkenyl).[52]

Smooth acyldemetallation is also observed in the case of more complex substrates containing other functional groups in addition to the acid chloride.[12,14,52,54,55] The acid chlorides of trichloroacetic, α,α-dichloro- and α-chlorocarboxylic acids react with organomanganese compounds to give the corresponding trichloromethyl-, α,α-dichloroalkyl- and α-chloroalkyl ketones in high yield. β-Chloro-containing acyl chlorides are subject to elimination of HCl in the presence of manganese complexes. On the other hand γ-chloro derivatives (and also substrates with a halogen atom removed even further from the COCl fragment) react in the usual way. A high yield of acyldemetallation product was also achieved on using acid chlorides of α-alkoxy- and α-alkylthiocarboxylic acids.

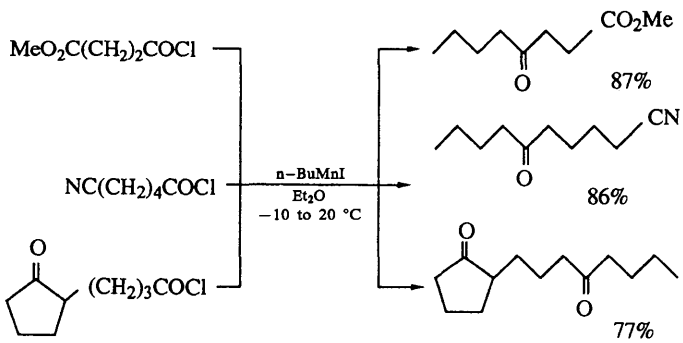




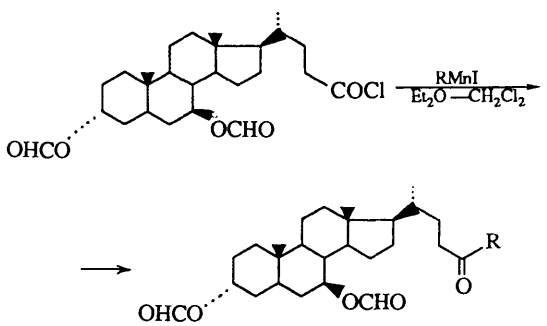




Reactions involving substrates containing ester, nitrile and keto groups are characterised by complete retention of these groupings and lead to keto-esters, ketonitriles and diketones.



The possibility of retaining two formate ester groups is shown using a steroid acid chloride as an example.[56]



88% (R = iso-Bu),
78.5% (R = Me_2C=CH),
73.5% (R = PrC≡C)

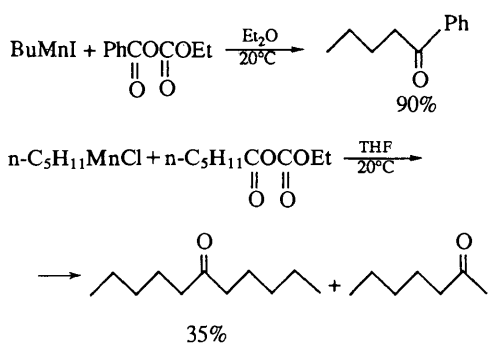
The less reactive carboxylic acid anhydrides[14,15,54,57] have been used in this reaction in addition to acid chlorides. Symmetrical anhydrides react with the complexes RMnI (in Et_2O) or RMnCl (in THF) to give the corresponding ketones in high yield. The yield of acyldemetallation product was reduced somewhat on replacing RMnX derivatives (R = Alk; X = Cl, I) by trialkyl manganates R_3MnM (M = Li, MgBr). It is reported that the latter react with transfer of all three organic fragments.

$$R^1MnX + (R^2CO)_2O \xrightarrow[20°C]{Et_2O \text{ or } THF} R^1COR^2 \quad 81—96\%$$

$R^1 = n\text{-}C_7H_{15}$, Ph;
R_2 = Et, iso-Pr, iso-Bu, t-Bu;
X = Cl, I.

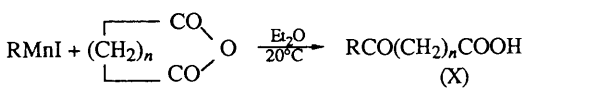
The reaction of $n\text{-}C_7H_{15}MnI$ with the mixed anhydride of a carboxylic acid and pivalic acid proceeds exclusively by replacing the t-butyl carboxylate group and leads to heptyl pentyl ketone (72% yield).[15]

Acyl ethyl carbonates, which may readily be obtained by treating carboxylic acids with phosgene in the presence of Et_3N, are efficient substrates for carrying out the acyldemetallation of organomanganese compounds.[14,15] These derivatives react with RMnI complexes in ether giving the corresponding ketones in high yield. On using THF or a THF—Et_2O mixture as solvent the yield of ketone was reduced due to a side reaction forming an ethyl ester.



The use of other mixed anhydrides of the form $R^1C(O)OC(O)ZR^2$ (ZR^2 = OMe, OPh, SEt) and $RC(O)OP(O)(OMe)_2$ in place of acyl ethyl carbonates gives poorer results.[15]

The reactions of alkyl σ-complexes of manganese with cyclic anhydrides of dicarboxylic acids is a convenient method of synthesising aliphatic keto-acids.[54]



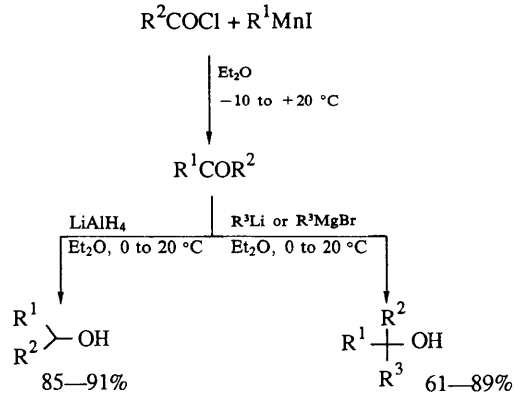
R	n	Yield (X), %
$n\text{-}C_7H_{15}$	2	77
n-Bu	3	55

The reaction of alkyl-, aryl- and alkenylmanganese iodides with ethyl chloroformate leads to the ethyl esters of alkyl-, aryl- and alkenylcarboxylic acids.[13]

$$RMnI + ClCOOEt \xrightarrow[20\ °C]{Et_2O} RCOOEt$$

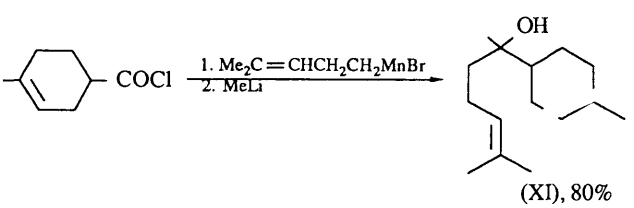
83% (R = $n\text{-}C_7H_{15}$),
77% (R = Ph),
70% ($R = Me_2C{=}CH$)

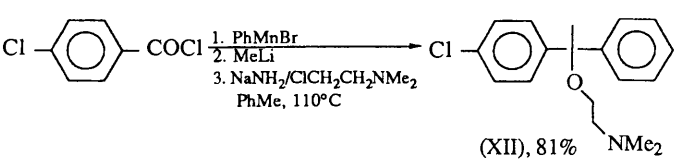
A more detailed study of the acyldemetallation of organomanganese compounds revealed several interesting features.[58] It turned out that the difference in reaction rates of RMnI derivatives with the initial acid chloride and with the ketone isolated from the reaction mixture was too small to guarantee conduct of the acylation without subsequent condenstion with the formation of a tertiary alcohol (which is observed in practically every case). In the reaction of BuMnI with BuCOCl (ether, 20 °C) the yield of BuCOBu is 80 and 92% after 5 and 10 min but in the reaction of BuMnI with BuCOBu the yield of Bu_3COH is 78 and 81% after the same times. It was shown that the acyldemetallation product formed *in situ* is a complex of the ketone with the metal halides present in solution (MnX_2 + LiX or MnX_2 + MgX_2, whre X = Cl, Br, I) which are practically unreactive towards RMnI unlike the free ketone. Treatment of such a complex with the more reactive organic compounds of lithium and magnesium and with $LiAlH_4$ and $NaBH_4$ leads to the formation of tertiary and secondary alcohols respectively in high yield. Various tertiary alcohols may therefore be synthesised directly from acid chorides by the sequential action on them of first organomanganese compounds and then organolithium or organomagnesium reagents.[58]



R^1 = Et, Bu, iso-Bu, $n\text{-}C_7H_{15}$;
R^2 = Et, iso-Bu, t-Bu, $n\text{-}C_5H_{11}$, Ph, $Me_2C{=}CH$;
R^3 = Me, Et, Bu, sec-Bu, Ph, $Me_2C{=}CH$, $MeCH{=}CH$, $CH_2{=}CHCH_2$.

The procedure developed has been used successfully to obtain biologically active compounds, viz. the diastereomeric (±-α-bisabolols (XI) and (±)-chlorphenoxamine (XII).[59]





3. 1,2- And 1,4-addition

The reaction of organomanganese compounds with aldehydes and ketones occurs similarly to the corresponding reaction of organolithium and organomagnesium compounds and leads to secondary or tertiary alcohols in high yield.[14,60,61] However, the σ-complexes of manganese react significantly more selectively than the lithium or magnesium derivatives. They are inert towards esters, nitriles and apparently several other functional groups, the preservation of which during a condensation at an aldehyde or ketone group has been shown in only a few examples.[14,62]

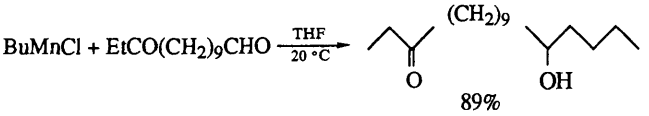
Reaction of alkyl-, alkenyl-, aryl- and alkynylmanganese halides with an equimolar mixture of an aldehyde and a ketone occurs only with the aldehyde. The initial ketone does not react.[60,61]

$$R^1MnX + R^2CHO + R^3COR^4 \longrightarrow R^1R^2CHOH + R^3COR^4$$
82—99%

R^1 = Me, Bu, n-C_7H_{15}, Ph, $Me_2C{=}CH$, $BuC{\equiv}C$;
R^2 = Bu, n-C_6H_{13}, t-Bu, Ph, $Me_2C{=}CH(CH_2)_2C(Me){=}CH$;
$R^3 = R^4$ = Pr; R^3 = Me, R^4 = n-C_5H_{11}; R^3 = Pr, R^4 = Ph;
$R^3 - R^4 = -(CH_2)_5-$; $R^3 = Me_2C{=}CH$, R^4 = n-C_7H_{15}.

X	Solvent	T, °C	Additive
Cl	THF	20	LiCl or MgClBr
Br	Et_2O	20	LiBr
I	Et_2O	−50	MgBrI

Under the same conditions aliphatic ketoaledhydes give secondary ketoalcohols.

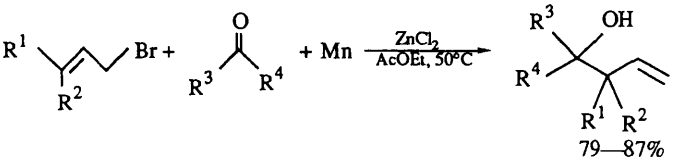


The temperature for carrying out a chemoselective condensation is determined by the reactivity of the manganese derivative which in its turn depends on the nature of the solvent and the metal salts in solution. It was found that complexes RMnX (X = Br, I) in ether in the presence of MgX_2 are more reactive than in the presence of LiX.[61] The reason for this is apparently that MgX_2, being a stronger Lewis acid, is coordinated at the oxygen atom of the carbonyl group, increasing its electrophilicity.

It is known that organic derivatives of trialkoxytitanium are used most frequently to achieve a high chemoselectivity in reactions of this type.[63—65] Organic compounds of Mn(II) at the same selectivity (>99%) give secondary alcohols in higher yield (5—10% more on average). In addition the reaction of σ-complexes containing alkenyl and secondary alkyl fragments becomes possible (the corresponding titanium reagents are unstable even at −78 °C.

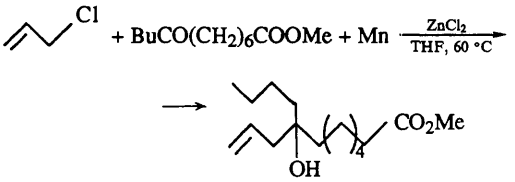
Allylmanganese halides, unlike alkyl-, alkenyl-, aryl- and alkynylmanganese halides, may be obtained by direct synthesis from metallic manganese and allyl halides.[66—68] The synthesis of allylmanganese halides in the presence of a carbonyl substrate, such as an aldehyde or ketone, is the most expedient and preparatively convenient.[67,68] This modification enables both the decomposition of the unstable allyl manganese complexes and the formation of 1,5-dienes by the Wurtz reaction, which reduce the yield of condensation products, to be reduced to a minimum.

Heating the carbonyl compound, allyl halide and metallic manganese in ethyl acetate or THF in the presence of 10 mol% $ZnCl_2$ leads to the preparation of the corresponding homoallyl alcohols in high yield.[68]

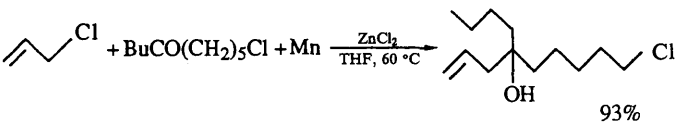


79—87%

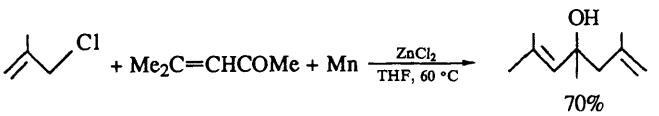
$R^1 = R^2$ = H, R_1 = Me, R^2 = H, Me;
R^3 = H, R^4 = n-C_6H_{13}, t-Bu, Ph;
R^3 = Me, R^4 = n-C_7H_{15}, $R^3 = R^4$ = Bu.



66%



93%

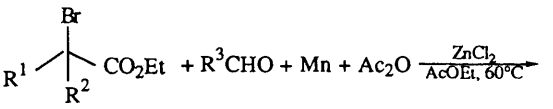


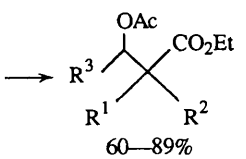
70%

The reaction is characterised by complete retention of ester and dimethylacetal groups, and of alkyl and aryl halogen atoms in the initial aldehyde or ketone. On using α,β-unsaturated ketones only 1,2-addition is observed. Crotyl and isoprenyl bromides react giving condensation products formed from the most substituted carbon atom of the allyl fragment.

Carrying out the reaction in THF in the absence of $ZnCl_2$ requires the use of a large excess (6—7 equiv.) of both manganese and allyl halide.[67] Furthermore, it is necessary to add 1 equiv. I_2 to the reaction mixture to achieve a high yield of the homoallyl alcohol.

In the presence of metallic manganese and 10 mol% $ZnCl_2$ it is possible to effect the condensation of α-bromocarboxylic acid esters with aldehydes and ketones by a type of Reformatsky reaction.[68] The use of acetic anhydride to acylate the alkoxide formed *in situ* inhibits the retroaldol reaction.





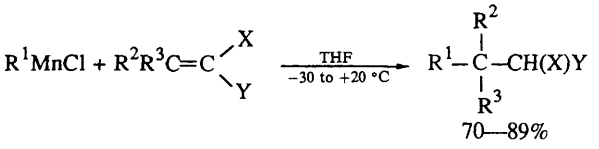
60—89%

R^1 = H, R^2 = H, n-C_6H_{13}; $R^1 = R^2$ = Me;
R^3 = n-C_6H_{13}, t-Bu, Ph.

The conjugate addition of σ-complexes of Mn(II) to an α,β-unsaturated carbonyl substrate was described for the first time by Gilman and collaborators[4] for the reaction of PhMnI and PhCH=CHCOPh. A detailed study of the reaction of alkyl-, aryl- and alkenylmanganese compounds with 2-cyclohexenone showed their unsuitability for the smooth synthesis of 3-substituted cyclohexanones. The latter were obtained in relatively low yield as a result of the competing processes of 1,2-addition and reductive dimerisation with the formation of 3,3′-bis(cyclohexanone).[69] The product ratio depended markedly on the type of complex (RMnX, R_2Mn, R_3MnLi or R_3MnMgX) and the nature of the solvent (Et_2O or THF).

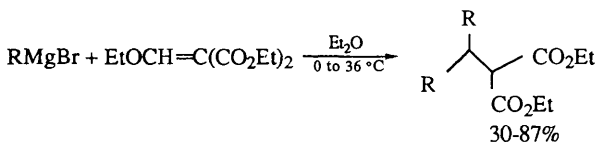
The reaction of cyclic α,β-unsaturated ketones with RMgX (R = Alk, Ar; X = Br, I) catalysed by manganese salts also proceeds nonselectively.[69–71]

In contrast to the α,β-enones, substrates containing a double bond activated by two electron-accepting groups (alkylidenemalonic, -cyanoacetic and -acetoacetic esters) react with RMnCl derivatives (R is alkyl, alkenyl, aryl, alkynyl) obtained from $MnCl_2$ and RMgCl in THF, forming conjugate addition products in high yield.[72] The yield is reduced when using the corresponding lithium reagents instead of RMgCl to obtain the organomanganese compounds.

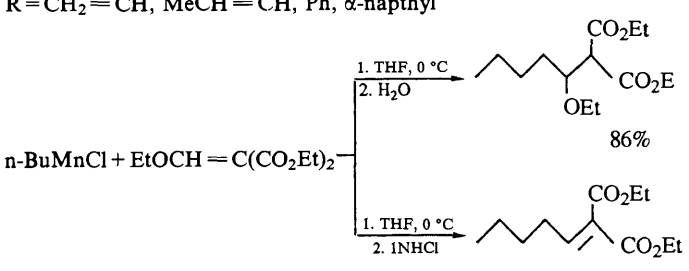


R^1 = Me, Bu, iso-Pr, $Me_2C=CH$, Ph, $BuC\equiv C$;
R^2 = H, R^3 = Me, Pr, Ph; R^2, R^3 = Me;
X, Y = CO_2Et, CN, COMe.

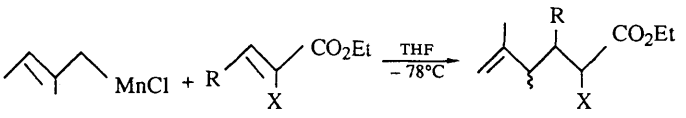
The initial Grinard reagents also give β-substituted alkylmalonic or alkylcyanoacetic esters on reaction with alkylidenemalonates or alkylidenecyanoacetates[73,74] though often in significantly lower yield (particularly with β,β-disubstituted substrates).[72] An even more clear difference in behaviour of the manganese and magnesium derivatives is displayed in reactions involving diethyl (ethoxymethylene)-malonate.[72,73,75]



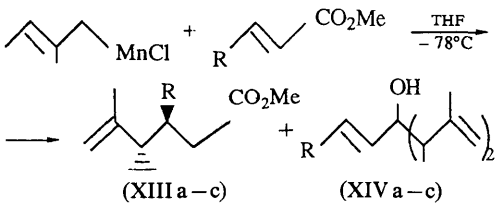
R = $CH_2=CH$, MeCH=CH, Ph, α-napthyl



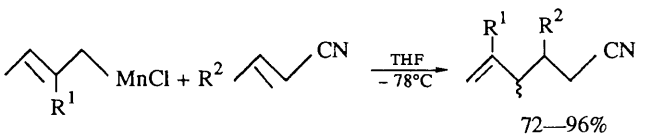
The introduction of γ-substituted allylic organomanganese compounds into the reaction leads to the formation of 1,4-addition products involving exclusively the γ-carbon atom of the reagent.[76] The esters of alkylidenemalonic, alkylidenecyanoacetic, maleic and fumaric acids containing a doubly activated double bond give 1,4-addition products. In contrast methyl crotonate, methyl 2-hexenoate and methyl cinnamate give the 1,2-addition products, the tertiary alcohols (XIVa–c), in addition to the 1,4-addition products (XIIIa–c). On changing from the ester to the nitrile the analogous 1,2-addition process does not take place.



R = n-C_6H_{13}, *E*-MeCH=CH; X = CO_2Et, CN.



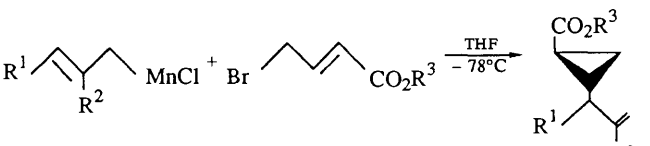
Compound	R	Yield (XIII), %	Yield (XIV), %
(a)	Me	69	18
(b)	Pr	45	39
(c)	Ph	27	36



R^1 = H, Me, Bu; R^2 = Me, Pr, Ph.

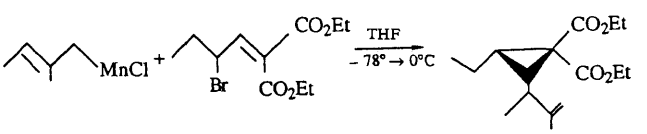
The reaction of allylic organomanganese compounds with esters of α,β-unsaturated monocarboxylic acids is characterised by a high stereoselectivity. Each of the products (XIIIa) and (XIIIb) is a single diastereomer with an *anti* disposition of alkyl groups at the β- and γ-carbon atoms.[77] The configuration of compounds (XIIIa) and (XIIIb) was confirmed by converting them into the 3,4-*cis* isomers of 3-alkyl-5-iodo-4,5-dimethylpentanolide by saponification and iodolactone formation.

The reaction of allylic complexes of manganese with alkyl 4-bromocrotonates is accompanied by cyclisation of the manganese enolates formed initially and leads to esters of allyl substituted cyclopropanecarboxylic acids.[42,78]



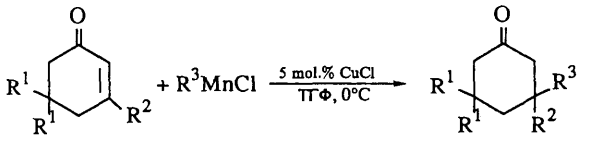
$R^1=R^2$=H; R^1 = Me, R^2 = H, Me, Bu; R^3 = Me, iso-Pr.

γ-Bromo-containing alkylidenemalonates and alkylidenecyano-acetates react similarly.[42]

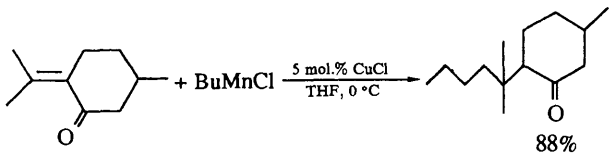


It should be noted that the corresponding α-, β- and γ-substituted crotonic acids give products of cross-coupling or condensation at the ester group (see section III.1).

The problem of the selective 1,4-addition of organomanganese reagents to α,β-unsaturated ketones may be resolved by conducting the reaction in the presence of catalytic quantities of copper salts.[79] The reaction of BuMnCl with 2-cyclohexenone (THF, 0 °C) leads to the preparation of 3-butylcyclohexanone in no more than 10% yield,[69] but in the presence of 0.1–5 mol% CuCl its yield becomes practically quantitative. The reactions of alkyl-, aryl- and alkenylmanganese chlorides with various conjugated enones (including those containing a tri- and even a tetrasubstituted double bond) catalysed by CuCl are efficient methods of synthesis of the corresponding β-branched alkyl ketones.

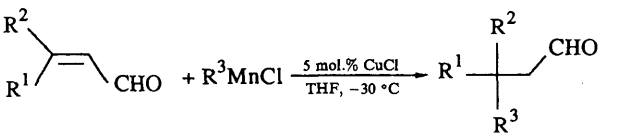


R^1 = H, R^2 = H, Me; R^1 = R^2 = Me;
R^3 = Me, n-Bu, iso-Pr, t-Bu, Ph, $Me_2C{=}CH$, $PrCH{=}CH$.



It must be recorded that the yield of 1,4-addition products when using RMnX is significantly greater in many cases than when using organocopper reagents of the type RCu, R_2CuLi and $R_2Cu(CN)Li_2$ and Grignard reagents under conditions of copper salt catalysis.[80]

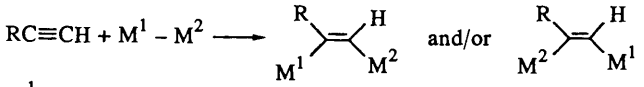
In the presence of catalytic quantities of CuCl the conjugated addition of manganese σ-complexes to β-mono- and β,β-disubstituted α,β-unsaturated aldehydes (the α,β-disubstituted substrates react giving a mixture of products of 1,4-addition and condensation at the aldehyde group).[81] The reaction course indicated is effected for organocopper compounds only on promotion with Me_3SiCl and leads to the formation of enol silyl ethers.[82,83]



R^1 = H: R^2 = Me, Bu, n-C_7H_{15}, Ph;
R^1 = Me: R^2 = Me, Bu, n-C_7H_{15}, Ph, $MeCH{=}CH$;
R^1 = $Me_2C{=}CH(CH_2)_2$, R^2 = Me;
R^3 = Me, Pr, n-C_7H_{15}, $Me_2C{=}CH(CH_2)_2$, Ph.

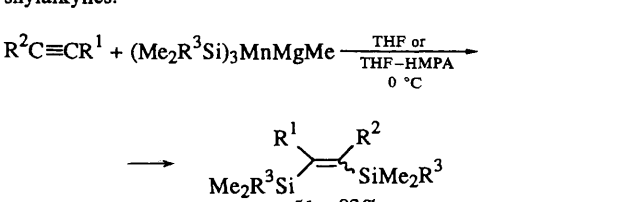
IV. Reactions of manganese derivatives containing Mn–Si and Mn–Sn bonds

The regio- and stereoselective addition of reagents with Si–Mg, Si–Al, Si–Zn,[84–86] Si–Cu,[87] Sn–Mg, Sn–Al, Sn–Zn,[88] or Sn–Cu [89,90] bonds to acetylene with the formation of 1,2-dimetallated alkenes has a high synthetic potential due to the possibility of further selective conversions at each of the two metal–carbon bonds.



M^1 = Me_2PhSi, Me_3Sn, Bu_3Sn, Ph_3Sn;
M^2 = MeMg, Et_2Al, $^1/_2Zn$, Cu, $^1/_2Cu$.

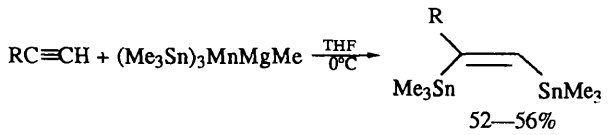
It was found that, in contrast to the "ate" complexes of manganese mentioned above, both $(Me_3Si)_3MnMgMe$ and $(Me_2PhSi)_3MnMgMe$, prepared by sequential treatment of Me_3SiLi or $Me_2PhSiLi$ with 1 equiv. MeMgI and 0.33 equiv. $MnCl_2$, give 1,2-disilylation products on reaction with terminal and 1-trimethylsilylalkynes.[91,92]



[(*E*)/(*Z*) from 33 : 67 to 65 : 35]

R^1 = H: R^2 = Me_3Si, n-C_6H_{13}, Ph, $PhCH_2O(CH_2)_2$, $(THP)O(CH_2)_2$;
R^1 = Me_3Si: R^2 = n-C_6H_{13}, $PhCH_2O(CH_2)_2$.
$(THP)O(CH_2)_2$(where THP is tetrahydropyranyl); R^3 = Me, Ph.

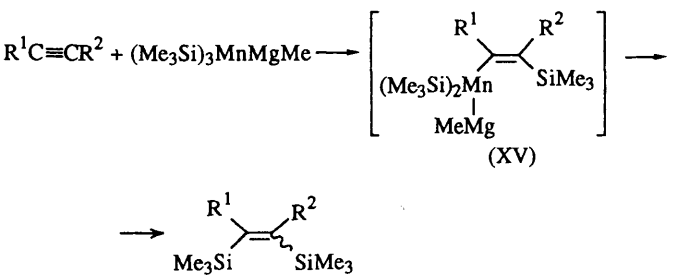
The stannylmanganese complex $(Me_3Sn)_3MnMgMe$ reacts analogously.



R = n-$C_{10}H_{21}$, $PhCH_2O(CH_2)_2$, $(THP)O(CH_2)_2$.

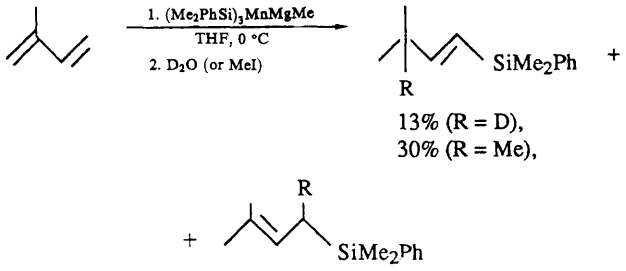
Replacement of $(Me_3Si)_3MnMgMe$ by the lithium derivative $(Me_3Si)_3MnLi$ leads, after hydrolysis, to a mixture of mono- and disilyated alkenes.

The reaction mechanism obviously includes a step for the *syn* addition of the Mn–Si fragment to the triple bond and the reductive elimination of zero-valent manganese from the alkenylmanganate intermediate (XV).



The proposed scheme is confirmed by the formation on reaction of $PhCH_2O(CH_2)_2C{\equiv}CMe$ and $(Me_3Si)_3MnMgMe$, after treatment with H_2O, D_2O and MeI, of the (*E*)-isomeric products of hydrolysis, deuterolysis and methylation of the complex (XV) (R^1 = $PhCH_2O(CH_2)_2$, R^2 = Me) at the C–Mn bond.[92]

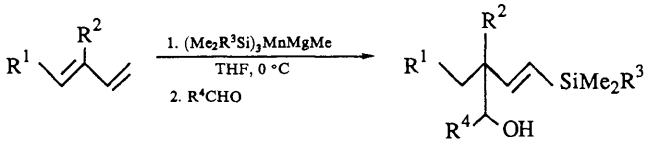
The reaction of $(Me_2PhSi)_3MnMgMe$ with 1,3-dienes (butadiene, isoprene, *trans*-piperylene) and subsequent deuterolysis gives in each case a mixture of γ-deuteroalkyenyl- and α-deuteroallylsilanes.[92,93] An analogous picture is also observed on replacing D_2O by MeI.



13% (R = D),
30% (R = Me),

65% (R = D),
60% (R = Me)

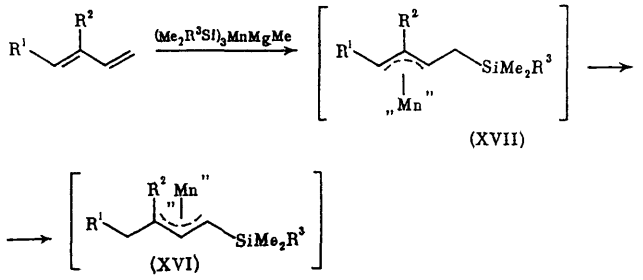
The use of aldehydes and ketones as electrophiles leads exclusively to the preparation of γ-substituted alkenylsilanes in high yield.



$R^1 = H$, $R^2 = H$, Me; $R^1 = Me$, $R^2 = H$; $R^3 = Me$, Ph;
$R^4 = Bu$, n-C_8H_{17}, Ph, *E*-MeCH=CH, *E*-PhCH=CH, Ph.

We note that, in contrast to the complexes $(Me_3Si)_3MnMgMe$ and $(Me_2PhSi)_3MnMgMe$, the lithium manganate reagents $(Me_3Si)_3MnLi$ and $(Me_2PhSi)_3MnLi$ do not react with conjugated dienes under the same conditions.

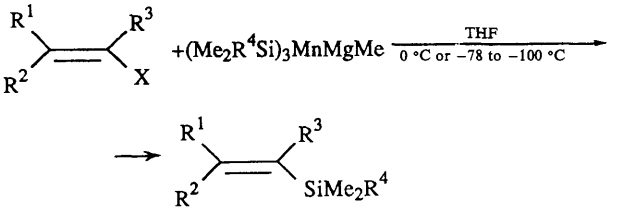
The synthesis of the indicated products of deuterolysis, alkylation and condensation indicates the participation of the allyl manganese intermediate (XVI) in the reaction. It is most probably formed by silylmanganation of the monosubstituted double bond in the diene and further isomeriation of complex (XVII) to complex (XVI) as a result of reversible β-elimination–addition of an Mn–H fragment.[92,93]



„Mn" = $(Me_2R^3Si)_2MnMgMe$

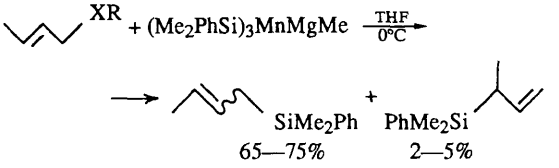
It is known that the diethylaluminosilane $Me_2PhSiAlEt_2$ is an efficient reagent for obtaining alkenyl- and allylsilanes from enol and allyl phosphates.[94,95] The silylmanganates $(Me_3Si)_3MnMgMe$ and $(Me_2PhSi)_3MnMgMe$ may also be used successfully for this purpose.

The reaction of these derivatives with alkenyl halides (bromides and iodides) is effected under mild conditions and leads to the corresponding alkenylsilanes in high yield.[92,96] In the cross-coupling process complete retention of both *trans* and *cis* geometry of the double bond is observed (to retain the *cis* geometry it is necessary to reduce the temperature from 0 to −78 or −100 °C). Alkenyl sulphides, enol phosphates and enol triflates also react in addition to the alkenyl halides.



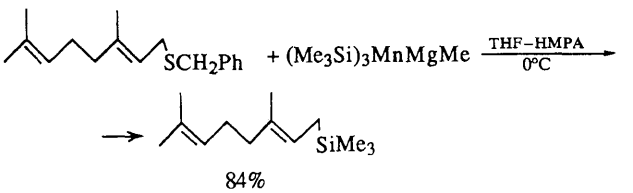
$R^1 = Me$, n-C_6H_{13}, n-$C_{10}H_{21}$, Ph, $R^2 = R^3 = H$;
$R^1 = R^3 = H$, $R^2 =$ n-$C_{10}H_{21}$, Ph;
$R^1 = Me$, n-$C_{10}H_{21}$, $R^2 = Me$, $R^3 = H$;
$R^1 = R^2 = H$, $R^3 = Pr$, n-C_6H_{13}, n-$C_{10}H_{21}$;
$R^1 - R^3 = -(CH_2)_4-$, $-(CH_2)_6-$, $R^2 = H$;
$R^4 = Me$, Ph;
X = Br, I, SMe, SPh, $OP(O)(OEt)_2$, $OP(O)(OPh)_2$, OSO_2CF_3.

Allyl sulphides and allylethers react forming allylsilanes.[92,96] Monosubstituted (α or γ) substrates give a mixture of regioisomeric silylation products with a predominance of the compound in which the Si atom is bound to the least substituted carbon atom of the allyl fragment. It should be noted that the regioselectivity of cross-coupling is significantly greater when using silylmanganate reagents than when using the complex $Me_2PhSiAlEt_2$.[92]



(*E*/*Z* from 5 : 1 to 20 : 1)

XR = SPh, OCH_2Ph, $OSiMe_2Bu$-t.



V. Conclusion

The organic compounds of Mn(II) are therefore efficient reagents for the selective formation of a carbon–carbon bond in acyl-, alkenyl- and allyldemetallation, and in 1,4- and 1,2-addition to aldehydes, ketones and esters. The availability and cheapness of the initial manganese halides, the possibility of obtaining *in situ* complexes of various types and their inertness towards several functional groups favourably distinguish the manganese derivatives from the corresponding derivatives of many other metals.

In addition, as follows from the data presented above, only a few examples are known of the use of manganese reagents in the synthesis of biologically active natural compounds. The stereochemistry of the condensation reactions involving γ-substituted σ-allylic complexes of Mn(II) (simple diastereoselectivity[97]) and α-chiral aldehydes and ketones (1,2-asymmetric induction[98]) are practically uninvestigated. The synthesis of organomanganese compounds from organic reagents containing aluminium or zinc has not as yet been described. The latter may contain functional groups.[99] The chemistry of enolates of Mn(II) is almost completely unstudied.

It may be expected that the development of these and other routes will enable organic derivatives of Mn(II) to be applied even more successfully to the solution of the problems of fine organic synthesis.

References

1. H Gilman, J C Bailie *J. Org. Chem.*, 1937, **2** 84
2. K N Anisimov, A A Ioganson, N E Kolobova *Usp. Khim.*, 1968, **37**(3) 380 [English translation in *Russ. Chem. Rev.*, 1968(3)]
3. P M Treichel *Comprehensive Organometallic Chemistry*, Pergamon Press, New York, 1982, Vol. 4, p. 1
4. H Gilman, R H Kirby *J. Am. Chem. Soc.*, 1941, **63** 2046
5. C Beerman, K Clauss *Angew. Chem.*, 1959, **71** 627
6. R Riemschneider, H G Kassahn, W Schneider *Z. Naturforsch., B*, 1960, **15** 547
7. K Clauss, H Bestian *Liebigs Ann. Chem.*, 1962, **654** 8
8. R Nast, H Griesshammer *Chem. Ber.*, 1957, **90** 1315
9. R P A Sneeden, H H Zeiss *J. Organomet. Chem.*, 1970, **22** 713
10. M Tamura, J Kochi *J. Organomet. Chem.*, 1971, **29** 111
11. G Cahiez, A Masuda, D Bernard, J F Normant *Tetrahedron Lett.*, 1976, 3155
12. G Cahiez, D Bernard J F Normant *Synthesis*, 1977, 130
13. G Cahiez, J F Normant *Bull. Soc. Chim. Fr. II*, 1977, 570
14. G Cahiez, J F Normant *Modern Synthetic Methods* (Edited by R Scheffold), Wiley, New York, 1983, Vol. 3, p. 173
15. G Friour, A Alexakis, G Cahiez, J F Normant *Tetrahedron*, 1984, **40** 683
16. G Cahiez, B Laboue *Tetrahedron Lett.*, 1989, **30** 3545
17. H Gilman, P G Jones, L A Woods *J. Am. Chem. Soc.*, 1954, **76** 3615
18. M Tamura, J K Kochi *Bull. Chem. Soc. Jpn.*, 1971, **44** 3063
19. A N Kasatkin, O Yu Tsypyshev, T Yu Romanova, G A Tolstikov *Metalloorg. Khim.*, 1989, **2**(4) 830 [English translation in *Organomet. Chem. USSR*, 1989(4)]
20. R A Andersen, E Carmona-Guzman, J F Gibson, G Wilkinson *J. Chem. Soc., Dalton Trans.*, 1976, 2204
21. G H Posner *Organic Reactions* (Edited by W G Dauben), Wiley, New York, 1975, Vol. 22, p. 253
22. G H Posner *An Introduction to Synthesis using Organocopper Reagents*, Wiley Intersci., New York, 1980, 140 pp
23. E J Corey, G H Posner *Tetrahedron Lett.*, 1970, 315
24. T Kauffmann, M Bisling *Tetrahedron Lett.*, 1984, **25** 293
25. A N Kasatkin, O Yu Tsypyshev, T Yu Romanova, G A Tolstikov *Mendeleev Commun.*, 1991, 62
26. A N Kasatkin, O Yu Tsypyshev, T Yu Romanova, G A Tolstikov *Metalloorg. Khim.*, 1991 (in press)
27. E Piers, I Nagakura *J. Org. Chem.*, 1975, **40** 2694
28. J P Marino, L J Browne *J. Org. Chem.*, 1976, **41** 3629
29. K Fugami, K Oshima, K Utimoto *Chem. Lett.*, 1987, 2203
30. A N Kasatkin, T Yu Romanova, O Yu Tsypyshev, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2623
31. A N Kasatkin, T Yu Romanova, O Yu Tsypyshev, G A Tolstikov *Metalloorg. Khim.* (in press)
32. H W Gschwend, H R Rodriguez *Organic Reactions* (edited by W G Dauben), Wiley, New York, 1979, **26** 1
33. S-J Murahashi, M Yamamura, K Yanagisawa, et al. *J. Org. Chem.*, 1979, **44** 2408
34. M Kumada *Pure Appl. Chem.*, 1980, **52** 669
35. E Negishi, A O King, N Okukado *J. Org. Chem.*, 1977, **42** 1821
36. S Baba, E Negishi *J. Am. Chem. Soc.*, 1976, **98** 6729
37. J F Normant *Pure Appl. Chem.*, 1978, **50** 709
38. N A Bumagin, I P Beletskaya *Usp. Khim.*, 1990, **59**(12) 2003 [English translation in *Russ. Chem. Rev.*, 1990(12)]
39. A N Kasatkin, T Yu Romanova, O Yu Tsypyshev, G A Tolstikov *Metalloorg. Khim.* (in press)
40. I V Kresteleva, A Yu Spivak, G A Tolstikov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 463
41. A N Nesmeyanov, K A Kocheshkov (Editors) *Metody Elementoorganicheskoi Khimii, Magnii, Berillii, Kal'tsii, Strontsii, Barii* (Methods in Organometallic Chemistry, Magnesium, Beryllium, Calcium, Strontium, Barium), Nauka, Moscow, 1963, 561 pp
42. A N Kasatkin, O Yu Tsypyshev, T Yu Romanova, G A Tolstikov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, **656**
43. A N Kasatkin, O Yu Tsypyshev, T Yu Romanova, G A Tolstikov *Metalloorg. Khim.*, 1989, **2** 837
44. G Cahiez, D Bernard, J F Normant *J. Organomet. Chem.*, 1976, **113** 107
45. G Cahiez, D Bernard, J F Normant *J. Organomet. Chem.*, 1976, **113** 99
46. A N Nesmeyanov, K A Kocheskov (Editors) *Metody Elementoorganicheskoi Khimii, Tsink, Kadmii* (Methods in Organometallic Chemistry, Zinc, Cadmium), Nauka, Moscow, 1964, 235 pp
47. D A Shirley *Organic Reactions* (Edited by R Adams), Wiley, New York, 1955, Vol. 8, p. 28
48. E Negishi *Organometallics in Organic Synthesis*, Wiley, New York, 1980, 532 pp
49. G A Tolstikov, F Kh Valitov, A V Kuchin *Dokl. Akad. Nauk SSSR*, 1982, **256** 1406
50. G H Posner, C E Witten *Tetrahedron Lett.*, 1970, 4647
51. G H Posner, C E Witten, P E McFarland *J. Am. Chem. Soc.*, 1972, **94** 5106
52. G Cahiez, B Laboue *Tetrahedron Lett.*, 1989, **30** 7369
53. Ya L Gol'dfarb, L M Smorgonskii *Zh. Obshch. Khim.*, 1938, **8** 1516
54. G Friour, G Cahiez, J F Normant *Synthesis*, 1985, 50
55. G Friour, G Cahiez, J F Normant *Synthesis*, 1984, 37
56. G Cahiez *Tetrahedron Lett.*, 1981, **22** 1239
57. G Cahiez, A Alexakis, J F Normant *Synth. Commun.*, 1979, **9** 639
58. G Cahiez, J Rivas-Enterrios, H Granger-Veyron *Tetrahedron Lett.*, 1986, **27** 4441
59. G Cahiez, J Rivas-Enterrios, P Clery *Tetrahedron Lett.*, 1988, **29** 3659
60. G Cahiez, J F Normant *Tetrahedron Lett.*, 1977, 3383
61. G Cahiez, B Figadere *Tetrahedron Lett.*, 1986, **26** 4445
62. C C Leznoff, V Yedidia *Can. J. Chem.*, 1980, **58** 287

63. M T Reetz *Organotitanium Reagents in Organic Synthesis*, Springer Verlag, Berlin, 1986, 236 pp
64. B Weidmann, D Seebach *Angew. Chem.*, 1983, **95** 12
65. M T Reetz *Topics in Current Chemistry*, Springer Verlag, Berlin, 1982, Vol. 106, p. 1
66. T Hiyama, M Obayashi, A Nakamura *Organometallics*, 1982, **1** 1249
67. T Hiyama, M Sawahata, M Obayashi *Chem. Lett.*, 1983, 1237
68. G Cahiez, P-Y Chavant *Tetrahedron Lett.*, 1989, **30** 7373
69. G Cahiez, M Alami *Tetrahedron Lett.*, 1986, **27** 569
70. M S Kharasch, J W Hancock, W Nudenberg, P O Tawney *J. Org. Chem.*, 1956, **21** 322
71. M S Kharasch, P O Tawney *J. Am. Chem. Soc.*, 1941, **63** 2308
72. G Cahiez, M Alami *Tetrahedron*, 1989, **45** 4163
73. T Cuvigny, H Normant *Bull. Soc. Chem. Fr.*, 1961, 2423
74. C Holmberg *Liebigs Ann. Chem.*, 1981, 748
75. S D Gupte, S V Sunthankar *J. Org. Chem.*, 1959, **24** 1334
76. A N Kasatkin, O Yu Tsypyshev, T Yu Romanova, G A Tolstikov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1154
77. A N Kasatkin, O Yu Tsypyshev, T Yu Romanova, et al. *Metalloorg. Khim.*, 1991 **4**(4) 200 [English translation in *Organomet. Chem. USSR*, 1991(4)]
78. A N Kasatkin, T Yu Romanova, O Yu Tsypyshev, G A Tolstikov *Metalloorg. Chem.*, 1989, **2**(2) 470 [English translation in *Organomet. Chem. USSR*, 1989(2)]
79. G Cahiez, M Alami *Tetrahedron Lett.*, 1989, **30** 3541
80. G H Posner *Organic Reactions* (Edited by W G Dauben), Wiley, New York, 1972, **19** 1
81. G Cahiez, M Alami *Tetrahedron Lett.*, 1989, **30** 7365
82. S Matsuzawa, Y Horiguchi, E Nakamura, I Kuwajima *Tetrahedron*, 1989, **45** 349
83. M Bourgain-Commercon, J-P Foulon, J F Normant *J. Organomet. Chem.*, 1982, **228** 321
84. H Hayami, M Sato, S Kanemoto, et al. *J. Am. Chem. Soc.*, 1983, **105** 4491
85. W Tückmantel, K Oshima, H Nozaki *Chem. Ber.*, 1986, **119** 1581
86. K Wakamatsu, T Nonaka, Y Okuda, et al. *Tetrahedron*, 1986, **42** 4427
87. I Fleming, T W Newton, F Roessler *J. Chem. Soc., Perkin Trans. 1*, 1981, 2527
88. J Hibino, S Matsubara, Y Morizawa, K Oshina *Tetrahedron Lett.*, 1984, **25** 2151
89. E Piers, J M Chong *J. Chem. Soc., Chem. Commun.*, 1983, 934
90. H Westmijze, K Ruitenberg, J Meiger, P Vermeer *Tetrahedron Lett.*, 1982, **23** 2797
91. J Hibino, S Nakatsukasa, K Fugami, et al. *J. Am. Chem. Soc.*, 1985, **107** 6416
92. K Fugami, J Hibino, S Nakatsukasa, et al. *Tetrahedron*, 1988, **44** 4277
93. K Fugami, S Nakatsukasa, K Oshima, et al. *Chem. Lett.*, 1986, 869
94. T H Chan, I Fleming *Synthesis*, 1979, 761
95. Y Okuda, M Sato, K Oshima, H Nozaki *Tetrahedron Lett.*, 1983, **24** 2015
96. K Fugami, K Oshima, K Utimoto, H Nozaki *Tetrahedron Lett.*, 1986, **27** 2161
97. R W Hoffman *Angew. Chem.*, 1982, **94** 569
98. M T Reetz *Angew. Chem.*, 1984, **96** 542
99. L Zhu, R M Wehmeyer, R D Rieke *J. Org. Chem.*, 1991, **56** 1445

Translated from *Uspekhi Khimii* 61 1002–1019 (1992) U.D.C. 541.64

The synthesis, properties, and applications of hydrophilic polymers and copolymers of hydroxyalkyl esters of acrylic and methacrylic acids

Z G Asadov, V S Aliev
Institute of Petrochemical Processes, Academy of Sciences of Azerbaijan

ABSTRACT. The scientific-technical and patent literature on the synthesis of hydroxyalkyl esters of acrylic and methacrylic acids by their catalytic reactions with epoxyalkanes, by the radical copolymerisation and polymerisation of presynthesised monomeric esters, and also by the chemical modification of polymerisation and copolymerisation products is surveyed. A wide variety of physicochemical properties of the polymers and copolymers based on the hydroxyalkyl esters of acrylic and methacrylic acids are described. The principal trends and prospects in the application of the high-molecular-weight products obtained in various branches of the national economy are indicated.

The bibliography includes 158 references.

Contents

I. Introduction 550
II. Synthesis of hydroxyalkyl esters of acrylic and methacrylic acids by the reaction of the monomeric acids with epoxyalkanes 550
III. Polymerisation of hydroxyalkyl esters of acrylic and methacrylic acids 551
IV. Copolymerisation of hydroxyalkyl esters of acrylic and methacrylic acids 553
V. Chemical modification of the polymers and copolymers of hydroxyalkyl esters of acrylic and methacrylic acids 556
VI. Properties and applications of the polymers and copolymers of hydroxyalkyl esters of acrylic and methacrylic acids 557

I. Introduction

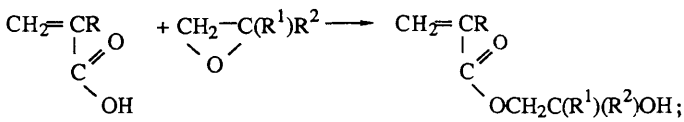
Water-soluble and hydrophilic polymers and copolymers are valuable products with unusual physicochemical characteristics. A specific feature of these compounds is the presence in their macromolecules of definite functional groups—hydroxy-, carboxy-, carbonylate, hydroxyalkyl, sulpho-, and other groups. The ratio of the hydrophilic and hydrophobic fragments in the macrochain determines the solubility in water and hydrophilicity of the polymers and copolymers. Here it is essential to bear in mind also the possibility of interchain and intrachain chemical bonds (the so called cross-links), which are formed in the synthesis of the macromolecular compounds or are introduced deliberately into the final product. They give rise to significant amendments to the physicochemical properties of the product, including a change in its solubility. These features must be taken into account in selecting approaches to the synthesis of the polymers and copolymers used to produce various materials with a specified range of physicochemical properties.

Water-soluble and hydrophilic polymers and copolymers are widely used in industry, agriculture, medicine, and science.

II. Synthesis of hydroxyalkyl esters of acrylic and methacrylic acids by the reaction of the monomeric acids with epoxyalkanes

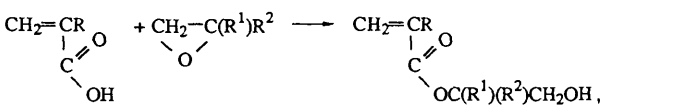
The hydroxyalkylation of acrylic (AA) and methacrylic (MAA) acids is of great applied importance because the final products of this reaction (unsaturated glycol esters) are valuable monomers from which it is possible to obtain polymeric materials with a wide variety of properties.

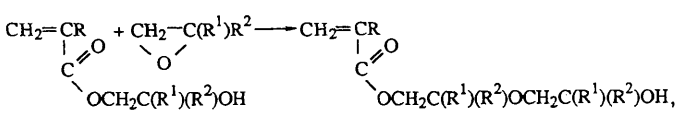
The addition of an epoxyalkane (EA) to AA and MAA, leading to the initiation of the formation of the hydroxyalkyl group, proceeds in accordance with the following scheme:

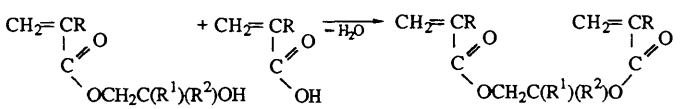


where R = H, CH_3, R^1 = H, CH_3, C_2H_5, R^2 = H, CH_3.

Apart from the formation of glycol monoesters, the following reactions are also possible theoretically:







The probability of each of these reactions is determined by the experimental conditions (molar ratio and concentrations of the reactants, temperature, nature of the reaction medium, etc.).

The addition of the epoxyalkane to AA and MAA in the presence of a catalyst is observed at temperatures below 100 °C. Inorganic and organic compounds of different classes have been proposed as catalysts. The weight of the catalyst is between 0.1 and 10% of that of the monomeric acid.

Among inorganic compounds, one may point to derivatives of tervalent iron: alkoxides (triethoxide, tri-δ-chlorobutoxide) and carboxylic acid salts (iron triacetate),[1] acetylacetonate and ethyl acetoacetate,[2] acrylate and methacrylate,[3] halides, $Fe(NO_3)_3$, $Fe(SCN)_3$, $Fe_2(CO_3)_3$, and $Fe_2(SO_4)_3$.[4,5] Mercury, chromium, copper, and iodine compounds are used as promoting agents in these reactions. Hydroquinone serves as a polymerisation inhibitor. In order to prevent the formation of quinone, compounds of alkali or alkaline earth metals, quaternary ammonium bases, amines, pyridine, and their salts are added. The yield of the monomeric esters exceeds 90% and their purity is 94–99%. The content of the unreacted monomeric acid is 0.2 wt.%. Hydroxyalkyl esters of AA and MAA are obtained also in the presence of other tervalent iron compounds,[6–10] for example, the hydroxide[9] and salts with aromatic carboxylic acids.[10] In the latter case, a small amount of diesters and dialkylene glycol monoacrylates and monomethacrylates is also formed.

$AlCl_3$ may be used as the catalyst of the hydroxyalkylation of AA and MAA;[11–16] $SnCl_4$ and BF_3 are unsuitable for this purpose, since they induce the polymerisation of the unsaturated acid even in the presence of an inhibitor.[11] A number of compounds of tervalent chromium (simple salts of aliphatic C_1-C_{36} acids and carbocyclic acids, coordination compounds with aliphatic or aromatic acids or *o*-hydroxyacids) have also been proposed.[17,18] When chromium is replaced by manganese and vanadium, the catalyst becomes ineffective. Chromium(III) halides[19,20] and chromium(III) salts of unsaturated aliphatic acid,[19] as well as Cr_2O_3 [19] and oxochlorochromium(III) acrylate and methacrylate[21] (the content of diesters in the products is 0.09%) have also been recommended.

Hydroxyalkyl acrylates and methacrylates (HOAA and HOAMA) can be obtained by the reaction of AA and MAA with an epoxyalkane in the presence of LiOH or $LiOH.H_2O$,[22] LiCl,[23] and lithium acrylate or methacrylate.[24] It is of interest that hydroxyalkyl methacrylates are formed with the involvement of potassium methacrylate, but potassium acrylate does not exhibit catalytic activity in the synthesis of hydroxyalkyl acrylates.[25] The use of titanium and zinc chlorides and alkoxides, their chelate compounds, and the products of their partial hydrolysis,[26] as well as vanadium compounds such as VCL_3, VCl_4, VOCl, $VOCl_3$, $V_2(SO_4)_3$, vanadyl sulphate, vanadyl acetylacetonate[27] (diesters are hardly formed as side products), and free iodine[28] has also been reported.

The esterification of AA and MAA by C_2-C_4 epoxyalkanes can be achieved under the influence for both an anion-exchange resin containing quaternary ammonium groups $[CH_2N^+(CH_3)_2C_2H_4OH]X^-$, where X^- is a univalent anion, for example the Dowex resin which is a copolymer of styrene with 8% of divinylbenzene[29–31] (the product contains 0.62% of the diglycol ester, 1.49% of the glycol diester, and 0.87% of the initial acid), as well as a cation-exchange resin of the sulphonic acid type with an aniline derivative.[32]

The hydroxyalkylation of AA and MAA is also possible in the presence of organic bases: triphenylphosphine, tributylphosphine, triethyl phosphite[33] (diacrylates and dimethacrylates are absent from the final product), cyclic and acylic compounds containing the paramagnetic nitroxy-group serving simultaneously as a polymerisation inhibitor,[34] carboxylic acid amides,[35] trialkylamines and dialkylanilines,[36–43] secondary aliphatic amines[37] (the content of diesters reaches 0.7% in the products), substituted ammonium and ammonium acrylate salts,[38] pyridine and alkylpyridines[42,44,45] and their salts with organic or inorganic acids,[43,44] quaternary pyridinium salts of the type of *N*-ethylpyridinium bromide[46] (the product does not contain appreciable amounts of diesters), and *N*-(carbamoyl-oxyalkyl)pyridinium halide or similar salts of other heterocyclic nitrogen-containing compounds[47] (high purity of the products and the absence of side products have been noted).

The hydroxyalkyl esters of AA and MAA are purified by fractional distillation,[48] where the polyalkylene glycols $HO[CH_2CH(R)O]_nH$ ($R = H, CH_3$; $n = 3-20$) may be added to prevent the formation of diesters,[49,50] or by distillation in the presence of polymerisation inhibitors (for example, hydroquinone) and various bases—alkali and alkaline earth metals, ammonia and its derivatives, amines or pyridines,[51] and hydrazine hydrate or β-hydroxyethylhydrazine.[52] In order to prevent the polymerisation of hydroxyalkyl acrylates and methacrylates during distillation, the liquid acrylate may be introduced into the mixture.[53] A procedure is available for the distillation of hydroxyalkyl esters of AA involving the addition of nitrosodiphenylamine in order to prevent their polymerisation during manufacture, transport, and storage.[54]

III. Polymerisation of hydroxyalkyl esters of acrylic and methacrylic acids

The existing publications on the polymerisation of hydroxyalkyl esters of AA and MAA are mainly devoted to processes involving the preparation of polymers of 2-hydroxyethyl methacrylate (2-HOEMA) (see, for example, the communications of Lavrov and co-workers[55–58]).

The radical polymerisation of 2-hydroxyethyl methacrylate can be achieved in bulk, in solution, and in emulsion (in organic solvents and in water). A number of procedures are used to obtain soluble polymers. For example, mixtures of dimethacrylates are removed from the aqueous solution of the monomer by their extraction with an organic solvent—preferentially hexane, heptane, and toluene. It is desirable that the polymerisation of 2-hydroxyethyl methacrylate be carried out in the presence of chain-transfer agents. The solubility of the 2-hydroxyethyl methacrylate polymer can be achieved also when the polymerisation is carried out in dilute solutions in organic solvents (benzene, chloroform) in which the monomer and the initiator dissolve, while the polymer itself does not dissolve and does not swell. The polymer is water-soluble also when the polymerisation is carried out in solvents such as dimethylformamide (DMF) and dimethyl sulphoxide (DMSO) as well as in water (for polymerisation in water, it is recommended that an oxidation-reduction initiating system of the type of persulphate salts–ascorbic acid be used). Peroxides, hydroperoxides, and azo-compounds can serve as radical initiators for the polymerisation of 2-hydroxyethyl methacrylate.[59] Application of the method described leads to the formation of a 2-hydroxyethyl methacrylate polymer with a molecular weight between 500 and 700 000.

High-molecular-weight polymers of 2-hydroxyethyl acrylate and methacrylate can be obtained without an initiator by freezing a mixture of an aqueous solution of the monomer with a hydrophobic

solvent of the type of alkyl acetates or dialkyl ethers and by irradiation from the ionised gas of a plasma discharge.[60]

In the study of the kinetics of the polymerisation of 2-hydroxyethyl methacrylate, features close to the classical ones are mainly observed. The order of the reaction in organic solvents with respect to the radical initiator, azobisisobutyronitrile (ABIBN), was found to be half. In ethanol, the reaction order with respect to the monomer was 1.2 and in dethylene glycol 0.9. In polymerisation in water initiated by the ammonium persulphate–ascorbic acid system, the reaction order was found to be unity with respect to 2-hydroxyethyl methacrylate. The order with respect to ammonium persulphate was found to be 0.8 and that with respect to ascorbic acid was zero.

The presence in the system of chain-transfer agents affects both the rate of polymerisation of 2-hydroxyethyl methacrylate and the possibility of the manifestation of the gel effect observed in polymerisation in bulk in the absence of chain-transfer agents.[59] The yield of the polymer obtained with the aid of ABIBN and methyl azobisisobutyrate then reaches 80% (at 70 °C).[61]

In the presence of ethylene glycol dimethacrylate (EGDMA) as the cross-linking agent, 2-hydroxyethylmethacrylate forms films[62] and gel-like products[63] as a result of polymerisation in water. These swell in water and in water–dioxane mixtures. The study of the kinetics of the radical polymerisation of 2-hydroxyethyl methacrylate in bulk in the presence of 0.07–1.00% of EGDMA (using ABIBN and dicyclohexyl prooxydicarbonate as the initiator) by heat flux microcalorimetry[64] showed that, for a conversion less than 10%, the polymerisation process obeys the classical rules, while for a higher conversion of the monomer a significant self-acceleration of the process is observed, its strength depending on the content of EGDMA and 2-hydroxyethyl methacrylate. For the 0.2% content of EGDMA, the polymers formed (yield 90–96%) are completely insoluble owing to their cross-linked structure. A decrease in the EGDMA content to 0.07% makes it possible to obtain soluble polymers with a molecular weight of 315 000–792 000.

The radical polymerisation of 2-hydroxyethyl methacrylate in the polyvinylpyrrolidinone (PVP) matrix in different solvents is of interest.[65] The study of the process kinetics showed that an increase in the rate of polymerisation in the absence of highly polar electron-donating solvents is induced by the complex formation reaction between polyvinylpyrrolidinone and monomer.

The conformational characteristics of the 2-hydroxyethyl-methacrylate polymer (isotactic) were investigated by Kim and co-workers using viscometric[66,67] and fluorescence[67] methods. It was established that the chain of the 2-hydroxyethyl methacrylate polymer is more expanded in the salt solution containing ions incorporated in the water structure. In terms of their disruptive effect on the conformation of the given polymer, anions can be arranged in the sequence $SO_4^{2-} < F^- < I^- < NO_3^- < SCN^-$. The polymer conformation is more sensitive to changes in the anion than in the cation. The conformational characteristics of the isotactic 2-hydroxyethyl methacrylate polymer in water–alcohol (methanol, ethanol, propanol, isopropyl alcohol, ethylene glycol) mixtures were detected from the change in the intensity of the fluorescence of auramine introduced into the polymer solution and in the specific viscosity of the solutions. It was shown that in water the 2-hydroxyethyl methacrylate polymer has a compact structure stabilised by the hydrophobic interactions of the CH_3 groups. The structure is disrupted by alcohols. The disruption of the complex compact structure is accompanied by a decrease in the fluorescence intensity and by an increase in the specific viscosity of the solution over a narrow range of variation of the solvent composition for all alcohols other than ethylene glycol. With increase in the length of the aliphatic group of the alcohol, the compact structure is disrupted for a lower content of the latter in water. The disruptive effect of ethylene glycol can be explained by the formation of hydrogen bonds between the polar groups of the 2-hydroxyethyl methacrylate polymer and the alcohol.

The viscous properties of aqueous solutions of isotactic 2-hydroxyethyl methacrylate polymer are influenced by urea and its derivatives (thiourea, methylurea, ethylurea, 1,3-dimethylurea, and tetramethylurea, and tetramethylurea).[68] Comparison of the excess molar heat capacities of the urea or its derivatives and of the ratio of the intrinsic viscosities $[\eta_{urea}]/[\eta_{water}]$ of solutions of the 2-hydroxyethyl methacrylate polymer in water containing urea or its derivatives and in pure water respectively shows, firstly, that in aqueous solutions the isotactic polymer has the structure of a compact statistical coil and, secondly, that the addition of urea or its derivatives leads to a disruption of the compact structure of the 2-hydroxyethyl methacrylate polymer. This can be explained by the breakdown of the water structure under the influence of urea or its derivatives and by the interaction between the polymer and the additive. The temperature variation of $[\eta_{water}]$ shows that at 20 °C the isotactic 2-hydroxyethyl methacrylate polymer has the most compact conformation.

The state of water in the hydrated 2-hydroxyethyl methacrylate polymer was studied by NMR spectroscopy and differential scanning calorimetry.[69] It was shown that the onset of the mobility of water corresponds to a temperature of approximately 180 K (below which the system is a glass). In specimens with a higher water content, an appreciable proportion of mobile water freezes at 230–260 K. Near 273 K, the behaviour of water is complex and above room temperature chemical exchange processes are manifested. The equilibrium water content in the 2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate polymers has been measured in distilled water and in phosphate buffer.[70] It was noted that in distilled water the equilibrium water content increases with increase in the hydrophilicity of the polymer and is almost independent of its molecular weight. In the buffer solution the degree of swelling and the amount of "frozen" water in the polymer are anomalously high, which can be explained by the ionisation of small amounts of methacrylic acid present in the polymers.

A macromonomer with two terminal COOH groups and OH side groups, having the formula $HOOCCH_2CH(COOH)S[CH_2C.(CH_3)COOCH_2CH_2OH]_nH$, was synthesised by the radical polymerisation of 2-hydroxyethyl methacrylate in tetrahydrofuran (THF) at 60 °C in the presence of thiomalic acid $HOOCCH(SH)CH_2COOH$.[71] It is used for the preparation of grafted polyamide copolymers.

The kinetics of the polymerisaiton of 2-hydroxypropyl methacrylate[39–41,72] and 2-hydroxypropyl acrylate (2-HOPA) [41,72,73] were investigated by the dilatometric method in ethanol with the process influenced by persulphate salts. In the case of 2-hydroxypropyl acrylate, the orders of the polymerisation reaction with respect to the monomer and initiator are close to the classical values (1 and 0.5), but in the case of 2-hydroxypropyl methacrylate the order with respect to the monomer is higher (1.77) and that with respect to the initiator is zero (because of its insolubility in ethanol, the persulphate is introduced in aqueous solution, which leads to the separation of the monomer and initiator phases). It was shown that the polymerisation of 2-hydroxypropyl methacrylate is described by the equation

$$1/0.77\ [M]^{0.77} = k\tau + 1/0.77\ [M]_0^{0.77}$$

where $[M]$ and $[M]_0$ are the current and initial concentations of the monomeric ester, k is the overall polymerisation rate constant, and τ is the time. The activation energy for this process was found to be 8.75 kcal mol^{-1} and the pre-exponential factor was 7.76×10^5.

In the study[73] of the effects of the nature of the reaction medium on the polymerisation of 2-hydroxypropyl acrylate at 50 °C with ammonium persulphate as the initator, it was established that the highest rate of reaction is observed in ethanol, THF, and DMSO and the lowest in acetone and DMF. The rate decreases further in the sequence water–isopropyl alcohol–methanol–1,4-dioxane, but under these conditions the final degree of conversion in methanol is much higher than in isoropyl alcohol. A lower rate of polymerisation of 2-hydroxypropyl acrylate was noted in acetonitrile.

The results of studies[73] of the kinetics of the polymerisation of 2-hydroxypropyl acrylate in ethanol–water and acetone–water binary mixtures indicate an inverse correlation between the rate of polymerisation and the volume fraction of water in the system, but in the case of the complete replacement of ethanol or acetone by water the rate of polymerisation increases. The 2-hydroxypropyl acrylate polymer is soluble in water only when its molecular weight is low.

The study[73] of the temperature variation of the polymerisation of 2-hydroxypropyl acrylate in ethanol with ammonium persulphate as the initiator at 40–70 °C showed that the rate of polymerisation increases as the temperature is reduced in the range from 40 to 65 °C. At 70 °C, the rate of polymerisation and the final degree of conversion of 2-hydroxypropyl acrylate have the minimum values in the experimental temperature range, which is probably associated with the predominance of the chain termination reaction.

The most effective initator, leading to the attainment of the optimum rates of the process and the optimum final conversion of 2-hydroxypropyl acrylate, is ammonium persulphate. Potassium persulphate exhibits a much lower initiating activity. Hydrogen peroxide occupies an intermediate position. ABIBN and benzoyl peroxide are fairly powerful initiators of the radical polymerisation of 2-hydroxypropyl acrylate. It has also been shown experimentally[73] that sodium sulphite and thiosulphate, which form redox systems with the persulphate salt, exhibit an activating affect on the polymerisation of 2-hydroxypropyl arylate.

Table 1. Rate constants for the polymerisation of 2-hydroxypropyl acrylate in ethanol (with ammonium persulphate as the initiator) at different temperatures.[73]

Constant	50 °C	55 °C	60 °C
k_i, s^{-1}	$7.24 \cdot 10^{-5}$	$11.06 \cdot 10^{-5}$	$13.85 \cdot 10^{-5}$
k_p	0.646	65.242	102.259
k_t	$5.388 \cdot 10^3$	$5.433 \cdot 10^5$	$8.531 \cdot 10^5$
k	$1.059 \cdot 10^{-3}$	$1.315 \cdot 10^{-3}$	$1.843 \cdot 10^{-3}$

2-Hydroxypropyl arylate is capable of photochemically initiated polymerisation (on irradiation with blue light). This makes it possible to employ the rotating sector method for the determination of the rate constants for the propagation (k_p) and termination (k_t) stages in the polymerisation process. These constants as well as the initation constant k_i, calculated by the inhibition method, are listed in Table 1 (k is the overall rate constant for the polymerisation of 2-hydroxypropyl acrylate).

The activation energy for the polymerisation process proved to be 10.37 kcal mol^{-1}. The Arrhenius equation assumes the following form:

$$k = 11.04 \cdot 10^7 \exp(-5220/T).$$

The activation energy for the initiation of the polymerisation of 2-hydroxypropyl acrylate with ammonium pesulphate as the initiator is 13.81 kcal mol^{-1}. The temperature variation of the initiation rate constant is described by the following equation:[73]

$$k_i = 17.69 \cdot 10^8 \exp(-6953/T).$$

IV. Copolymerisation of hydroxyalkyl esters of acrylic and methacrylic acids

Most of the published studies on the copolymerisation of the hydroxyalkyl esters of AA and MAA are devoted to the 2-hydroxyethyl methacrylate copolymers. The results of studies of its copolymerisation with a number of other methacrylate esters have been described:[74–79] methyl methacrylate (MMA),[74,79] ethyl methacrylate (EMA),[75,78] butyl methacrylate (BMA),[74,75,79] tributyltin methacrylate,[76] lauryl methacrylate,[77] and decyl methacrylate.[79] The copolymerisation is carried out in solution[74,77,79] or in bulk.[75] The solvents employed are methanol,[74,79] benzene, THF, t-butyl alcohol, and DMF.[77] The initiators used are benzoyl peroxide,[75] ABIBN,[77] and ammonium persulphate[79] (temperature 50–70 °C). With increase in the mole fraction of 2-hydroxyethyl methacrylate in the copolymer, its intrinsic viscosity also increases (the molecular weights reach one million and above[75]). There is a parallel increase in the swelling coefficient of the copolymer, its values being in the range 21.27–27.14 in the case of the copolymers with ethyl and butyl methacrylates. It was established that the introduction of up to 10% of alkyl methacrylate into the chain greatly alters the solubility and the physicomechanical properties of the polymer. The copolymers form transparent films with good adhesion to glass and metal. The copolymerisation constants (r_1 and r_2), calculated by the Kelen–Tudes, Feynman–Ross, and Ezrielev methods and from data based on the $Q-e$ scheme, are presented in Table 2.

The copolymerisation of 2-hydroxyethyl methacrylate with both 2-hydroxyethyl arylate (2-HOEA) and acrylic and methacrylic acids and their sodium or potassium salts has also been investigated.[80] Dispersion (derivatives of cellulose or anhydrosorbitol ethers served as dispersing agents) of 2-hydroxyethyl methacrylate together with an aqueous solution of the comonomer in an organic solvent immiscible with water (benzene, heptane, hexane, $CHCl_3$, CCl_4, xylene) makes it possible to obtain powdered water-soluble copolymers.

The copolymerisation of 2-hydroxyethyl methacrylate with acrylic acid has been investigated[81] in water at 20 °C in the presence of the ammonium persulphate–ascorbic acid initiating system. It was shown that, with increase in the overall concentration of the monomers from 0.4 to 1.0 M, the rate of reaction rises from 3.6×10^{-5} to 3.5×10^{-4} mol $litre^{-1}$ s^{-1}. The copolymerisation constants are 1.55 and 0.36 respectively. The best unit alternation effect in the

macrochain is observed for a 2-hydroxyethyl methacrylate mole fraction in the mixture of comonomers of 0.2–0.4.

It has been shown[82] that the rate of copolymerisation of 2-hydroxyethyl methacrylate with *N*-vinylsuccinimide increases with increase in the ester content in the initial mixture. The rate of copolymerisation in benzene is significantly higher than in DMSO and the copolymerisation constants, calculated taking into account the influence of the preterminal unit differ, which leads to different microstructures of the copolymers. According to ^{1}H NMR data the probability of the formation of the $M_1M_2M_1$ triads is greater in benzene.

Table 2. Constants for the copolymerisation of 2-hydroxyethyl methacrylate (r_1) with other monomers (r_2).

Comonomer (solvent)	r_1	r_2	Refs.
Methyl methacrylate (methanol)	0.96	0.5	[74]
	0.81±0.10	0.45±0.03	[79]
Butyl methacrylate (methanol)	0.52	0.62	[74]
	0.76±0.14	0.61±0.06	[79]
Decyl methacrylate (methanol)	0.66±0.05	2.65±0.01	[79]
Lauryl methacrylate			
(benzene)	11.2	0.7	[77]
(THF)	2	1	[77]
(t-butyl alcohol)	1.6	0.5	[77]
(DMF)	0.8	0.8	[77]
Tributyl methacrylate	2.45	0.39	[76]
Acrylic acid (water)	1.55	0.36	[81]
N-Vinylsuccinimide			
(benzene)	7.36±1.66	0.09±0.02	[82]
(DMSO)	8.5	0.05	[82]
Styrene			
(butanol, propanol, DMF)	0.59	0.53	[85]
(toluene)	1.65	0.50	[85]
Acrylamide (water)	0.98	0.14	[87]
p-Nitrophenyl acrylate (alcohol)	1.4	0.7	[96]
N-acryloyloxyethylsuccinimide (alcohols)	1.0	0.8	[96]

Lavrov et al.[83] synthesised the copolymer of 2-hydroxyethyl methacrylate with *N*-vinylamidosuccinic acid. The study of the properties of aqueous solutions of the copolymer by the viscometric titration method showed that an increase in the viscosity of the solution is observed up to a degree of ionisation $\alpha = 0.85$, which indicates the uncoiling of the macrocoil. The maximum size of the macromolecules exhibiting polyelectrolyte properties is observed at pH 7.5–8.5 ($\alpha = 0.85-0.95$). On further increase in the pH of the medium, the molecules assume a more twisted conformation.

The 2-hydroxyethyl methacrylate–N-vinyl-2-pyrrolidinone copolymer was obtained in the form of a hydrogel with the aid of ABIBN at 70 °C.[84] It was shown by optical and refractometric methods that the degree of hydration of the copolymers and their linear expansion on hydration increase in the ranges 10–80 and 5–40% respectively with increase in the content of the second comonomer units in the copolymer from 0 to 75%. The permeability of the swollen hydrogels to oxygen increases with increasing degree of hydration.

The copolymerisation constants have been determined[85] for the 2-hydroxyethyl methacrylate–styrene system in solutions in butanol, propanol, DMF, and toluene (Table 2).

The possibility of obtaining cross-linked (in the form of hydrogels) and non-cross-linked 2-hydroxyethyl methacrylate–acrylamide (AAM) copolymers by radical copolymerisation in water initiated by the ammonium persulphate–ascorbic acid system has been demonstrated.[86] Methylenebisacrylamide and triethylene glycol dimethacrylate were used as cross-linking agents. It was established that the introduction of acrylamide units into the polymer chain increases the water-absorbing properties of the product. Calculation of the probability of the distribution of the units of the comonomers from the copolymerisation constants determined by the Kelen–Tudes method[87] (Table 2) indicates a tendency towards the alternation of the units to give the ratio acrylamide:2-hydroxyethyl methacrylate = 2:1.

The copolymers of 2-hydroxyethyl methacrylate with sodium 2-acrylamidomethylpropanesulphonate (2-AA-2-MPSNa) having different compositions (78:22, 60:40, 40:60, and 20:80) have been synthesised.[88] The heterogeneity of the copolymers was investigated by the isotachophoresis method — the separation of aqueous buffer solutions into series of consecutive zones in conformity with their electrophoretic mobility. Aqueous solutions of the 60:40 and 40:60 copolymers at copolymer concentrations in excess of 10% separate into two phases. The upper layer contains the copolymer enriched in 2-AAM-2-MPSNa and the lower is enriched in 2-hydroxyethyl methacrylate. The effective electrophoretic mobilities increase with increase in the mole fraction of 2-AAM-2-MPSNa to 0.5–0.6 and are almost independent of the composition of the copolymer for high contents of 2-AAM-2-MPSNa.

Polymers with a degree of polymerisation of approximately 300 and free from betaine groups have been obtained[89] by the polymerisation of 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, or 2-hydroxypropyl methacrylate with methyl acrylate and *N,N*-dimethyl-*N,N*-diethylaminoethyl methacrylate in 10–20% KOH solution at 65–90 °C or in an emulsion at 50–70 °C with subsequent hydrolysis of the final product in an alkaline medium.

High-molecular-weight acrylic copolymers with $[\eta] = 12-17$, which are suitable as flocculating agents, have been synthesised[90] by the copolymerisation of hydroxyethyl acrylate or methacrylate and the vinyl monomer $CH_2=CR^1COY(CH_2)_n.N^+R^2R^3R^4X^-$ (where R^1 = H, CH_3; R^2-R^4 = alkyl; X^- = acid residue), for example, methacryloyloxyethyltrimethylammonium chloride, in a thin layer on a moving strip under the influence of UV light in the presence of non-ionic surfactants and a photoinitiator. The polymer layer is continually removed from the strip.

Copolymers of 2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate with vinyl acetate (VA) have been obtained by the radiation method[91] in the presence of cross-linking agents, for example ethylene glycol.

The radical copolymerisation of 2-hydroxyethyl methacrylate monomers containing active functional groups (*p*-nitrophenyl acrylate and *N*-acryloyloxyethylsuccinimide) initiated by ABIBN has been investigated[92] in alcohol in order to produce reactive carriers for the immobilisation of proteins, enzymes, and aminoacids. The copolymerisation constants were determined by the Feynman–Ross and Ezrielev methods (Table 2).

Polymeric products with a high mechanical strength have been obtained[93] by the suspension copolymerisation of 2-hydroxyethyl

methacyrlate with the monomers $\{CH_2=CRCOO(CH_2CH_2O)_n.[CH_2CH(CH_3)O]_m\}_3P=O$ (where R = H, CH_3; m = 0–30; n = 0–3; $m + n \geqslant 1$) in 50:50 to 10:90 ratios.

The radical copolymerisation of 2-hydroxyethyl methacrylate with both *N,N'*-diethyl-*N*-(4-vinylphenylethyl)ethylenediamine and with its self-condensation product (initiated by lithium diisopropylamide in THF at 20 °C) in benzene, ethanol, and *o*-dichlorobenzene has been described.[94]

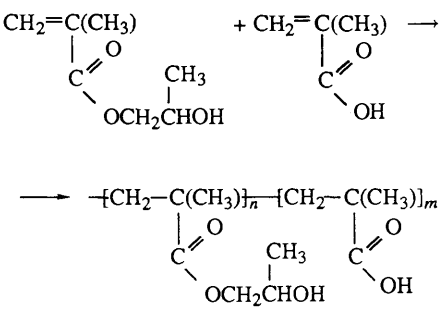
Terpolymers based on hydroxyalkyl acrylates and methacrylates (with C_6-C_{12} alkyl groups) and styrene (α- or *p*-methylstyrene) have been obtained in solution in ketones with the reaction initiated by peroxides.[95,96] Mono-, di-, or tri-alkyl acrylates and methacrylates (with C_2-C_{18} alkyl groups) [95] or acrylic (methacrylic) acid were used as the third comonomer. The copolymers are suitable for coatings and have a narrow molecular weight distribution and a molecular weight less than 4000.[96] The OH groups in the copolymer are partly esterified by treatment with natural or synthetic aliphatic acids in the presence of a catalyst.[95]

Copolymers used as current conducting salts, flocculants, and additives to cosmetic compositions have been obtained[98] by the radical copolymerisation of hydroxyalkyl arylates and methacrylates in an aqueous medium at 40–100 °C with the monomers $[R^1R^2R^3N^+CH(R^4)CH(R^5)OH]A^-$, where R^1 = C_2-C_4 alkenyl, n = 1–18, X = O or NH, R^6 = H or CH_3, R^2 = C_1-C_{18} hydroxyalkyl, R^3 = C_2-C_4 alkenyl or C_1-C_{18} alkyl, R^4, R^5 = H or C_1-C_{28} alkyl, and A = anion.

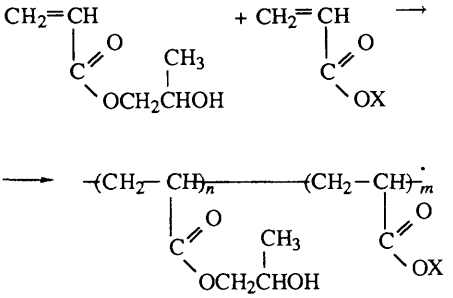
Copolymers of 2-hydroxyethyl acrylate, vinyl acetate, and ethylene, whose microstructure was investigated by ^1H and ^{13}C NMR, have also been synthesised.[98] It was shown that, for a 2-hydroxyethyl acrylate content of 5%, its units are not distributed statistically. For a vinyl acetate content of 25%, ethylene–vinyl acetate–vinyl acetate and ethylene–vinyl acetate–ethylene triads are formed in the chain, but there are no ethylene–vinyl acetate–hydroxyethyl acrylate and hydroxyethyl acrylate–ethylene–vinyl acetate triads. With increase in the molecular weight of the fractions of the copolymer with 25% of vinyl acetate, isolated by gel-permeation chromatography, the content of 2-hydroxyethylacetate also increases.

As can be seen from the data presented above, 2-hydroxyethyl methacrylate and its analogues are very active monomers in copolymerisation reactions. This is confirmed also by the Alfrey–Price parameters quoted in the literature:[81–83] Q = 1.16, e = 0.30 and Q = 0.80, e = 0.20.

The radical polymerisation of 2-hydroxypropyl methacrylate with methacrylic acid[39–41]



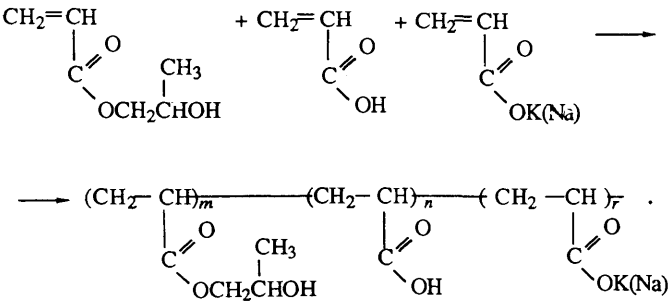
and of 2-hydroxypropyl acrylate with both acrylic acid and acrylate salts[73]



where X = H, K, or Na, has been achieved. The initiator was ammonium persulphate.

It has been shown that the highest solubility of the 2-hydroxypropyl methacrylate–methacrylic acid copolymer in water is achieved when the product is obtained in organic media, which is due to its lower molecular weight. With increase in the mole fraction of both 2-hydroxypropyl methacrylate and 2-hydroxypropyl acrylate in the copolymer, its solubility in water is impaired. The constants for the copolymerisation of 2-hydroxypropyl methacrylate and methacrylic acid proved to be 0.99 and 0.31, which indicates the higher reactivity of the ester. In the copolymerisation of 2-hydroxypropyl acrylate with acrylic acid, the difference between the reactivities of the comonomers is much greater (r_1 = 17 and r_2 = 0.02), the overall order of the reaction with respect to the comonomers being 2 and that with respect to the initiator (ammonium persulphate) being 0.7. Alkali metal acrylates (potassium and sodium acrylates) exhibit a much higher reactivity in copolymerisation with 2-hydroxypropyl acrylate than does acrylic acid. Thus the constants for the copolymerisation of 2-hydroxypropyl acrylate and potassium acrylate are 1, 10, and 0.96.

The ternary copolymers of 2-hydroxypropyl acrylate, acrylic acid, and the alkali metalacrylates indicated above have been synthesised:[73]



It is of interest that, in order to attain the best solubility of both binary and ternary copolymers involving 2-hydroxypropyl acrylate in water, it is desirable to obtain the acrylate salts *in situ* (by the reaction of acrylic acid and alkali), without isolating them from aqueous solution, to make them undergo the polymerisation reaction initiated by ammonium persulphate.

There have been a number of studies on the graft polymerisation of hydroxyalkyl esters of acrylic and methacrylic acids. Graft copolymers based on 2-hydroxyethyl methacrylate and poly(vinyl

alcohol) (PVA) have been obtained[99] in DMSO using hydroperoxides and azo-initiators. The process characteristics indicate a matrix reaction mechanism. The activating effect of the hydrogen-bonded complex between 2-hydroxyethyl methacrylate, the initiator, and the OH groups of PVA on the course of the reaction has been demonstrated.[100]

The graft copolymerisation of 2-hydroxyethyl methacrylate (in DM using ABIBN) on unsaturated polyurethane, obtained from poly(ethylene glycol) (M = 1500), methylenebis-4-phenylene isocyanate, *cis*-but-2-ene-1,4-diol, and butane-1,4-diol (in a mixture of DMSO with 4-methyl-2-pentanone as the solvent) has been carried out.[101] 2-Hydroxyethyl methacrylate can be grafted also on a polyurethane in the form of an emulsion (with t-butyl-hydroperoxide as the initiator)[102] or a film (under the influence of γ-irradiation).[103] In the latter case, the degree of grafting increases with increase in the swelling time of the film. 2-Hydroxyethyl methacrylate is grafted with an induction period of 0.5–1 h.

Studies on the photografting of 2-hydroxyethyl methacrylate on polyvinylpyrrolidinone (PVP) have been carried out.[104–107] The component ratio was 70–95:30–5. The photosensitiser was benzoyl peroxide. With increase in the PVP content, the degree of conversion of 2-hydroxyethyl methacrylate and the maximum rate of its polymerisation diminish. At the same time, the gel formation time is reduced. On irradiation with UV light, the compositions harden in a thin layer, which makes it possible to obtain hydrophilic coatings and films with valuable properties. The formation of highly permeable copolymers with a network structure has been established. 2-Hydroxyethyl methacrylate can be grafted to PVP also electrochemically.[108] An initiator-free polymerisation of 2-hydroxyethyl acrylate and methacrylate in the presence of 10–40% of PVP (molecular weight 12000) at 50–80 °C has also been described.[109] The formation of the graft copolymer is observed at a temperature as low as 50–60 °C, while homopolymerisation of the ester does not occur under analogous conditions. The yield of the copolymer and the content of the gel-fraction in the system increase with increase in temperature and with decrease in the content of PVP in the initial mixture. The rate of polymerisation increases with increasing PVP content. Dilution of the mixture of the ester and PVP with hydroxylated solvents (water, cyclohexanol, ethanol, ethylene glycol, and diethylene glycol) increases the rate of polymerisation compared with polymerisation in bulk.

Chinese investigators have achieved[110] the graft copolymerisation of 2-hydroxyethyl methacrylate on polyethylene membranes initiated by ^{60}Co γ-rays in ethanol solution at 25 °C. The initial rate of grafting was proportional to the ester concentration and the irradiation intensity raised to powers of 1.0 and 0.5 respectively. The apparent activation energy in the range 25–66 °C and the frequency factory for the graft copolymerisation are 8.0 kcal mol^{-1} and 1.505 × 10^7 respectively. The dependence of the apparent grafting rate constant k on the absolute temperature is described by the equation

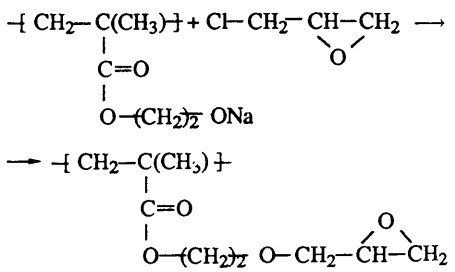
$$\ln k = 16.5269 - 4026(1/T).$$

It is suggested[111] that macroporous sorbents can be obtained by the polymerisation of 2-hydroxyethyl methacrylate initiated by ABIBN at 60–110 °C (or thermally at 100–150 °C or by exposure to radiation) in the presence of a copolymer of 2-hydroxyalkyl methacrylate (C_2–C_4 alkyl group) and a polyvinyl monomer, for example, C_2–C_4 alkylene dimethacrylate, as the carrier.

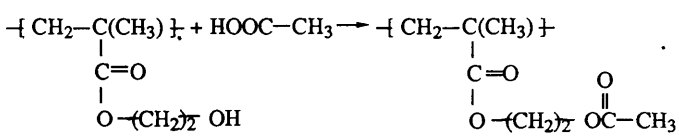
Gel-free hydroxylated graft copolymers, ensuring an effective distribution of metallic pigments without additives, are obtained[112] by the copolymerisation of monomers containing hydroxy-groups (2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, and 2-hydroxypropyl methacrylate) and carboxy-groups (monoesters of maleic fumaric acids, acrylic acid, and methacrylic acid) in the presence of an acrylic polymer contaning ethoxy-groups, the ratio of the numbers of COOH groups in the monomer and of the epoxy-groups in the acrylic polymer ranging from 1:0.5 to 0.5:1. Grafting occurs as a result of the condensation fo the epoxy- and carboxy-groups.

V. Chemical modification of the polymers and copolymers of hydroxyalkyl esters of acrylic and methacrylic acids

One of the methods for the chemical modification of 2-hydroxyethyl methacrylate polymers involves the carrying out of polymer-analogue transformations via the hydroxy- or ester groups. The course of the reaction is inferred from the results of elemental and functional as well as IR spectroscopic analyses. The hydroxy-group in the 2-hydroxyethyl methacrylate units can react with alkali metals to form alkoxides and with acids and acid anhydrides to form esters.[113,114] When the 2-hydroxyethyl methacrylate units interact with maleic anhydride, ethylene glycol methacrylate maleates are formed.[115] The reaction with thionyl chloride leads to 2-chloroethyl methacrylate units. The reaction with phosgene can yield 2-chlorocarbonyloxyethyl methacrylate fragments. 2-Hydroxyethyl methacrylate oligomers react with diisocyanates to form polyurethanes.[115] Glycidyl ethers have been obtained by the reaction of the sodium alkoxide derived from the 2-hydroxyethyl methacrylate units with epichlorohydrin:[116]



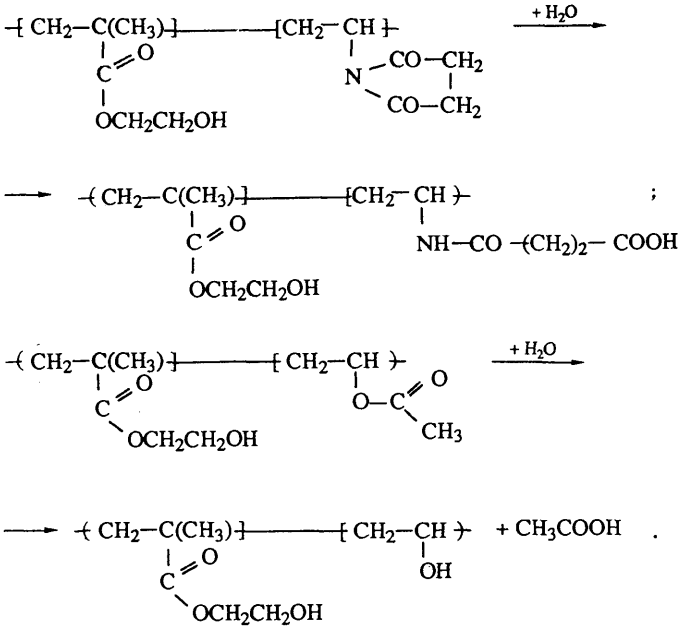
2-Hydroxyethyl methacrylate polymers enter into the acetal formation reaction involving the hydroxy-group. It has been suggested that this reaction be carried out with acetic acid in pyridine:[114]



The ester group in the 2-hydroxyethyl methacrylate units is very resistant to the action of hydrolysing agents. Alkaline hydrolysis of polymeric 2-hydroxyethyl methacrylate gels proceeds at a low rate only above 100 °C and acid hydrolysis with sulphuric acid under the

same conditions is slower still.[114] The possibility of hydrolysis at temperatures below 100 °C appears only when a non-cross-linked polymeric 2-hydroxyethyl methacrylate is used. In this case, the reaction is carried out in water (heterogeneous hydrolysis) or in a DMSO–water mixture (homogeneous hydrolysis) at 60–80 °C.[117,118] The kinetics of the alkaline hydrolysis of the polymer obey rules governing second-order reactions. In a heterogeneous medium, the hydrolysis is appreciably slower. At 20 °C, the 2-hydroxyethyl methacrylate units in the chain are not hydrolysed in either homogeneous or heterogeneous media.[117]

The *N*-vinylsuccinimide (VSI) and vinyl acetate units differ appreciably in their hydrolytic stability from the 2-hydroxyethyl methacrylate units,[117,119] which creates conditions for specific hydrolysis involving the vinylsuccinimide and vinyl acetate units in copolymers of 2-hydroxyethyl methacrylate with vinylsuccinimide and vinyl acetate, in which 2-hydroxyethyl methacrylate units are retained. The reaction results in the formation of copolymers of 2-hydroxyethyl methacrylate with *N*-vinylamidosuccinimic acid[117,118] and vinyl alcohol:[119]

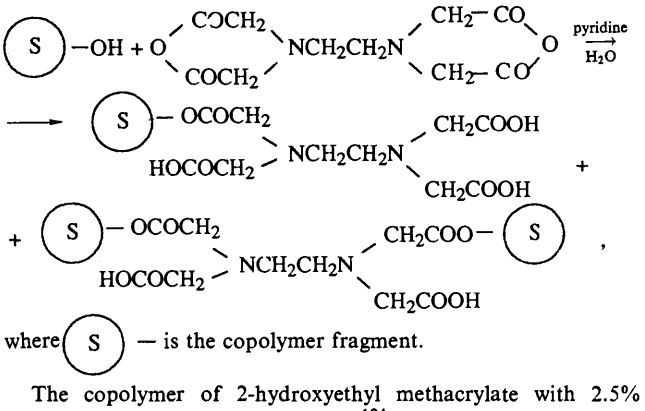


The degree of reaction involving the vinyl succinimide or vinyl acetate units is affected by the structure of the macrochain. The high reactivity of 2-hydroxyethyl methacrylate in copolymerisation with vinyl succinimide[120] and vinyl acetate[121] leads to single vinyl succinimide or vinyl acetate units separated by several 2-hydroxyethyl methacrylate units, which facilitates the interaction of the vinylsuccinimide or vinyl acetate units with the OH^- ion and permits their complete hydrolysis.

2-Hydroxyethyl methacrylate polymers can react with amines (ethanolamine, aniline, hydroxylamine), but the reaction is very slow even at 100 °C. The reaction with hydrazine proceeds most effectively.[114]

The reaction of the copolymer of 2-hydroxyethyl methacrylate and ethylene glycol dimethacrylate with the organosilicon compounds $(XR_m)_nSiR_{4-n}$, where X = NH_2, CO, COOH, HCO, etc., R and R′ = alkyl, n = 0–20, n = 1–3, has been described.[122]

By treating the copolymer of 2-hydroxyethyl methacrylate and ethylene glycol dimethyacrylate with dianhydride-complexones, it is possible to obtain chelating macromolecular products:[123]

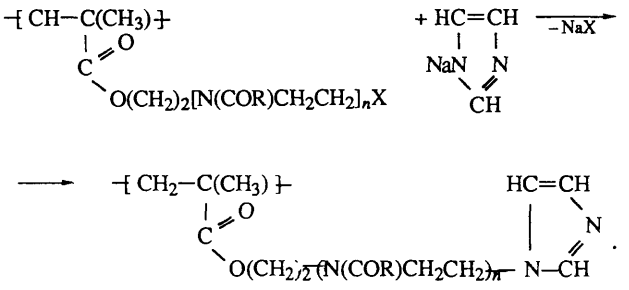


where (S) — is the copolymer fragment.

The copolymer of 2-hydroxyethyl methacrylate with 2.5% of methyl acrylate has been synthesised[124] and the interaction of gels of this copolymer with calcium ions has been shown that 2590 μg of calcium ions is absorbed per gramme of the gel at pH 8.5, while at 5.5 the gel collapses, which promotes the removal of calcium ions.

When the OH groups in the 2-hydroxyethyl methacrylate polymer are replaced by halogens (Br, Cl) and the product interacts with 2-R-oxazoline at 80–120 °C, polar graft copolymers are formed[123,125] with the units $-CH_2C(CH_3)COOCH_2CH_2.[N(COR)CH_2CH_2]_nX$, where R = H, C_1–C_3 alkyl, or phenyl, X = Br or Cl, and n = 1–20.

On treatment with sodioimidazole in methanol, THF, or DMF, the above haloderivatives of the polymeric 2-hydroxyethyl methacrylate give rise[123,126] to a product containing 0.9 mmol g^{-1} of imidazole groups:



Reactions in an aqueous medium on thin films of the cross-linked gel of the copolymer of 2-hydroxyethyl methacrylate with 2-isopropenylanthraquinone have been investigated[127] by UV and fluorescence spectroscopy. It was shown that fragments of anthrahydroquinone and of its tautomer (oxanthrone) are formed simultaneously on irradiation with near UV light.

VI. Properties and applications of the polymers and copolymers of hydroxyalkyl esters of acrylic and methacrylic acids

Polymers based on 2-hydroxyethyl methacrylate have many valuable properties: they are non-toxic, biologically compatible, and transparent and they adhere effectively to various substrates.

They are therefore recommended for use in the preparation of contact lenses, hydrogels for different purposes, membranes, films, adhesives, coatings, etc.[115,128–131]

The copolymers of 2-hydroxyethyl methacrylate with acrylic and methacrylic acids, methyl, butyl, and 2-hydroxypropyl methacrylates, as well as *N*-vinylpyrrolidinone,[132] N-1-(2-pyrrolidinonyl)ethylacrylamide,[133] styrene, and ethyl vinyl malonate are used for the manufacture of contact lenses.[115,129] Multicomponent copolymerisation is usually carried out in special moulds using a cross-linking agent (ethylene glycol dimethacrylate, etc.).[130,134]

Hydrophilic gels based on the 2-hydroxyethyl methacrylate polymers are used as carriers for physiologically active compounds,[135] the immobilisation of enzymes,[136,139] medicinal drugs,[140–143] and antigens and immunogenic substances,[130] for the preservation of enzymes and aromatic essential oils,[130] and in the manufacture of ion-exchange resins for the separation of biologically active substances.[130]

It has been established that the activity of immobilised enzymes depends on the gel structure. The introduction of a hydrophilic monomer into the polymeric 2-hydroxyethyl methacrylate gel increases appreciably the activity of the cells by virtue of the formation of a more porous gel structure, while the addition of a hydrophobic monomer lowers the activity of the cells immobilised in the gel as a result of the formation of a more rigid and finely porous gel structure.[138]

Ternary copolymers of 2-hydroxyethyl methacrylate, methyl methacrylamidoglycolate, and methyl methacrylate, deposited on a support, can be used[144] to eliminate specific pathological effectors from biological liquids of patients. These copolymers may contain covalently bound biologically active compounds capable of adsorbing the effectors.

The copolymers of 2-hydroxyethyl methacrylate with methyl methacrylate,[145,146] acrylamide,[147] and methyl acrylate[148,149] swell effectively in water. Thus the swellability of the 2-hydroxyethyl methacrylate–methyl acrylate copolymer in alkaline solutions reaches 3600% relative to the volume in an acid solution.[148]

2-Hydroxyethyl methacrylate-based gels are used to prepare implant for example, urinary bladder prostheses,[150] and catheters.[151] Membranes permeable to salts,[152–155] sugars,[152,154] urea,[154,155] dextran,[154] etc. have been developed on the basis of 2-hydroxyethyl methacrylate homopolymers and copolymers partly cross-linked with the aid of ethylene glycol dimethacrylate. Antithrombogens can be obtained by grafting 2-hydroxyethyl methacrylate on polystyrene, polyethylene, polytetrafluoroethylene, polyurethanes, PVA, and collagen.[130]

The copolymer of 2-hydroxyethyl methacrylate, methyl methacrylate, as well as sodium alginate can be used for the microencapsulation of immobilised cells,[156] while the copolymer of 2-hydroxyalkyl, acrylate and alkyl acrylate or methacrylate can be used for the microencapsulation of medicinal preparations.[157] The high capacity of 2-hydroxyethyl methacrylate polymers and copolymers for adhesion to various supports has led to its use for the preparation of coatings and adhesives.[130] The copolymers with methyl and butyl methacrylates, acrylic and methacrylic acid, etc. are used as aqueous compositions, solutions, and powdered compositions. 2-Hydroxyethyl methacrylate polymers and copolymers are employed in the preparation of transparent materials with a satisfactory wear resistance, hardness, and resistance to the appearance of turbidity,[130] and also for the preparation of compositions susceptible to thermal hardening[130] and photohardening.[158]

The copolymers of 2-hydroxypropyl methacrylate with methyl acrylate,[39,40] 2-hydroxypropyl acrylate, and potassium and sodium arylates as well as ternary copolymers of 2-hydroxypropyl acrylate with the above acrylate salts and acrylic acid[73] exhibit effective petroleum displacing properties. The copolymers of 2-hydroxypropyl acrylate with both potassium acrylate and acrylic acid exhibit bactericidal properties in relation to sulphate reducing bacteria evolving hydrogen sulphide, which stimulates the corrosion of metallic equipment in petroleum deposits.[73] In addition, the 2-hydroxypropyl acrylate–acrylic acid copolymer is an effective insulating agent, which to a large extent prevents the losses of drilling solutions and this increases the rate of drilling of petroleum and gas bore-holes.[73]

The hydroxyalkyl esters of acrylic and methacrylic acids are extremely promising and interesting monomers. A convenient method for the synthesis of these substances is believed to be the catalytic interaction of acrylic and methacrylic acids with the corresponding epoxyalkane. Homopolymers and copolymers with a wide range of exceptionally valuable properties can be synthesised from these esters. The homopolymers are obtained by the radical polymerisation of the hydroxyalkyl esters of acrylic and methacrylic acids, while the copolymers are obtained by the radical copolymerisation of the esters with monomers of different nature or by the chemical modification of homopolymers and copolymers. As a result of the above chemical reactions, it is possible to synthesise specifically high-molecular-weight compounds containing in their chains functional groups of the same or several different types. Depending on the chosen method of synthesis, there are then extensive possibilities for the regulation of the microstructure of the copolymers, i.e. of the nature of the alternation of the comonomer units in the chain.

Most of the studies published in this field have been devoted to the synthesis and applications of the polymers and copolymers of the esters synthesised by the reaction of methacrylic acid with epoxyethane. However, bearing in mind the comparative scarcity of epoxyethane and the much greater amounts of epoxypropane available as the starting material as well as certain difficulties involved in work with epoxyethane (its virtually gaseous state, explosive nature, high toxicity, and lower reactivity as a consequence of its symmetrical structure compared with hydroxypropane, which is an asymmetric epoxy-derivative), one may expect a growth of interest in the immediate future in the synthesis and application of the polymers and copolymers of the hydroxypropyl esters of acrylic and methacrylic acids. The results of studies included in this review and carried out at the Institute of Petrochemical processes of the Azerbaijan Academy of Sciences by the present authors and their co-workers are consistent with such forecasts.

References

1. Th Volker, H Walter, BRD P. 1 147 938
2. H Ito, K Kimura, Japanese P. 26 606; *Ref. Zh. Khim.*, 1970, 1N85P
3. W Gruber, BRD P. 1 255 104
4. M Murayama, US P. 3 441 599
5. M Murayama, US P. 1 137 071
6. M Murayama, Japanese P. 8970; *Ref. Zh. Khim.*, 1971, 7N91P
7. M Murayama, K Abe, Japanese P. 14 087; *Ref. Zh. Khim.*, 1973, 14N85P
8. M Murayama, BRD P. 1 568 838

9. T Matsuda, S Takamatsu, Japanese Appl. 54-39 008; *Ref. Zh. Khim.*, 1980, 6N61P
10. N Simizu, H Taiki, S Matsumoto, Japanese P. 56-161 349; *Ref. Zh. Khim.*, 1983, 8N59P
11. H J Wright, J F Bremmer, Australian P. 280 288
12. H J Wright, J F Bremmer, B.P. 1 066 086
13. H J Wright, J F Bremmer, US P. 3 150 167
14. H J Wright, J F Bremmer, French P. 1 390 843
15. H J Wright, J F Bremmer, Dutch P. 128 262
16. R L Routon, US P. 3 441 598
17. Y Kanbara, Japanese Appl. 61-27 945; *Ref. Zh. Khim.*, 1987, 2N42P
18. R Steckler, US P. 3 875 211
19. S Nezu, A Miyamoto, A Aozima, Japanese Appl. 57-38 747; *Ref. Zh. Khim.*, 1983, 8N58P
20. W Kunze, H Brachel, H Gattner, BRD P. 1 518 642
21. A A Gololobova, A P Sineokov, Z S Salakhetdinov, et al. USSR P. 505 627; *Ref. Zh. Khim.*, 1977, 3N80P
22. Y Tanizaki, Y Kubo, Japanese P. 21608; *Ref. Zh. Khim.*, 1972, 16N57P
23. Th H Cour, US P. 3 174 995
24. Y Tanizaki, Y Kubo, Japanese P. 47-51 338; *Ref. Zh. Khim.*, 1974, 12N75P
25. J-F Nemec, E L Wolffe, Sh N Lewis, US P. 3 314 983
26. H Ito, K Kimura, Japanese P. 2686; *Ref. Zh. Khim.*, 1970, 5N99P
27. A Itoi, M Kawamata, T Ono, et al., Japanese Appl. 56-87 537; *Ref. Zh. Khim.*, 1982, 10456P
28. N Murayama, Japanese P. 12 643; *Ref. Zh. Khim.*, 1968, 19N74P
29. H S R Bearden, Dutch P. 136 048
30. H S R Bearden, French P. 1 357 423
31. H S R Bearden, B.P. 1 003 346
32. Y Hamamoto, Japanese P. 17 682; *Ref. Zh. Khim.*, 1971, 12N78P
33. C Suling, H Wilms, E Roos, BRD P. 1 568 487
34. Kh-M A Brikenshtein, A A Berlin, A A Radugina, et al., USSR P. 749 823; *Ref. Zh. Khim.*, 1981, 7N44P
35. F Meier, N V Kutepow, BRD P. 1 248 036
36. W Gruber, H Walter, BRD Appl. 2 345 394; *Ref. Zh. Khim.*, 1975, 22N74P
37. Y Takayama, S Saito, Japanese P. 685; *Ref. Zh. Khim.*, 1970, 6N21P
38. H Ito, K Kimura, Japanese P. 27 083; *Ref. Zh. Khim.*, 1971, 15N94P
39. A Yu Yusubov, Candidate's Thesis in Chemical Sciences, Institute of Petrochemical Processes, Academy of Sciences of the Azerbaijan SSR, Baku, 1985, 149 pp
40. V S Aliev, Z G Asadov, A Yu Yusupov, et al. *Azerb. Khim. Zh.*, 1986, (2) 55–60
41. V S Aliyev, Z G Asadov, A Yu Yusubov, et al. *MACRO'87: 31st IUPAC Macromolecular Symposium: Abstracts of Papers, Microsymposium 1,* Merseburg, 1987, p. 117
42. A Yu Yusubov, A D Agazade, G A Akhmedova, Z G Asadov *Khimiya i Tekhnologiya Neftekhimicheskogo Sinteza i Vysokomolekulyarnykh Soedinenii* (The Chemistry and Technology of Petrochemical Synthesis and High-Molecular-Weight Compounds), Baku, 1988. Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 13.01.89, No. 326-V89
43. E Chadwick, B.P. 970 202
44. A J Simpson, B.P. 998 394
45. A Obami, S I Mekhtiev, P D Shikhalizade, et al. *Azerb. Khim. Zh.*, 1984, (4) 21–24
46. I Girvan, M A John, B.P. 1 096 035
47. R Dowbenko, R M Christenson, US P. 3 431 294
48. E G Stepanov, B A Saraev, V A Podgornova, et al. *Promyshlennost' Sinteticheskogo Kauchuka,* 1975, (6) 5–7
49. M Murayama, G Abe, Japanese P. 41 524; *Ref. Zh. Khim.*, 1972, 1N63P
50. M Murayama, K Abe, US P. 3 709 929
51. M Murayama, Japanese P. 8971; *Ref. Zh. Khim.*, 1971, 7N92P
52. S Suzuki, S Miura, H Tatemichi, Japanese P. 4850; *Ref. Zh. Khim.*, 1967, 24N77P
53. Y Kanbara, S Asano, V Isozaki, et al., Japanese Patent Application 63-41 441; *Ref. Zh. Khim.*, 1988, 7N27P
54. N Ito, K Suzuki, Japanese P. 44-76 893; *Ref. Zh. Khim.*, 1980, 6N59P
55. N A Lavrov *Khimicheskaya Tekhnologiya, Svoistva i Primenenie Plastmass* (Chemical Technology, Properties, and Applications of Plastics), Leningrad, 1989, pp. 77–84
56. N A Lavrov *Khimicheskaya Tekhnologiya, Svoistva i Primenenie Plastmass* (Chemical Technology, Properties, and Applications of Plastics), Leningrad, 1984, pp. 17–21
57. N A Lavrov, A F Nikolaev, N A Astaf'eva, USSR P.1 353 780; *Byul. Izobret.*, 1987, (43)
58. N A Lavrov, A F Nikolaev *Zh. Prikl. Khim.*, 1986, **59**(11) 2691–2693
59. T Mulavasic, U Osredkar, I Anzur, et al. *Vestn. Sloven. Kem Drus.*, 1986, **33**(2) 123–132
60. Y Osada, T Yamamoto, Y Kondo, Japanese Appl. 59-202 204; *Ref. Zh. Khim.*, 1986, 3S426P
61. W T K Stevenson, R A Evangelista, R L Broughton, et al. *J. Appl. Polym. Sci.*, 1987, **34**(1) 56–83
62. N A Peppas, H J Moynihan, L M Lucht *J. Biomed. Mater. Res.*, 1985, **19**(4) 397–411
63. Th P Davis, M B Huglin *Makromol. Chem. Rapid Commun.*, 1988, **9**(1) 39–43
64. D I Val'dman, A B Kochnov, A I Val'dman, et al. *Vsesoyuznaya Konferentsiya "Radikal'naya Polimerizatsiya": Tezisy Dokladov, Gor'kii* (All-Union Conference on "Radical Polymerisation". Abstracts of Reports, Gorky), Gorky, 1989, p. 142
65. O V Suberlyak, V I Skorokhodov, A I Soshko *Kinetics of the Polymerisation of 2-Hydroxyethyl Methacrylate in the Presence of Polyvinylpyrrolidinone,* Kiev, 1985, 8 pp. Article Deposited at UkrNIINTI, 30.05.85, No. 1166
66. W G Kim, M S Jhon *J. Polym. Sci.*, 1988, **A26**(3) 859–864
67. W G Kim, S H Jeon, M S Jhon *J. Polym. Sci., Polym. Chem. Ed.*, 1987, **A25**(2) 467–474
68. S H Jeon, M S Jhon *J. Polym. Sci.*, 1989, **A27**(1) 237–244
69. G Smyth, F X Quinn, V J McBrierty *Macromolecules,* 1988, **21**(11) 3198–3204
70. W T Stevenson, M V Sefton *J. Appl. Polym. Sci.*, 1988, **36**(7) 1541–1553
71. J Chujo, H Kobayashi, Y Yamashita *Polym. Commun.*, 1984, **25**(9) 278–280

72. G A Akhmedov, A Yu Yusubov, Z G Asadov *Khimiya i Tekhnologiya Neftekhimicheskogo Sintesa i Vysokomolekulyarnykh Soedinenii* (The Chemistry and Technology of Petrochemical Synthesis and High-Molecular-Weight Compounds), Baku, 1988. Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 13.01.89, No. 326-V89
73. G A Akhmedova, Candidate's Thesis in Chemical Sciences, Institute of Petrochemical Processes, Academy of Sciences of the Azerbaijan Republic, Baku, 1991, 203 pp
74. A V Tkachev, V A Tverskoi *Copolymerisation of Hydroxyethyl Methacrylate with Methacrylic Monomers,* Cherkassy, 1987, 2 pp. Article Deposited at the ONIITEKhIM, 13.11.87, No. 1243-KhP87
75. M S Choudhary, I K Varma *J. Polym. Sci., Polym. Chem. Ed.,* 1985, **23**(7) 1917–1929
76. J R Dharia, C P Pathak, G N Babu, S K Gupta *J. Polym. Sci.,* 1988, **A26**(2) 595–599
77. R Ito, K Uchida, T Kitano, E Yamada, T Matsumoto *Polym. J.,* 1985, **17**(6) 761–766
78. D Briggs, B D Rather *Polym. Commun.,* 1988, **29**(11) 6–8
79. A V Tkachev, V A Tverskoi *Vsesoyuznaya Konferentsiya "Radikal'naya Polimerizatsiya". Tezisy Dokladov, Gor'kii* (All-Union Conference on "Radical Polymerisation". Abstracts of Reports, Gorky), Gorky, 1989, p. 36
80. T Atano, S Kanefusa, S Kadovni, Japanese Appl. 59-135 201; *Ref. Zh. Khim.,* 1985, 13S373P
81. N A Lavrov, A F Nikolaev, T S Bocharova *Zh. Prikl. Khim.,* 1989, **62**(10) 2401–2403
82. N A Lavrov, A F Nikolaev *Zh. Prikl. Khim.,* 1988, **61**(7) 1648–1650
83. N A Lavrov, A F Nikolaev, V M Chudnova *Zh. Prikl. Khim.,* 1988, **61**(7) 1646–1648
84. G Kossmehl, J Volkheimer, H Schafer *Makromol. Chem.,* 1989, **190**(6) 1253–1262
85. J Lebduška, J Snuparekml, K Kaspar *Chem. Prum.,* 1986, **36**(9) 472–475
86. N A Lavrov, N M Grinberg *Khimicheskaya Tekhnologiya Svoistva i Primenenie Plastmass* (Chemical Technology, Properties and Applications of Plastics), Leningrad, 1988, pp. 37–40
87. V Konsulov, D Kirova, N Grozeva *Khimiya Industriya,* 1987, **59**(5) 216–218
88. L R Whitlock, L M Wheeler *J. Chromatogr.,* 1986, **368**(1) 125–134
89. R P Foss, US P. 4 749 762
90. A Yada, Sh Matsumoto, Y Kawamori, Y Adachi, US P. 4 762 862
91. M S Ramakrishna, D D Deshpande, G N Babu *Angew. Makromol. Chem.,* 1985, **130** 171–178
92. N A Lisovtseva, G F Zvereva, G V Dubinkina *Vsesoyuznaya Konferentsiya "Radikal'naya Polimerizatsiya". Tezisy Dokladov, Gor'kii* (All-Union Conference on "Radical Polymersiation". Abstracts of Reports, Gorky), Gorky, 1989, p. 19
93. S Tani, K Kogo, Y Nodzaki, K Osima, Japanese Appl. 198 606; *Ref. Zh. Khim.,* 1990, 6S557P
94. Y Nabeshima, T Tsuruta *Makromol. Chem.,* 1989, **190**(7) 1635–1647
95. D Briche, D Guymord, Ph Persisse, J P Pouget, French Appl. 2 601 023; *Ref. Zh. Khim.,* 1989, 7S620P
96. V R Kamath, US P. 4 777 280
97. H-H Goeretz, A Oftring, F Voget, BRD Appl. 3 725 449; *Ref. Zh. Khim.,* 1989, 22S556P
98. M F Grenier-Loustalot, M Audenaert, J Boutillier, D Lecacheux *Eur. Polym. J.,* 1989, **25**(4) 411–418
99. O S Zaikina, S M Romaniv *Vtoraya Konferentsiya Molodykh Uchenykh Khimicheskikh Fakul'tetov RPI i LGU, Riga* (The 2nd Conference of Young Scientists from the Faculties of Chemistry at the Riga Polytechnic Institute and Leningrad State University, Riga), Riga, 1987, p. 68
100. O V Suberlyak, O S Zaikina, S M Romaniv *Kompozitsionnye Polimernye Materialy,* Kiev, 1989, (41) 51–54
101. S H O Egbow *Angew. Makromol. Chem.,* 1987, **148**(2329) 79–86
102. O Murai, T Sakai, Japanese Appl. 1 110 506; *Ref. Zh. Khim.,* 1990, 6S562P
103. B Yansen, G Ellinghorst *J. Biomed. Mater. Res.,* 1985, **19**(9) 1085–1099
104. O V Suberlyak, M L Sheketa, A I Soshko *Photopolymerisation of Liquid Compositions Based on 2-Hydroxyethyl Methacrylate and Polyvinylpyrrolidinone,* Kiev, 1985, 7pp. Article Deposited at UkrNIINTI, 23.08.85, No. 1515
105. L Sheketa, B I Bardak *Materialy 3-i Konferentsii Molodykh Uchenykh Khimiko-Tekhnologicheskogo Fakul'teta RPI, Riga* (Proceedings of the 3rd Conference of Young Scientists at the Faculty of Chemical Engineering of the Riga Polytechnic Institute, Riga), Riga, 1989, p. 78
106. O V Suberlyak, M L Sheketa *Plast. Massy,* 1989, (8) 15–17
107. O V Suberlyak, M L Sheketa, A I Soshko *Zh. Prikl. Khim.,* 1988, **61**(8) 1877–1880
108. M S Kurilo, M M Tsyunok, M M Blazhkivskii *Vestn. L'vov Politekh. Inst.,* 1989, (231) 31–33
109. O V Suberlyak, M Sh Poretskaya, G M Yaremko *Ukr. Khim. Zh.,* 1988, **54**(10) 1109–1111
110. Fang Yue-e, Shi Tianyi, Wang Wenfeng, Shi Fang *J. Appl. Polym. Sci.,* 1989, **38**(5) 821–828
111. J Coupek, S Vozka, A Frydrychova, V Smigol, Czech. P. 260 852; *Ref. Zh. Khim.,* 1990, 4S667P
112. K Das Suryya, S Porter, R Dowbenko, EEC Appl. 0 307 504; *Ref. Zh. Khim.,* 1990, 4S666P
113. N A Lavrov *Khimicheskaya Tekhnologiya Svoistva i Primenenie Plastmass* (Chemical Technology, Properties and Applications of Plastics), Leningrad, 1988, pp. 32–37
114. S Sevcik, J Stamberg, P Schmidt *J. Polym. Sci. C,* 1967, (16) 821–831
115. N A Lavrov, A F Nikolaev *Plast. Massy,* 1984, (8) 55–57
116. F Ibragimov, T I Usmanov, T G Gafurov *Vysokomol. Soedin., Ser. A,* 1970, **12**(11) 2621–2624
117. N A Lavrov, V M Chudnova, A F Nikolaev *Zh. Prikl. Khim.,* 1986, **59**(7) 1554–1558
118. A F Nikolaev, N A Lavrov, S G Bondarenko, V Bondarenko, USSR P. 891 689; *Otkrytiya. Izobreteniya,* 1981, (47) 111
119. N A Lavrov, A F Nikolaev, Yu V Solomatin *Zh. Prikl. Khim.,* 1987, **60**(11) 2616–2618
120. N A Lavrov, V M Bondarenko, A F Nikolaev, S N Sautin *Vysokomol. Soedin.,* 1981, **23** 142–144
121. N A Lavrov, A F Nikolaev, Yu V Solomatin *Zh. Prikl. Khim.,* 1987, **60**(1) 167–170
122. W Schössler, J Coupek, F Hiepe DDR P. 256 720; *Ref. Zh. Khim.,* 1988, 22S569P

123. J Kahovec, M Jelinkova, J ACoupek *Polym. Bull.*, 1987, **18**(6) 495–499
124. M R Van de Mark, N D Lian, M Brandon, E C Eckstein *J. Polym. Sci.*, 1987, **C25**(8) 327–330
125. J Kahovec, M Jelinkova, J A Coupek, Czech. P. 253 004; *Ref. Zh. Khim.*, 1989, 13S512P
126. M Jelinkova, J Kahovec, J A Coupek, Czech. P. 251 117; *Ref. Zh. Khim.*, 1989, 3S669P
127. Y Takahashi, V Foyle, J E Guillet, *IUPAC 32nd Int. Symp. Macromol. Kyoto, Prepr-Kyoto,* 1988, p. 185
128. N A Lavrov, A F Nikolaev *Plast. Massy,* 1984, (4) 10–12
129. O Wichterle, D Lim *Nature,* 1960, **185** 117
130. N A Lavrov *Khimicheskaya Tekhnologiya, Svoistva i Primenenie Plastmass* (Chemical Technology, Properties, and Applications of Plastics), Leningrad, 1987, pp. 26–36
131. N A Lavrov *Khimicheskaya Tekhnologiya, Svoistva i Primenenie Plastmass* (Chemical Technology, Properties, and Applications of Plastics), Leningrad, 1989, pp. 77–84
132. S G Starodubtsev, O K Boiko, N P Pavlova, V A Kabanov *Plast. Massy,* 1985, (1) 30–33
133. J Vacik, B Obereigner, D Souckova, J Kudelkova, K Smetana *IUPAC 32-nd Int. Symp. Macromol. Kyoto, Prepr.-Kyoto,* 1988, p. 591
134. O V Suberlyak, O S Zaikina, I G Tkhir, A I Soshko *Plast. Massy,* 1985, (11) 27–29
135. H Singh, P Vasudeva, A R Pay *J. Sci. Ind. Res.*, 1980, **39**(3) 162–171
136. P Yoshida, M Kumakura, I Kaetsu *J. Macromol. Sci. A. Chem.*, 1980, **14**(4) 555–569
137. M Kumakura, I Kaetsu *J. Polym. Sci., Polym. Lett. Ed.*, 1983, **21**(8) 609–613
138. M Kumakura, I Kaetsu *J. Appl. Polym. Sci.*, 1983, **28**(12) 3759–3765
139. M Kumakura, I Kaetsu *J. Dispers. Sci. Technol.*, 1983, **34**(2) 147–159
140. K F Mueller, W R Good *AIChE Symp. Sec.*, 1981, **77**(206) 42–51
141. J M Collett, D Attwood, J M Wodd *Am. Chem. Soc., Polym. Prepr.*, 1983, **24**(1) 62–63
142. N M Franson, N A Peppas *Am. Chem. Soc., Polym. Prepr.*, 1983, **24**(1) 53–54
143. J Kopecek *Abstracts of Papers, 194th American Chemical Society National Meeting,* New Orleans, 1987, p. 753
144. J H Me Jain, R D Jarrett, US P. 4 737 544
145. C Migliaresi. L Nicodemo, L Nicolais, P Passerini *J. Biomed. Mater. Res.*, 1984, **18**(2) 137–146
146. C Migliaresi, L Nicodemo, L Nicolais, P Passerini *Polymer,* 1984, **25**(3) 686–689
147. N A Lavrov, F A Kuz'mina, M V Vinogradov *Khimicheskayo Tekhnologiya, Svoistva i Primenenie Plastmass* (Chemical Technology, Properties and Applications of Plastics), Leningrad, 1988, pp. 148–151
148. L Pinchuk, E C Eckstein, M R Van de Mark *J. Appl. Polym. Sci.*, 1984, **29**(5) 1749–1760
149. J Verhoeven, R Scheffer, J A Bowstra, H E Junginger *Polymer,* 1989, **30**(10) 1946–1950
150. L Pinchuk, E C Eckstein *J. Biomed. Mater. Res.*, 1981, **15**(2) 183–189
151. K Ito, Y Masuda, T Shintani *Polym. J.*, 1983, **15**(8) 557–583
152. M F Refogo, F L Leong *IUPAC 28th Macromolecular Symposium. S. l.*, Amherst, 1982, p. 725
153. I G Tkhir, O V Suberlyak, V P Stadnik, A I Soshko *Zh. Prikl. Khim.*, 1983, **56**(10) 2250–2254
154. S Wisniewski, Wan Kim Sung *J. Membr. Sci.*, 1980, **6**(3) 299–308
155. S C Yoon, M S Jhon *J. Appl. Polym. Sci.*, 1982, **27**(12) 4661–4668
156. E V Lamberti, R Evangelista, M A Wheatley, et al. *Polym. Biometer. Proc. Symp.*, New York–London, 1984, pp. 39–50
157. T Fukuda, I Takeuchi, I Fukumori, Japanese Appl. 1 113 322; *Ref. Zh. Khim.*, 1990, 5S566P
158. H Ahne, W Plundrich, BRD Appl. 3 630 954; *Ref. Zh. Khim.*, 1989, 3S668P

Translated from *Uspekhi Khimii* **61** 1025–1046 (1992) U.D.C. 547.458.68:541.49:543.454(048.8)

Induced optical activity in cyclodextrin complexes

Yu A Zhdanov, Yu E Alekseev, E V Kompantseva, E N Vergeichik
Scientific-Research Institute of Physical and Organic Chemistry, Rostov State University
Pyatigorsk Pharmaceutical Institute

ABSTRACT. The phenomenon of induced optical activity (IOA) is briefly described. The IOA that occurs in complexes of cyclodextrins (CYDs) with achiral and chiral organic molecules is examined. The types of information obtained using chiroptical spectroscopic methods are described. It is shown how these methods in conjunction with the theoretical representation of this phenomenon can be used to obtain information about the fine structure of the complexes, including the orientation of the "guest" molecule in the cavity of the "host" molecule, the formation of two-guest complexes, and the selection of chiromers by complexation.

The bibliography includes 188 references.

Contents

I.	Introduction	563
II.	Induced optical activity	563
III.	Information obtained from interpretation of the chiroptical properties of cyclodextrin complexes	564
IV.	Conclusion	572

I. Introduction

Rapid progress in the chemistry of cyclodextrins has occurred because of the unique ability of these compounds to react with a large number of organic and inorganic compounds to form complexes of the type "host–guest" (H–G),[7] which are classed as virtual topological isomers,[8] and it is very closely related to the development of a new topic–supramolecular organic chemistry.[9] As a result of this property CDXs can be used as models of enzymes,[3,10] catalysts of chemical reactions,[11] modifiers of pharmaceutical compounds,[12–14] and in a number of other areas of science and industry.[14]

One of the most important properties of CDXs that distinguishes them from the majority of synthetic hosts, such as podands, coronands, cryptands, etc.,[7] is their chirality, namely the property that distinguishes a compound from its mirror image.[15] It is true that the overall chirality of CDX molecules is regarded as insignificant because of their symmetrical structure,[16] but sufficient information has been collected for the chiral field of the CDX cavity to be considered capable of inducing optical activity in the electronic transitions of the guest molecule. In this review an attempt is made for the first time to correlate these data in order to demonstrate the potentialities of chiroptical methods, induced optical rotatory dispersion (IORD), and principally induced circular dichroism (ICD) for studying the fine structure of CDX complexes.

II. Induced optical activity

Induced optical activity (IOA) denotes[17] the induction of optical activity in the molecules of an achiral compound (the chromophore) when they are in contact with the molecules of a chiral compound (the inducer). The main consequence of this interaction is asymmetric perturbation of the electronic transitions of the chromophore by the chiral field of the inducer, with the result that the transitions become optically active and are exhibited in the optical rotatory dispersion (ORD) or induced optical rotatory dispersion (IORD) spectra and circular dichroism (CD) or induced circular dichroism (ICD) spectra. The asymmetric perturbation can be so intense that it stabilises certain chiral conformers of the chromophore, thus intensifying the parameters of the ICD spectra by many times. This occurs in many CDX complexes (see below). The phenomenon of ICD occurs for low-molecular-weight chromophores, such as saturated and aromatic ketones,[18–21] aliphatic nitrites,[20–21] azulenes,[22] and free-radical hydrazines[23] in the presence of the following inducers: 2,3-butanediol,[18] menthol,[19,27] diethyl tartrate,[20] nopinone,[22] 2-octanol,[23] and *N*-cetyl-α-phenylethylamine.[24] Metal complexes can also be subject to induced optical activity[18,25–29] from butanediols,[18,26] ethyl tartrates,[25] amino alcohols,[27,29] and amino acids.[28]

High-molecular-weight inducers, in particular biopolymers, have proved more effective than low-molecular-weight inducers. Thus, polypeptides give rise to strong IOA in dyes[30,31] and bile pigments,[32] while nucleic acids produce IOA in dyes.[33–35] Carbohydrates also give rise to IOA, with both monosaccharides (in ketones[36] and metal complexes[37]) and particularly polysaccharides being active. The IOA of pyrene and tetracyanonaphthodimethane in triacetylcellulose films,[38] azo dyes and bacterial polysaccharides.[39] and chitosan[40] can be given as an example. The IOA in the complexation of amylose with iodine[41] and in the complexation of anionic polysaccharides with cationic dyes[42,43] have been studied in particular detail. The IOA produced by the cyclic oligosaccharides—cyclodextrins—is discussed in the present review. Synthetic chiral polymers also give rise to IOA,[44–47] and the inducer and chromophore can be present in the same polymer molecule.[45] The induction of optical activity by supermolecular chiral structures such as liquid crystals[48,49] and micelles[50–52] is worthy of note.

The degree of IOA depends primarily on the structure of the inducer and chromophore. If the chirality of the inducer were the only condition for IOA to occur, there would be an infinite number of inducer–chromophore systems with IOA, which does not correspond to reality. It is evident that the chirality of the inducer is a necessary but incomplete condition for IOA to occur. However, for the present it is not possible to give comprehensive details of the precise conditions (they will be briefly reviewed in the concluding section). It may simply be stated that one of the sufficient

conditions for IOA to occur is an ordered supermolecular organisation in the system polymeric inducer–chromophore which restricts the number of rotational and translational degrees of freedom of the chromophore. In fact, the most intense IOA has occurred in systems with internally organised polymeric inducers that have sections of regular spiral conformation of the polymer chain, which evidently gives rise to a chiral configuration of the chromophore molecules (the formation of an internally asymmetric chromophore). This situation occurs, for example,[43] in the system sodium carboxymethylcellulose (anionic polysaccharide, inducer)–safranine T (cationic dye, chromophore), in which the value of the apparent molar ellipticity [θ] in the ICD spectrum is 10^5.

The nonspecific inducer–chromophore interactions that occur when chromophores are dissolved in chiral solvents[18,19,21–23,26,36] or in achiral solvents with chiral additives[19,20,24,25,27–29,36,37] constitute the opposite extreme for IOA. It is thought that the inducer–chromophore interaction is a dispersion interaction, which is expressed as dispersion-induced optical activity and hence dispersion-induced circular dichroism (DICD).[37]

Since information about the relative configuration of guest–host molecules in CDX complexes may be derived from the chiroptical properties of the complexes based on a correlation between the structure and the rotational properties (see below), a brief consideration of the general theory of IOA is worthwhile.

The central model of the quantum mechanical theory of optical activity (OA) is the Rosenfeld equation[53,54]

$$R_{0k} = I_m\left\{\left\langle\psi_0\left|\overline{\mu}\right|\psi_k\right\rangle\left\langle\psi_k\left|\overline{m}\right|\psi_0\right\rangle\right\},$$

where R_{0k}, the rotatory strength of the kth electronic transition of a molecule, is generated when electric ($\overline{\mu}$) and magnetic ($\overline{m}$) dipole transition moments occur in it. The rotatory strength of the transition corresponds to the strength of the oscillator in the theory of electronic spectra and is therefore determined as the area under the band of the corresponding Cotton effect in the CD spectrum. The Rosenfeld equation, like the Schrödinger equation, requires a knowledge of the exact form of the wave functions of the ground (ψ_0) and excited (ψ_k) states of the molecule, which is known to be impracticable. That is why the quantum mechanical theory of OA is essentially a combination of different approximated approaches to the solution of the Rosenfeld equation.

The arbitrary division of a chiral molecule into achiral residues—oscillators or chromophores—forms the basis of all these approximations. At the same time it is thought that the optical activity of the electronic transitions of a given chromophore is induced by the nearest chiral centre, namely, it is induced optical activity.

One of the most widely used approximations for calculation is the Kirkwood–Tinoco theory of polarisabilities,[54–57] which is based on the rather broad assumption that it is possible to generate the rotatory strength R solely the interactions of the electric dipole transition moments of the chiral residue (inducer) and that of the chromophore. Since the electric dipole transition moment is proportional to the polarisability of the respective residue, it may be replaced experimentally by the more accessible polarisability of this residue. This theory is discussed in greater detail in Section III.

All the approaches to an approximate solution to the Rosenfeld equation essentially calculate the intramolecular IOA, so they can in principle also be used[58] to estimate intermolecularly induced optical activity, namely, IOA.

III. Information obtained from interpretation of the chiroptical properties of cyclodextrin complexes

The chiroptical properties of CDX complexes with various chromophores or guest molecules have been studied as follows:

Chromophore (guest)	Refs.
Carboaromatic compounds	59–119
benzene derivatives (including dyes)	59–88
napthalene derivatives (including dyes)	83, 85–87, 89–108
other carboaromatic derivatives	100, 109–119
Heteroaromatic compounds (including nucleic acids and their heteroaromatic components)	72, 73, 120–141
Organometallic compounds (ferrocence and its derivatives)	8, 101, 142–145
Metal complexes	81, 146–150
Carbonyl derivatives of alicyclic compounds (including prostaglandins)	151–155
Drugs	64, 65, 68, 72, 73, 128–131, 155–157

The vast majority of the above compounds fall into the category of carbo- and hetero-aromatic compounds, which is typical of COX complexes.[1,2]

Because of the symmetrical structure of CDX molecules as mentioned above,[17] their chiral cavities should not have a very marked ability to cause IOA. Another reason for this may be the generally low stability constants of these complexes,[1,2] which indicate that the chromophore is held insufficiently firmly in the CDX cavity. The experimentally determined values of [θ] lie in the region of 0.4–43 000 deg cm^2 dmol^{-1}, and in the majority of cases they gravitate to the upper end of this range, i.e., they are unexpectedly high. It is true that on the whole they are values of apparent molar ellipticity that are calculated assuming complete complexation of the guest. With the most frequently occurring guest–host molar ratio of 1 : 100 and stability constants of CDX complexes in the region of 30–3000 M^{-1} there is no doubt that complete complexation occurs.

In the vast majority of cases, studies have been made of the spectra of aqueous solutions of complexes, which are buffered in the case of proteolytic guest molecules. It has been shown, however,[142] that complexation is also possible in solutions of alcohols (ethylene glycol, diethylene glycol, triethylene glycol, etc.).

The information obtained from studies of the chiroptical properties of CDX complexes is analysed below in an order corresponding to the increase in its quantitative content.

1. Information similar to that obtained from electronic absorption spectra

The chiroptical spectra—ORD spectrum (Fig. 1*a*) (dependence of the molar rotation [M] on the wavelength λ) and CD spectrum (Fig. 1*b*) (dependence of the dichromic absorption ΔE or molar ellipticity [θ] on wavelength)—of a given chiral compound correspond to the electronic absorption spectrum of the same compound (Fig. 1*c*) in the form of a Cotton effect (positive Cotton effects are shown). If the compound is transparent in a given spectroscopic region, only a section of the electronic transition occurs in the ORD spectrum in the form of the so-called plain ORD curve (curve *AB* in Fig. 1*a*) and there is no Cotton effect in the CD spectrum or peak in the electronic absorption spectrum.

CDX complexes are particularly convenient for a study of their chiroptical properties, since CDXs as inducers (hosts) are transparent in the accessible spectroscopic region, while the chromophores (guests) listed above have at least one electronic transition in this region.

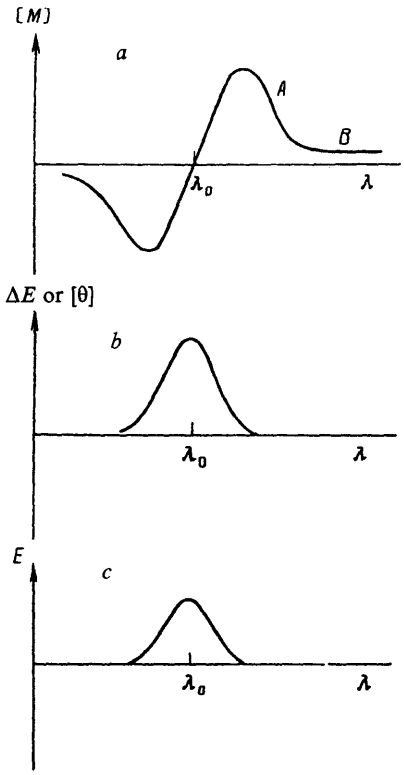
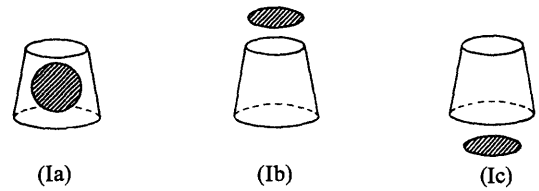


Figure 1. Cotton effects of a chiral compound with an electronic transition at λ_0 (*c*) in the ORD (*a*) and CD (*b*) spectra.

The ORD spectra of all CDXs comprise intense positive plain curves which mask possible induced Cotton effects (ICEs) of the chromophores in the ORD spectra of CDX complexes. Therefore, such spectra have little informative value. Thus, in the first study[108] on complexation with CDXs using chiroptical methods, ORD spectroscopy was used, with dyes serving as chromophores. In this case the Cotton effects appeared as weak deviations from a plain positive ORD curve on the sections of the spectrum corresponding to absorption of the dye in the UV spectrum. These deviations were largest for the dye Congo red and α-CDX. The assumption made from these observations that a complex is formed was, however, disrupted by Takeo and Kuge,[71] who used CD spectroscopy. It appeared that the deviations from the plain ORD curve discussed by Sensse and Kramer[108] were of the same order as the background noise of the instrument.

The ORD spectrum of a CDX complex contains additional rotatory contributions of the CDX molecule both through the slight change in conformation of the CDX on complexation and through induction of optical activity in the CDX molecule on the part of the guest molecule. The question concerning the methods of obtaining this information from the ORD spectra of CDX complexes still remains open.

In studies of the chiroptical properties of CDX complexes with azo dyes, much more accurate results in the form of several induced bands of the Cotton effect corresponding in wavelength to the electronic transitions of the dye were obtained.[106,107] It is true that the occurrence of an induced Cotton effect in the ICD spectra of a mixture of the guest and CDX in aqueous solution is merely an indication of complexation, which does not have to result in the formation of a G–H complex (1a) but may be restricted to conventional molecular complexes † of type (1b) or (1c).



In the studies of Suzuki and Sasaki[106,107] structures of type (1a) were unequivocally chosen because of additional information obtained from ^{1}H NMR spectra. This choice can be made with sufficient assurance when the following arguments are applied:

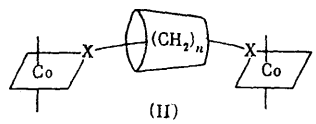
1. the cavity of the CDX molecule is hydrophobic[1–3] since it is formed by C–O–C and C–H bonds. Hence, the formation of complexes of type (1a) is assisted by guest molecules or their residues of a hydrophobic nature.

2. The size of the guest molecule must not exceed the diameter of the CDX molecule.[1–3]

3. The degree of IOA rises to a maximum in complexes of type (Ia), since contact between the inducer and chromophore is greatest in this case.

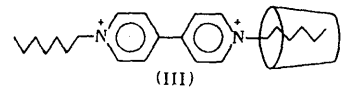
Thus, in a study of the ICD spectra of β-CDX complexes with hydrophobic uracil derivatives,[131] the choice was made in favour of structures of type (Ib) and (Ic) on the basis of the small values of [θ]. A similar choice was made by Blais et al.[134] in a study of the IORD spectra of β-CDX complexes with hydrophobic derivatives of isonicotinic acid.

Complexation of CDXs with a chromophore has only a slight effect on its chiroptical properties if a part of the chromophore contained in the cavity of the CDX is transparent in the spectroscopic region used. Thus, in the spectra of rotaxanes (II)[146–148]



(II)

X = N, S,



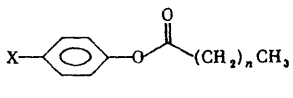
(III)

obtained as a mixture of diastereomers a very weak induced Cotton effect has been detected[146] in the visible region, which is probably

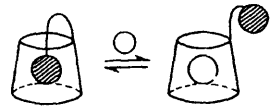
† Here and subsequently we shall use the standard notation[1–3] of a CDX molecule as a truncated cone on whose base are located the secondary hydroxyl groups and on the opposite side are located the primary hydroxyl groups of the CDX's α-*D*-glucopyranose residues.

caused because there is only a weak interaction between the chelate centres and hydroxyl groups in the CDX [contribution from complexation of type (Ib) and (Ic)]. At the same time pure diastereomers of (II) exhibit very strong Cotton effects[147,148] in this region of the spectrum, due to the chirality of these chelate centres. The even more intense induced Cotton effect in the case of the related heptylviologen complexes (III) is evidently caused by the large contribution from complexation of type (Ib) and (Ic).[122] It is interesting to note that in this case complexation cannot be detected in the Raman spectrum or ^{1}H NMR spectrum.

Competition between the aromatic and acyclic residues of *p*-substituted phenyl alkanoates (IV) for inclusion in the cavity of CDXs has been observed[76] in the ICD spectra as a progressive decrease in intensity of the aromatic induced Cotton effects with increase of n, while inclusion of the aromatic residue still occurs when $n = 6$ for α-CDX and at $n = 5$ for β-CDX. In all of these examples inclusion of the hydrophobic aliphatic residues is preferred, which clearly demonstrates the hydrophobic nature of the CDX cavities.



(IV)

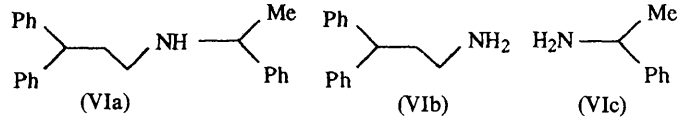


(Va) (Vb)

Complexation of CDX with a spectroscopically transparent guest can be detected in ICD spectra if at the same time a spectroscopically opaque guest is displaced from the CDX cavity. This situation occurs[81,92,136,138] in CDX complexes of type (Va) which are functionalised with an opaque chromophore (naphthyl,[92] a nucleic base,[136,138] nitrophenylacyl[81]). When a transparent chromophore (sodium 1-adamantanecarboxylate,[81,92,136,138] cyclododecanol,[92] 1-adamantylammonium chloride[81]) is added in increasing concentration to aqueous solutions of these complexes, the induced Cotton effect in the ICD spectrum gradually disappears as a result of the formation of complex (Vb). A more complex example of this type is provided by complex (Va) with an *N*-methylacetyl residue as a chromophore located in the cavity.[153] The induced Cotton effect of this complex in the region of amide absorption decreases with the addition of conjugated cyclohexanone derivatives, but an induced Cotton effect appears and then increases at the longer-wavelength region of conjugated carbonyl. Furthermore, this competing complexation can be used to determine the stability constants of CDX complexes with transparent chromophores (see below).

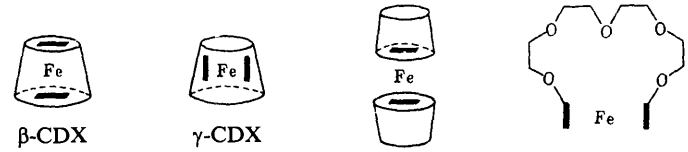
Qualitative information on complexation obtained from ICD spectra is by no means limited to these examples. This information is particularly useful for studying the complexation of CDXs with pharmacological compounds. Thus, the IOA which occurred in ORD[134] and CD[78,131,155] spectra constituted decisive evidence for the complexation of CDXs with derivatives of isonicotinic acid,[134] uracil,[131] indomethacin,[78] and prostaglandins.[155]

The fruitful approach of modelling in the interpretation of ICD spectra has been demonstrated[82] by a comparison of the ICD spectra of complexes of β-CDX with the drug fendiline (VIa) and models of its residues, 3,3-diphenylpropylamine (VIb) and 1-phenylethylamine (VIc). From the similarity between the ICD spectra of complexes of β-CDX with fendiline (VIa) and with 3,3-diphenylpropylamine (VIb) it was possible to conclude that the diphenyl residue of fendiline was included in the β-CDX cavity.



(VIa) (VIb) (VIc)

A semi-quantitative interpretation of ICD spectra using absolute values of the dichroic absorption ΔE or molar ellipticity [θ] may in certain cases provide a fairly reliable assessment of the stability of the respective complexes. In principle a direct correlation between the stability constants K and the corresponding values of ΔE or [θ] is not to be expected, since the latter incorporate the rotatory strength[53] (see the Rosenfeld equation), which is known not to depend on K but which is governed by the geometry of the G–H complex. Thus, in studies of the complexation of ferrocene with CDXs using ICD[8,142–144] it has been established that a strong induced Cotton effect occurs in the β-CDX complex, a weak effect occurs in the γ-CDX complex, while the α-CDX complex does not exhibit IOA, although according to other information complexes are formed in all cases. The proposed structures (VIIa–c) have geometries that are too diverse for comparison to be made from the magnitudes of the induced Cotton effects. Of these the structure (VIIa) has been demonstrated[145] by means of modelling. The ferrocene-containing crown ether (VIId),



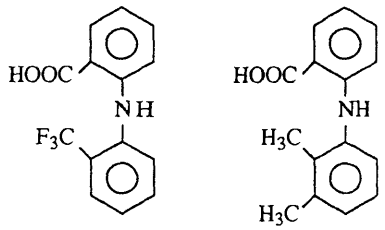
β-CDX (VIIa) γ-CDX (VIIb) α-CDX (VIIc) (VIId)

which can only be included equatorially, exhibited an induced Cotton effect when complexed with β-CDX that was opposite in sign to that of complex (VIIa). This correlation between the geometry of the complex and the sign of the corresponding induced Cotton effect will be discussed in detail below.

However, in certain systems (same chromophore—different CDXs, same CDX—structurally related chromophores) with similar fixed geometries a qualitative correlation between [θ] and the stability of the complex may occur. For example, in the complexation of α- and β-CDX with cyclohexanone[151] and cyclopentanone[154] the magnitudes of the induced Cotton effects of the α-CDX complexes proved to be greater than those for the β-CDX complexes. This result is consistent with the cavity sizes of the two CDXs.

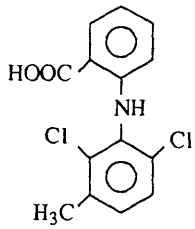
In a number of complexes of structurally related chromophores (VIIIa–c) with β-CDX a parallel decrease in intensity of the induced Cotton effect and stability of the complexes has been observed.[64] However, this pattern no longer occurs for the similar derivatives (VIIId), which are more extensively varied,[63] although [θ] increases with an increase in size of the CDX cavity, i.e., in the series α-CDX < β-CDX < γ-CDX. For *ortho* compounds [θ] is

considerably lower than for *meta* and *para* derivatives, which is apparently due to the nonplanar structure of the chromophore

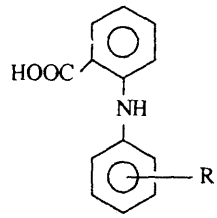


(VIIIa)

(VIIIb)

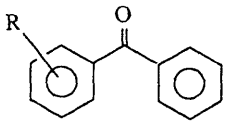


(VIIIc)

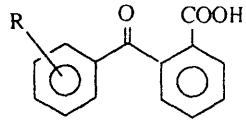


(VIIId)

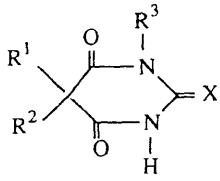
in the first case. There is also no correlation between [θ] and K in complexes of substituted benzophenone (IXa) and benzoic acids (IXb), barbiturates and thiobarbiturates (X),[128,129]



(IXa)



(IXb)



(X)

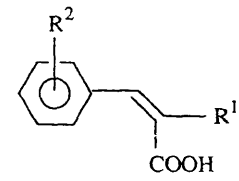
$R^1 = CH_3(CH_2)_n$ ($n = 0-6$), Ph;
R^2 = MeEt, R^3 = H, Me; X = O, S.

and probably in the majority of similar cases. Consequently, assumption of a correlation between [θ] and K should be treated with considerable caution, even if it is supported by matching the size of the chromophore and the radius of the CDX, the study of molecular molecules being particularly useful in this case.

According to the theory of optical activity, a more intense electronic transition corresponds to a lower rotatory strength and vice versa. Therefore, the anisotropy factor g—the ratio of the dichroic absorption ΔE to the extinction coefficient E or the equivalent ratio involving [θ]—may be regarded as a generalised characteristic of a chiral molecule:

$$g = \Delta E/E = \theta/3300E.$$

Cases where there is agreement between g and the stability of complexes are, however, fairly rare. They occurred in a number of phenylanthranylic acids (VIIIa–c)[64] and (VIIId)[65] and cinnamic acids (XI),[70]



(XI)

R^1 = H, Me;
R^2 = Me, Cl, OH, NO_2

but not in barbiturates (X).[129] A comparison of the values of g obtained at different CDX concentrations with the literature data was used[78] to estimate the stability of β-CDX complexes with the drug indomethacin. The use of g instead of [θ] evidently has no particular advantages.

The stability constant K—the most reliable criterion of the stability of a complex—may be determined by means of ICD using the same methods as for UV spectroscopy, since in essence the CD spectra represent a modification of the UV spectra (see Figs. 1*b* and 1*c*). The simplest method of Hildebrand and Benesei[158,159] used in several studies[60,67,69,85,143] has been applied quite extensively together with the modification of Scott[160] used by Otagiri et al.[124] and the modification of Rose and Drago[161] used by Harata.[75] The approximation of Mack[162] was used in three studies[87,98,101] while the approximation of Monk[163] was used by Formoso.[135,137]

The least squares method has become the most widely used of the calculation methods.[62,74,92,154] Individual cases are represented by the adjustment method[156] and nonlinear regression analysis.[130] Computational methods will probable find considerable application as a result of the computerisation of chemical calculations. In certain studies[63,136,138,153] no indication of the method of determination is given.

All these methods are applicable to complexes with an established or assumed 1 : 1 composition. In certain cases the composition was determined[60,67,70,120,142] using ICD with the method of continuous variations of the composition. Calculation of K from the ICD data at different temperatures made it possible[67,74,75,85] to determine the thermodynamic parameters of complexation. The phenomenon of displacement of an opaque chromophore by a transparent chromophore from the CDX cavity was used[81,92] to determine K for the complex of a transparent chromophore with CDX by means of ICD spectroscopy. The possibility of determining the composition of complexes polarimetrically was demonstrated by Giordano et al.[152]

2. Specific information

In this section an analysis is made of the specific information on CDX complexes which in principle cannot be obtained by methods other than chiroptical spectroscopy methods and which is based on the pseudoscalar property of the Cotton effect—its sign. The quality of such information is considerably improved by the applicaton of OA theory.

Interpretation of the CD spectra of CDX complexes with chiral chromophores[73,74,135–141,150–152,154–157] is frequently made difficult because the small induced Cotton effects are masked by the more intense inherent Cotton effects of the chromophore. In some cases[73] it is possible to limit this by recording the CD spectra of CDX complexes with both enantiomers of the chromophore, and the absence of mirror reflection properties suggests that complexation is occurring. A lack of change in the CD spectrum of one of the enantiomers of a chromophore when CDX is added to it may indicate[73] the absence of complexation. Otherwise[137] it may be a reliable indication of complexation, while the extent of change between the CD spectra of the initial enantiomer of the chromophore and its mixtures with different CDXs is proportional[155] to the degree of complexation. The changes in the CD spectra of a pure enantiomer on addition of CDX may be significant if the chromophore contains achiral residues that can undergo complexation and bulky chiral residues, such as in the case of *p*-nitrophenylglycoside.[74] Calculation of the stability constants in these cases[73,74,135–137,154] is complicated by the fact that the apparent values of [θ] include the inherent and induced ellipticity of the chromophore.

The superior sensitivity of CD spectroscopy over UV spectroscopy is particularly evident in the case of CDX complexes with chiral chromophores. Thus, according to the data from differential UV spectroscopy,[164] β-CDX selectively complexes the monophosphates of adenosine and inosine, while according to the data of CD spectroscopy[135,137] this type of complexation occurs for all nucleotides. Thus the idea of using CDXs as probes for the structural analysis of nucleic acids can be rejected. From the CD spectra of CDX complexes with chiral guests it is possible to distinguish drugs qualitatively,[73] especially between chiral and achiral ones, while it is possible to identify cocaine quantitatively.[156] The complex of a chelated pyridoxal aldimine with γ-CDX has been successfully used[150] for studying the kinetics of the stereodifferentiating transamination of phenylpyruvic acid with pyridoxamine.

Let us now consider the correlation between the magnitude and sign of rotation of the Cotton effect, on the one hand, and the geometry of the inclusion of the guest, on the other hand. Specific definition of the Rosenfeld equation in terms of the geometric parameters of specific chiral molecules, based on the classical theory of interacting oscillators[165,166] and the principle of pairwise interactions,[167] led Kirkwood[168] to develop the first "practical" quantum-mechanical theory of optical activity that could be used to calculate the rotational parameters of simple chiral molecules. Starting from the concept of a molecule as a combination of arbitrarily discrete groups (chromophores) that are not exchanging electrons with each other (this concept was subsequently developed as the "discrete chromophore model"),[169] Kirkwood represented[56,168] the rotatory strength of such a molecule as the sum of several terms, one of which represents the interaction between electric dipole transition moments of different chromophores (which is true under certain conditions) and replaced these values with the polarisabilities of the respective groups, which are proportional to them, the latter being values that are more easily obtained experimentally. Kirkwood derived a relatively simple formula for calculating rotatory strength. Tinoco[55] subsequently developed the theory of Kirkwood in relation to polymers and put forward a more general equation for rotatory strength. Harata[62,90] used the Kirkwood–Tinoco equation in a form that was suitable for calculating the rotatory strengths of cyclodextrin complexes in the jth transition from the ground state 0 to an excited state a:

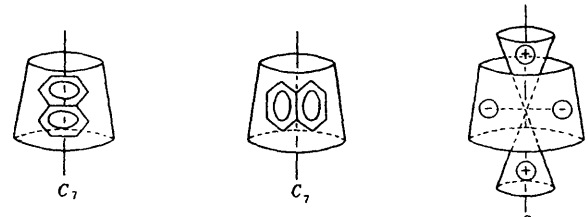
$$R_{0aj} = \frac{\pi \nu_a \nu_0^2 \mu_{0a}^2 \left(\alpha_{33} - \alpha_{11}\right)_j \left(GF\right)_j}{c\left(\nu_0^2 - \nu_a^2\right)},$$

$$\left(GF\right)_j = \left[\frac{1}{r_j^3}\vec{e}_{0a}\vec{e}_j - \frac{3\left(\vec{e}_{0a}\vec{r}_j\right)\left(\vec{e}_j\vec{r}_j\right)}{r_i^2}\right]\vec{e}_{0a}\vec{e}_j\vec{r}_j,$$

$\vec{e}_{0a}$ is the unit vector along the electric dipole transition $\vec{\mu}_{0a}$ of the guest chromophore; ν_a is the corresponding frequency; $\vec{e}_j$ is the unit vector along the axis of symmetry of the jth group; r_j is the distance from the chromophore to the jth group with frequency ν_0; α_{33} and α_{11} are the electric polarisabilities, corresponding to the parallel and perpendicular axes of symmetry of the jth group.

The origin of the system was located in the centre of the CDX molecule, while the z axis passed up along the C_7 axis (in the case of β-CDX). The C–O and C–C bonds in the α-*D*-glucopyranose residue of the β-CDX molecule were regarded as the jth groups with the corresponding tabular values of α_{11} and α_1. The frequency ν_0 of the host was taken from the absorption spectrum of cyclohexanol as a model compound while the values of μ_{0a} for the ^1L_a and ^1B_b transitions of the naphthalene ring for which r was calculated were taken from literature data. The details of the calculations are given in a study of Shimizu et al.[60] For the complexes of β-CDX with naphthalene derivatives that were studied, the calculated values of R differed from the experimental values by a factor of several times, which suggests that there was a small interaction in this case, but the predicted signs proved to be correct. As a result the following rule was developed (the rule of Harata):

If the electric dipole transition moment μ in the chromophore is aligned parallel to the C_7 axis of the symmetry of the β-CYD molecule, the corresponding induced Cotton effect is positive (+ICE). When μ is aligned perpendicular to this axis the induced Cotton effect is negative (−ICE). On the basis of this rule it was concluded that inclusion of the guest was axial (XIIa) rather than equatorial (XIIb), since the induced Cotton effect of the ^1L_a transition directed along the long axis of the naphthalene molecule proved to be positive. The rule of Harata is evidently valid for all CDXs.



(XIIa) (XIIb) (XIIc)

Shimizu et al. subsequently performed similar calculations of the rotatory strengths of β-CDX complexes with substituted benzenes[59,60] and azanaphthalenes.[120] Without starting the rule of Harata as such, the authors merely concluded that inclusion of these chromophores was axial. The rule of Harata was used to establish the form of inclusion of aromatic chromophores in CDX complexes,[77,79,93,119] and to postulate a "lid-type" complex (Ib) between 1,3,6,8-pyrenetetrasulphonate anion and β-CDX[111] with induced Cotton effects of the same sign as well as an axial complex between β-CDX and a nickel complex of a 14-membered macrocyclic

tetraamine.[149] In the latter case, because of the correspondence between the Cotton effect and the $d-d$ transitions, the method was considered to be useful in studying $d-d$ transitions.

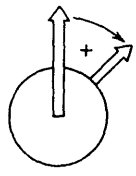
The reverse problem—to establish the direction (polarisation) of the electric of the electric dipole transition moment from the ICD spectra of CDX complexes of known structure—was resolved in four studies.[94,96,102,109] The method used for this was an improvement on those proposed previously which were technically more complex methods for determination of the direction of polarisation in oriented polymer films[170] or in cholesteric liquid crystals.[171] However, the new method is not suitable for chromophores of low symmetry or when there are strongly overlapping transitions of opposite sign.[120]

The rule of Harata has been stated more graphically[83] as a sector rule (XIIc) similar to the octant, quadrant, and sector rules in the quantitative theory of optical activity:[172–174] *if the electric dipole moment of a transition of an aromatic guest lies within a hypothetical double cone, the centre of which coincides with the centre of the CYD, and the generants form angles of 30° with the C_7 axis, the rotatory strength and the corresponding induced Cotton effect will be positive, while the same parameters that are induced by an electric dipole transition moment outside this cone will be negative. The maximum positive anisotropy factor g is approximately twice as high as the maximum negative g, corresponding to the maximum, negative induced Cotton effect of the electric dipole moment of the transition perpendicular to the C_7 axis.* This is in agreement both with the Kirkwood–Tinoco calculations[60] and with the experimental results.[83]

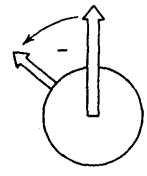
The eminent theoretician in the field of IOA, P E Schipper, having given the equation for the induced rotatory strength of a guest in a generalised form according to the model of interacting oscillators, demonstrated[175] that the correlation between the geometry of the complex and the sign of the induced Cotton effect, corresponding to the rule of Harata, is derived automatically from this equation on the basis of general selection rules for chromophores in perturbing fields.[176]

It was also possible to use the rule of Harata to assign the vibrational bands of aromatic chromophores in complexes of monosubstituted benzenes[61,66] and the 4,4-bipyridyl radical.[123]

The theory of interacting oscillators[17,177,178] represents the interaction of two chromophores that are identical or have a similar structure in terms of exciton theory[179] and it predicts the so-called Davydov splitting of the corresponding absorption band of the interacting chromophores. In the UV spectrum this splitting is insignificant and frequently does not occur, whereas in CD spectra the Davydov (exciton) splitting appears as a double Cotton effect of opposite sign, the so-called exciton couplet, which is positive (Fig. 2*a*) or negative (Fig. 2*b*) depending on whether the relative configuration of the electric dipole of the transition of these chromophores forms part of a right-handed (XIIIa) or left-handed (XIIIb) spiral respectively in the Newman projection.[17,177]



(XIIIa)



(XIIIb)

The electric dipoles of transitions approximate to the projections of planes of rings in the case of aromatic and heteroaromatic chromophores or to C=O bonds for carbonyl chromophores.

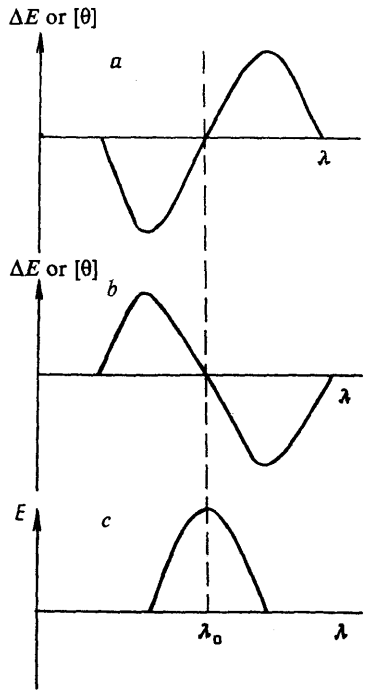
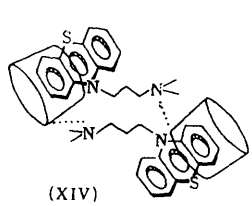


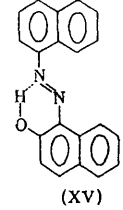
Figure 2. CD spectra with positive (*a*) and negative (*b*) exciton couplets by the absorption band at λ_0 in the UV spectrum (*c*).

The simple and graphic rule of exciton chirality has been extended to a determination of the absolute and relative configuration of natural compounds.[180] It has also recently successfully "started to work" in the field of CDX complexes, primarily in cases of the dimerisation of one-guest complexes or the formation of two-guest complexes.

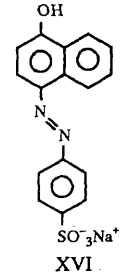
In a study of the complexation of β-CDX with phenothiazine tranquillisers it transpired[124] that 1:1 complexes with chlorpromazine and related derivatives with long alkyl substituents on the nitrogen atom have excited couplets in their ICD spectra, which may suggest that dimers (XIV) are formed through hydrogen bonding of the alkyl chains. An analogous dimeric structure was assigned[117] to a complex between β-CDX and benz[*b*]anthracene on the basis of similar arguments.



(XIV)

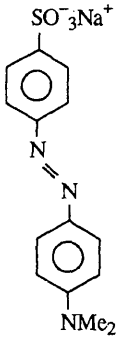


(XV)

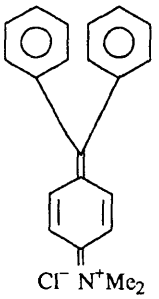


XVI

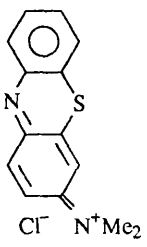
Reaction of chloropromazine with γ-CDX in aqueous solution gives a 2:1 complex (two-guest complex),[125] which was supported[115] by the observation of a negative exciton couplet in the ICD spectrum corresponding to a negative angle between the two chromophores as in structure (XIIIb), i.e., a laevospiral chirality of the guest dimer [(*S*)-chirality according to Cahn, Prelog, and Ingold]. Similar phenomena were observed in complexes of γ-CDX with a number of dyes such as roccellin (XV),[104] tropaeolin 000 (XVI),[103] methyl orange (XVII),[87,88] crystal violet (XVIII),[87] methylene blue (XIX),[87] and acridine orange (XX),[100] and the exciton couplets occurred in both the visible and ultraviolet regions of the spectrum.



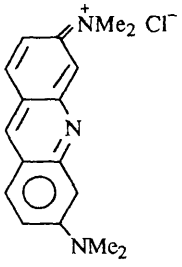
(XVII)



(XVIII)



(XIX)

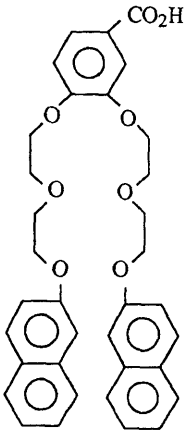


(XX)

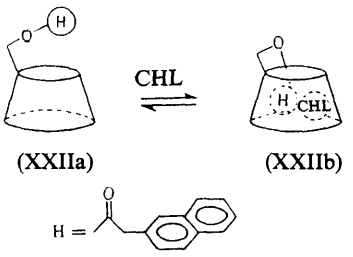
When β-CDX or γ-CDX is added to a mixture of a donor (naphthalene derivatives) and acceptor (nitrobenzene derivatives), a change in colour of the solution occurs and two Cotton effects of opposite sign (possibly an exciton couplet) appear in the charge-transfer region of the ICD spectrum, suggesting that a D^+A^- complex enters the CDX cavity.[85]

In the case of luminescent guests, the formation of two-guest complexes is also detected in the luminescence spectra. Thus, the formation of a (pyrene)$_2$-γ-CDX complex, detected by Kobayashi et al.[113] from its negative exciton couplet in the CD spectrum, was confirmed[114] by the presence of an excimer band in the luminescence spectra. The formation of an (anthracene-2-sulphonate)$_2$-γ-CDX complex with a positive exciton couplet was established in a similar manner,[16] but no excimer band was observed because of rapid photodimerisation of the dimer.

It was shown[100] that naphthalene and also the bis(naphthyl) derivative (XXI) form two-guest complexes with γ-CDX that can be readily detected from the excimer emission in their luminescence spectra. There are no exciton couplets, however, in the corresponding ICD spectra. Such a situation is possible when the naphthalene rings are situated parallel to each other in the CDX cavity, corresponding to the configuration of an achiral dimer.



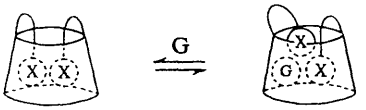
(XXI)



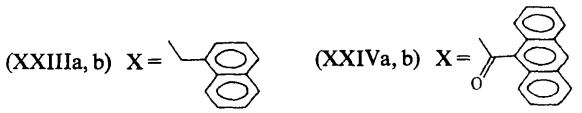
(XXIIa) (XXIIb)

Interesting results were obtained with functionalised γ-CDX. Contrary to expectation, the addition of the transparent chromophore cyclohexanol (CHL) to an aqueous solution of the derivative (XXIIa) increases[91,101] the intensity of the induced Cotton effect in the ICD spectrum, apparently because of the formation of a two-guest complex (XXIIb). A similar result was obtained[101] when the naphthalene residue in the host molecule (XXIIa) was replaced by an azobenzene or ferrocene residue.

In the ICD spectrum of a modified γ-CDX (XXIIIa) with two naphthalene residues there is a positive exciton couplet with its centre at 270 nm which corresponds to the ^1L_a absorption band of naphthalene and an excimer emission in the fluorescence spectrum, which is consistent with structure (XXIIIa). When transparent guests (adamantanecarboxylic acid, cyclohexanol, borneol) are added, the exciton couplet disappears but the excimer emission remains, suggesting that there is a conversion to structure (XXIIIb).[92,98,99] The similar conversion (XXIVa) → (XXIVb) was detected[115] by the same methods for a dianthracene derivative of γ-CDX (XXIVa).



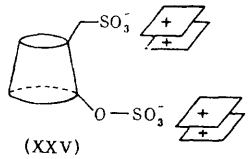
(XXIIIa) (XXIVa) (XXIIIb) (XXIVb)



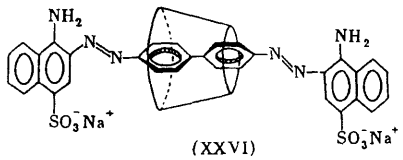
(XXIIIa, b) X = (XXIVa, b) X =

A special case occurs for the complex of acridine orange (XX) with the disulphate of β-CDX,[133] in whose spectrum a strong exciton couplet has been detected in the visible region of absorption of the dye. However, the intensity of this couplet is sensitive to pH and the ionic strength of solution, which is inconsistent with the occurrence of two dye molecules in the β-CDX cavity. It follows from the fact that such a couplet is absent from the ICD spectrum of a complex of acridine orange (XX) with glucose sulphate[181] while it is present in complexes of spiral conformations of sodium carboxymethylcellulose

with acridine orange[185] and safranine T[43,183] that the complex of β-CDX disulphate with acridine orange should be assigned structure (XXV) (the rectangles correspond to planar dye molecules).



(XXV)



(XXVI)

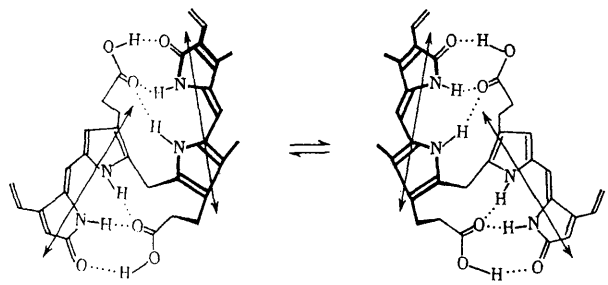
The presence of a chiral excimer can be recorded using circularly polarised luminescence spectroscopy (CPL spectroscopy),[184,185] which measures the emission anisotropy factor g_{em}.

$$g_{em} = 2(I_L - I_R)/(I_L + I_R),$$

where I_L and I_R are the intensities of emission of left- and right-handed circularly polarised light respectively. The method has so far not been widely developed mainly because of the elaborate recording equipment, and in the area of interest to use it has been used in two instances—for recording the chiral excimers of pyrene in the cavities of γ-CDX[110,112] and modified γ-CDX[110] and also for 1,3-dinaphthylpropanes in the cavity of modified γ-CDX.[110]

The dimeric guest in two-guest complexes is essentially a chromophore with its own internal[172,173] chirality (if, of course, the monomers are not parallel to each other) and therefore the components of exciton couplets are characterised by high [θ] values ($10^3 - 10^4$). With regard to the direction of chirality of the guest, it would appear that it should always be the same because of the uniform chirality of the CDX cavity. However, this is not so. While, for example, dimers of pyrene and acridine orange with γ-CDX have (*S*)-spiral chirality, the dimer of naphthalene is achiral, whereas in complex (XXIIIa) with covalently bonded naphthalene residues (*R*)-spiral chirality occurs, as in complex (XXIVa). The dimer of tropaeolin 000 (XVI) in the cavity of γ-CDX has (*S*)-chirality while in the cavity of β-CDX it has (*R*)-chirality. It is evident that the direction of this form of induced chirality is determined not only by the direction of spiral chirality of the cavity but also by the translational and rotational degrees of freedom of the guest in the host cavity.

However, ICD spectra of one-guest CDX complexes with exciton couplets have been recorded. Thus, the dye Congo red forms a one-guest complex with γ-CDX that exhibits a positive exciton couplet in its ICD spectrum.[87] This can be explained by the formation of the complex (XXVI) with one of several chiral conformers of the guest molecule located in the chiral cavity. The most studied[139–141] example of this type is complexation of CDX with the bile pigment bilirubin, which exists in aqueous solution as a mixture of interconvertible enantiomeric conformers—laevospiral (XXVIIa) and dextrospiral (XXVIIb).

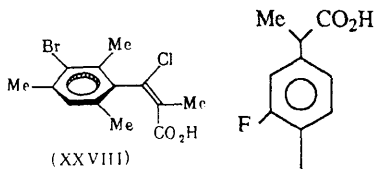


(XXVIIa) (XXVIIb)

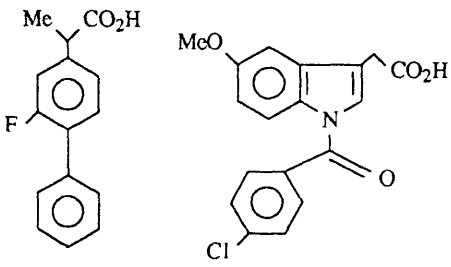
(The arrows denote the calculated directions of the electric dipole transition moments of the pyrromethene chromophores, the relative configuration of which corresponds to sections of a left- and right-handed spiral).

On complexation of bilirubin with α-, β-, and γ-CDX, negative exciton couplets were recorded with a centre at 460 nm corresponding to the absorption of bilirubin, which indicates that in the CDX cavity the specific chiral conformer (XXVIIa) has been selected from the racemate (XXVIIa, b) in aqueous solution. On similar complexation benzil and diacetyl have no exciton couplets in their ICD spectra but the high intensities of the recorded single Cotton effects ([θ] values up to 40 000 deg cm^2 dmol^{-1}) have led to the assumption[139–141] that in these cases also selection of one of the chiral conformers occurs during complexation.

Intense Cotton effects ([θ] of the order of 2600–11 900 deg cm^2 dmol^{-1}) also occurred in the complexation of cinnamic acids (XI) with α- and β-CDX. Since all the recorded intense Cotton effects were positive and the optically active (*R*)-β-(3-bromo-2,4,6-trimethyl-β-chloromethylacrylic acid (XXVIII) had a positive Cotton effect in its CD spectrum, the authors came to the fairly plausible conclusion that the guests (XI) were held in the CDX cavities as (*R*)-conformational enantiomers.



(XXVIII)



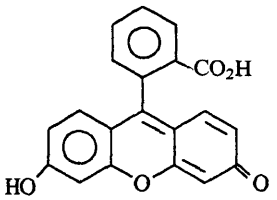
(XXIX) (XXX)

The same configuration is also selected[140] in the complexation of biphenyl derivatives with β-CDX.

An analysis of the literature data given in the present review in relation to the possible selection of chiral conformers of guest molecules when they are included in CDX cavities as indicated by high-intensity Cotton effects showed that this situation is highly probable for flurbiprofen (XXIX),[68] indomethacin (XXX),[78] and

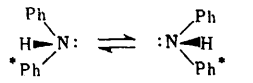
substituted barbiturates (X).[132] In the case of flurbiprofen (XXIX) this selection may occur with respect not only to the conformational enantiomer but also the configurational enantiomer (see below) because it has a chiral centre. The presence of a maximum in the region of 530 nm in the CPL spectrum of the complex of fluorescein (XXXI) with β-CDX has also been interpreted[126] as the selection of one of the chiral conformer of fluorescein during complexation.

Thus, the following conclusion is suggested: any sufficiently complex molecule having even one residue with restricted rotation can undergo complexation with CDXs as one of its rotational enantiomers. This phenomenon has been called[154] chiral conformational discrimination induced by complexation.



(XXXI)

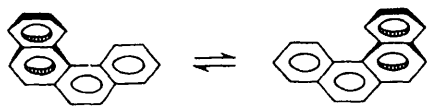
We should also note the ability of CDXs to select one of the two enantiomorphic pyramidal conformations (XXXIIa, b) of substituted diphenylamines.[65] Because of this property there is reason to expect the selection of configurational enantiomers of the type $R_1R_2R_3N$ when they are complexed with CDXs.



(XXXIIa) (XXXIIb)

The selection of configurational enantiomers has been demonstrated[151] using ICD in the complexation of racemates of 2- and 3-methylcyclohexanol with α- and β-CDX. The resolution of racemic esters[186] and sulphinyl compounds[187] using CDXs provides indirect evidence for the ability of CDXs to select configurational enantiomers of guest molecules, although the low optical yields (1–15%) indicate the limited enantiodifferentiating ability of CDX molecules with respect to small guest molecules. This conclusion has been supported[154] in the case of the complexation of α-CDX with cyclopentanol derivatives.

The enantiodifferentiating ability of CDXs probably increases for large guest molecules. At least one example of this kind is known, which relates, admittedly, to chiral conformational discrimination induced by complexation[140]—the appearance of a very intense Cotton effect ($[\theta] \simeq 40\,000$ deg cm^2 dmol^{-1}) in the ICD spectrum of the complex between γ-CDX and the racemate of 4-helicene, both enantiomers of which (XXXIIIa, b) are interconverted in solution.



(XXXIIIa) (XXXIIIb)

When the enantiodifferentiating ability of the CDX is weak, the observed ICD spectrum of the complex between CDX and racemate evidently represents the sum of the ICD spectra of the corresponding diastereomers provided that complete complexation occurs. With absolute enantiodifferentiation the opposite enantiomer is present in solution while the observed ICD spectrum essentially represents the optical activity induced by the CDX cavity in complexation of the guest enantiomer through additional hydrophobic interactions and/or hydrogen bonding of the guest with the hydroxyl groups of the host.[151] The high values of [θ] that occur for 4-helicene (XXXIIIa, b) may be due to the additional chiral distortion of the flexible conformational changes of a guest in the form of achiral and chiral molecules and a racemate in complexation with CDXs are discussed in detail by Boiswin et al.[154]

Thus, the data presented here provide a sufficiently convincing illustration of the ability of CDXs to distinguish between chiromers (conformational and configurational isomers).

IV. Conclusion

The material presented here shows that progress in the chemistry of CDXs is impossible without chiroptical spectroscopic methods[188] (ORD, CD, and CPL spectroscopy as well as infrared CD spectroscopy in the future). The most widely used method is ICD, with which it is possible to derive a variety of information about CDX complexes. Thus, an induced Cotton effect provides an indication of the complexation of a given chromophore with given CDXs, while small values of [θ] (less than 1000 deg cm^2 dmol^{-1}) most likely suggest the formation of conventional molecular complexes of type (Ib) and (Ic) and large values of [θ] (1000–10 000 deg cm^2 dmol^{-1}) indicate the presence of guest–host complexes (Ia). The shift in [θ] values to the upper end of this range may signify an increase in stability of the complex and/or a restriction of the rotational and translational degrees of freedom of the guest molecule in the CDX cavity. Even higher values of [θ] or the appearance of an exciton couplet may signify chiral conformational discrimination induced by complexation. This relates to complexes with a 1:1 composition which can be determined from the ICD spectra in the same way as the stability constants of the complexes.

If the directions of the electric dipole transition moments of an asymmetric chromophore are known, the nature of inclusion of the chromophore (axial or equatorial) in the CDX cavity can be established from the rule of Harata. If the nature of inclusion of the complex is known, the reverse problem—to establish the directions of the electric dipole transition moments of a chromophore—can be solved using the same rule.

Exciton couplets in the ICD spectra may also suggest that dimerisation of one-guest complexes is occurring or two-guest complexes are being formed.

Some of the information derived from ICD spectra (the complexation, composition, and stability constant of the complex) may also be obtained by other methods. However, the information (the geometry of the complex, dimerisation of complexes, chiral conformation discrimination induced by complexation) obtained from the pseudoscalar property of the Cotton effect—its sign—is unique, since it is impossible (or extremely difficult) to obtain it by other methods.

References

1. J Szeitli *Cyclodextrins and their Inclusion Complexes*, Acad. Kladó, Budapest, 1982, 296 pp
2. M L Bender, M Komiyama *Cyclodextrin Chemistry. Chemical Reactivity and Structure Concepts in Organic Chemistry*, Springer, Berlin–Heidelberg–New York, 1978, Vol. 6, 96 pp
3. V T D'Souza, M L Bender *Acc. Chem. Res.*, 1987, **20** 146
4. I Tabushi *Frontiers of Chemistry* (Edited by J K Laidler), Pergamon, Oxford, 1985, p. 275

5. A A Shteinman *Zh. Vses. Khim. Obshch. Ova im D I Mendeleeva*, 1985, **30** 514
6. D French *Adv. Carbohydr. Chem.*, 1957, **12** 189
7. *Chemistry of Guest–Host Complexes* (Translated into Russian), Mir, Moscow, 1988, 511 pp
8. V I Sokolov *Metalloorg. Khim.*, 1988, **1**(1) 25 [English translation in *Organomet. Chem. USSR*, 1988(1)]
9. J-M Lehn *Biomimetric Chemistry. Studies in Organic Chemistry, 13* (Edited by Z Yoshida, N Ise), Elsevier, Amsterdam, 1983, p. 163
10. R Breslow *Biomimetric Chemistry. Studies in Organic Chemistry, 13* (Edited by Z Yoshida, N Ise), Elsevier, Amsterdam, 1983, p. 1
11. Yu Sh Gol'dberg *Izbrannye Glavy Mezhfaznogo Kataliza* (Selected Chapters on Phase-Transfer Catalysis), Zinatne, Riga, 1989, p. 432
12. N P Sugrobova, E A Obol'nikova, G I Samokhalov, et al. *Khim.-farm. Zh.*, 1987, (9) 111
13. V G Belikov, E V Kompantseva *Farmatsiya*, 1983, (3) 54
14. V G Belikov, E V Kompantseva, Yu K Botezait-Belyi *Khim.-farm. Zh.*, 1986, (5) 525
15. E Ruch *Acc. Chem. Res.*, 1972, **5** 49
16. J F Stoddart *Chem. Soc. Rev.*, 1979, **8** 85
17. A D Buckingham, P J Stiles *Acc. Chem. Res.*, 1974, **7** 258
18. B Bosnich *J. Am. Chem. Soc.*, 1967, **89** 6143
19. J Bolard *J. Chim. Phys.*, 1969, **66** 389
20. E Axelrod, G Barth, E Bunnelberg *Tetrahedron Lett.*, 1969, (57) 5031
21. K Noack *Helv. Chim. Acta*, 1969, **52** 2501
22. A Tajiri, H Hirayama, M Hatano *Chem. Phys. Lett.*, 1980, **70** 22
23. S Sur, J P Colpa, L R Walker, et al. *Chem. Phys. Lett.*, 1985, **118** 522
24. S Takenaka, M Sugiyama, N Tokura *J. Chem. Soc., Perkin Trans. 2*, 1976, (5) 555
25. S F Maison, B J Norman *Chem. Commun.*, 1965, 335
26. B Bosnich *J. Am. Chem. Soc.*, 1966, **88** 2606
27. H G Brittain *Inorg. Chem.*, 1980, **19** 3473
28. H G Brittain *Inorg. Chem.*, 1981, **20** 3007
29. X Yang, H G Brittain *Inorg. Chem.*, 1981, **20** 4273
30. E R Blout *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry* (Translated into Russian), Mir, Moscow, 1970, p. 284
31. H Yamamoto, A Nakazawa, T Hayakawa, M Mitsuishi *Polymer J.*, 1984, **16** 791
32. G Blauer *Isr. J. Chem.*, 1983, **23** 201
33. K Yamaoka, R A Resnik *J. Phys. Chem.*, 1966, **70** 4051
34. K Yamaoka *Biopolymers*, 1972, **11** 2537
35. K F Kuhlman, C W Mosher, R F Hammen *Biochem. Biophys. Res. Commun.*, 1980, **92** 1172
36. L D Hayward, R N Totty *Can. J. Chem.*, 1971, **49** 624
37. P E Schipper, A Rodger *J. Am. Chem. Soc.*, 1985, **107** 3459
38. Y J I'Haya, T Yunoki *Bull. Chem. Soc. Jpn.*, 1972, **45** 3065
39. K Ogawa, M Hatano *Carbohydr. Res.*, 1978, **67** 527
40. H Yamamoto *Makromol. Chem.*, 1984, **185** 1613
41. T Handa *Biopolymers*, 1980, **19** 723
42. A L Stone *Chemistry and Molecular Biology of the Intercellular Matrix. Vol. 3. Glycosaminoglycans and Proteoglycans* (Edited by E A Balazs), Acad. Press, New York–London, 1970, p. 1067
43. Yu A Zhdanov, Yu E Alekseev, L P Vakhrushev, et al. *Dokl. Akad. Nauk SSSR*, 1986, **289** 103
44. D S Sherrington, R Sclaro, E Chiellini *J. Chem. Soc., Chem. Commun.*, 1982, (19) 1103
45. A Altomare, C Carlini, R Solaro *Polymer*, 1982, **23** 1355
46. J Beaumais, J C Fenyo, G Miller *J. Polym. Sci.*, 1980, **18** 1367
47. R N Majumdar, C Carlini, R Nocci, et al. *Makromol. Chem.*, 1976, **177** 3619
48. P L Rinaldi, M Wilk *J. Org. Chem.*, 1983, **48** 2141
49. F D Saeva, G R Olin *J. Am. Chem. Soc.*, 1973, **95** 7882
50. N Nakashima, H Fukushima, T Kunitake *Chem. Lett.*, 1981, (9) 1207
51. J N Perrin, M Wilsey *Chem. Commun.*, 1971, (14) 769
52. J N Perrin, P Idsvoog *J. Pharm. Sci.*, 1970, **59** 1525
53. L V Vilkov, Yu A Pentin *Fizicheskie Metody Issledovaniya v Khimii. Resonansyne i Elektroopticheskie Metody* (Physical Methods of Research in Chemistry. Resonance and Electrooptical Methods), Vyssh. Shkol., Moscow, 1989, p. 177
54. E Charney *Optical Rotatory Dispersion and Circular Dichroism. The Molecular Basis of Optical Activity*, Wiley and Sons, New York, 1979, 364 pp
55. I Tonoco, Jr *Adv. Chem. Phys.*, 1962, **4** 113
56. J Cosman *Introduction to Quantum Chemistry* (Translated into Russian), Izd. Inostr. Lit., Moscow, 1960, Ch. 15
57. A P Klyagina, I F Golovanova *Metalloorg. Khim.*, 1990, **3**(3) 503 [English translation in *Organomet. Chem. USSR*, 1990(3)]
58. H Falk, W Jungwirth, N Müller *Monatsh. Chem.*, 1984, **115** 455
59. H Shimizu, A Kaito, M Hatano *Bull. Chem. Soc. Jpn.*, 1981, **54** 513
60. H Shimizu, A Kaito, M Hatano *Bull. Chem. Soc. Jpn.*, 1979, **52** 2678
61. H Yamaguchi, S Abe *J. Phys. Chem.*, 1981, **85** 1640
62. K Harata *Bioorg. Chem.*, 1981, **10** 255
63. M Otagiri, J H Perrin, K Uekama, et al. *Pharm. Acta Helv.*, 1976, **51** 343
64. K Ikeda, K Uekama, M Otagiri *Chem. Pharm. Bull.*, 1975, **23** 201
65. K Ikeda, K Uekama, M Otagiri, et al. *J. Pharm. Sci.*, 1974, **63** 1168
66. H Yamaguchi, N Ikeda *Z. Phys. Chem.*, 1978, **109** 173
67. N Matsuura, S Takenaka, N Tokura *J. Chem. Soc., Perkin Trans. 2*, 1977, (11) 1419
68. M Otagiri, T Imar, F Hirayama, et al. *Acta Pharm. Suec.*, 1983, **20** 11
69. S Takenaka, N Matsuura, N Tokara *Tetrahedron Lett.*, 1974, (26) 2325
70. K Uekama, M Otagiri, Y Kanie, et al. *Chem. Pharm. Bull.*, 1975, **23** 1421
71. K Takeo, T Kuge *Stärke*, 1972, **24** 281
72. S M Han, N Purdie *Anal. Chem.*, 1984, **56** 2822
73. S M Han, W M Atkinson, N Purdie *Anal. Chem.*, 1984, **56** 2827
74. K Harata *Bioorg. Chem.*, 1980, **9** 530
75. K Harata *Bull. Chem. Soc. Jpn.*, 1978, **51** 2737
76. G B Borona, R Fornasier, P Scrimin, et al. *J. Chem. Soc., Perkin Trans. 2*, 1985, (3) 367
77. N Kobayashi *J. Chem. Soc., Chem. Commun.*, 1989, (16) 1126
78. J Szejtli, L Szente *Pharmazie*, 1981, **36** 649
79. Yu Hu, L-K Guo, M-Kh Tonch *Huaxue Xuebao*, 1984, **42** 246; *Ref. Zh. Khim.*, 1984, 22B1280

80. A Meister, G Wenz *Minutes of the 5th International Symposium on Cyclodextrins*, Edition of Santé, Paris, 1990, p. 188
81. K Fujita, T Ueda, T Imoto, et al. *Bioorg. Chem.*, 1982, **11** 72
82. A Stadler-Szoke, M Vikmon, J Szejtli, et al. *J. Inclus. Phenom.*, 1985, **3** 71
83. M Kaitar, Cs. Horvath-Toro, E Kuthi, et al. *Acta Chim. Acad. Sci. Hung.*, 1982, **110** 327
84. R J Bergeron, P McPhie *Bioorg. Chem.*, 1977, **6** 465
85. N Kobayashi, R Saito, A Ueno, et al. *Makromol. Chem.*, 1983, **184** 837
86. N Kobayashi, A Ueno, T Osa *J. Chem. Soc., Chem. Commun.*, 1981, (7) 340
87. H Hirai, N Toshima, S Uenoyama *Polym. J.*, 1981, **13** 607
88. R J Clarke, J H Coates, S F Lincoln *Carbohydr. Res.*, 1984, **127** 181
89. K Harata *Bull. Chem. Soc. Jpn.*, 1979, **52** 1807
90. K Harata, H Uedaira *Bull. Chem. Soc. Jpn.*, 1975, **48** 375
91. A Ueno, Y Tomita, T Osa *J. Chem. Soc., Chem. Commun.*, 1983, (17) 976
92. F Moriwaki, H Kaneko, A Ueno, et al. *Bull. Chem. Soc. Jpn.*, 1987, **60** 3619
93. M Ata, H Yamaguchi *J. Chem. Soc., Chem. Commun.*, 1983, (1) 3
94. M Ata, H Yamaguchi *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, 1983, (2) 297
95. J Szejtli, E Bolla-Pustai, M Kajtar *Pharmazie*, 1982, **37** 725
96. H Yamaguchi, N Ikeda, F Hirayama, et al. *Chem. Phys. Lett.*, 1978, **55** 75
97. T Yorozu, M Hoshino, M Imamura *J. Phys. Chem.*, 1982, **86** 4422
98. A Ueno, F Moriwaki, T Osa, et al. *Bull. Chem. Soc. Jpn.*, 1986, **59** 465
99. A Ueno, F Moriwaki, T Osa, et al. *Tetrahedron Lett.*, 1985, **26** 3339
100. N Kobayashi, Y Hino, A Ueno *Bull. Chem. Soc. Jpn.*, 1983, **56** 1849
101. A Ueno, T Osa *J. Inclus. Phenom.*, 1984, **2** 555
102. N Kobayashi, S Minato, T Osa *Makromol. Chem.*, 1983, **184** 2123
103. R J Clarke, J H Coates, S F Lincoln *J. Chem. Soc., Faraday Trans. 1*, 1984, **80** 3119
104. R J Clarke, J H Coates, S F Lincoln *J. Chem. Soc., Faraday Trans. 1*, 1986, **82** 2333
105. M Suzuki, Y Sasaki *Chem. Pharm. Bull.*, 1981, **29** 585
106. M Suzuki, Y Sasaki *Chem. Pharm. Bull.*, 1984, **32** 832
107. M Suzuki, Y Sasaki *Chem. Pharm. Bull.*, 1979, **27** 1343
108. K Sensse, F Kramer *Chem. Ber.*, 1969, **102** 509
109. H Yamaguchi, K Ninimiya *Spectrochim. Acta, Part A*, 1981, **37** 119
110. K Kano, H Matsumoto, Y Yoshimura, S Hashimoto *J. Am. Chem. Soc.*, 1988, **110** 204
111. N Kobayashi *J. Chem. Soc., Chem. Commun.*, 1988, (14) 918
112. K Kano, H Matsumoto, S Hashimoto, et al. *J. Am. Chem. Soc.*, 1985, **107** 6117
113. N Kobayashi, R Saito, H Hino, et al. *J. Chem. Soc., Chem. Commun.*, 1982, (12) 706
114. N Kobayashi, R Saito, H Hino, et al. *J. Chem. Soc., Perkin Trans. 2*, 1983, (7) 1031
115. F Morikawa, A Ueno, T Osa, et al. *Chem. Lett.*, 1986, (11) 1865
116. T Tamaki, T Kokuba *J. Inclus. Phenom.*, 1984, **2** 815
117. H Yamaguchi, M Higashi *J. Inclus. Phenom.*, 1987, **5** 725
118. H Yamaguchi, M Fukuda, H Takeshita, et al. *J. Chem. Soc., Faraday Trans. 2*, 1982, **78** 193
119. N Ikeda, H Yamaguchi *Chem. Phys. Lett.*, 1978, **56** 167
120. H Shimizu, T Kaito, M Hatano *J. Am. Chem. Soc.*, 1982, **104** 7059
121. H Yamaguchi, A Uchuda, F Yoneda, et al. *J. Chem. Soc., Faraday Trans. 2*, 1981, **77** 947
122. M Kodaka, T Fukaya *Bull. Chem. Soc. Jpn.*, 1986, **59** 2032
123. N Aoyagi, Y Kubozono, M Ata, et al. *Chem. Phys. Lett.*, 1986, **131** 201
124. M Otagiri, K Uekama, K Ikeda *Chem. Pharm. Bull.*, 1975, **23** 188
125. K Takamura, S Inoue, F Kusa *Chem. Lett.*, 1983, 233
126. H G Brittain *Chem. Phys. Lett.*, 1981, **83** 161
127. S P Jones, D J W Grant, J Hadgraft, et al. *Acta Pharm. Tech.*, 1984, **30** 213
128. S M Han, N Purdie *Anal. Chem.*, 1984, **56** 2825
129. M Otagiri, T Miyai, K Uekama, et al. *Chem. Pharm. Bull.*, 1976, **24** 1146
130. A L Thakkar, P B Kuehn, J H Perrin, et al. *J. Pharm. Sci.*, 1972, **61** 1841
131. Yu A Zhdanov, E V Kompantseva, N N Samarskova, et al. *Oblastnoe Soveshchanie po Fizike i Organicheskoi Khimii s Uchastiem Vuzov Severnogo Kavkaza* (Regional Conference on Physics and Organic Chemistry with the Participation of the Higher Institutes of Education of the Northern Caucusus), Rostov-on-Don, 1989, p. 74
132. L Sargi, J Blais, G Mahuzier, et al. *Minutes of the 5th International Symposium on Cyclodextrins, Paris: 28, 29, 30th March 1990*, Editions de Santé, Paris, 1990, p. 294
133. K Nishida, S Ishida, H Watanabe *Colloid Polym. Sci.*, 1976, 254 481
134. J Blais et al. *J. Photochem. Photobiol.*, 1988, **2** 455
135. C Formoso *Biopolymers*, 1974, **13** 909
136. K Nagai, K Hayakawa, K Kanematsu *J. Org. Chem.*, 1984, **49** 1022
137. C Formoso *Biochem. Biophys. Res. Commun.*, 1973, **50** 999
138. K Nagai, K Hayakawa, S Ukai, et al. *J. Org. Chem.*, 1986, **51** 3931
139. G Le Bas, C DeRango, G Tsoucaris *Cyclodextrins* (Edited by J Szejtli), D Reidel, Dordrecht, 1982, p. 245
140. G Le Bas, G Tsoucaris *Mol. Cryst. Liq. Cryst.*, 1986, **137** 287
141. D A Lighter, J K Gawronski, K Gawronski *J. Am. Chem. Soc.*, 1985, **107** 2546
142. N Kobayashi, T Osa *Chem. Lett.*, 1986, (3) 421
143. A Harada, S Takahashi *Chem. Lett.*, 1984, (12) 2089
144. A Harada, S Takahashi *J. Chem. Soc. Chem. Commun.*, 1984, (10) 645
145. N Kobayashi, T Osa *Minutes of the 5th International Symposium on Cyclodextrins*, Edition de Santé, Paris, 1990, p. 196
146. H Ogino *J. Am. Chem. Soc.*, 1981, **103** 1303
147. K Yamanari, Y Shimura *Chem. Lett.*, 1982, (12) 1959
148. K Yamanari, Y Shimura *Bull. Chem. Soc. Jpn.*, 1983, **56** 2283
149. N Kobayashi, X Zao, T Osa, et al. *J. Chem. Soc., Dalton Trans.*, 1987, (7) 1801
150. L Casella, M Gulotti, F Piemontesi, et al. *Croat. Chem. Acta*, 1989, **62** 351
151. M Otagiri, K Ikeda, K Uekama, et al. *Chem. Lett.*, 1974, 679

152. F Giordano, O Azzolina, S Collina, et al. *Minutes of the 5th International Symposium on Cyclodextrins*, Edition de Santé, Paris, 1990, p. 665
153. G M Borona, R Fornasier, P Scrimin, et al. *Carbohydr. Res.*, 1986, **147** 205
154. M Boiswin, A Rassat, G Le-Bas, et al. *Croat. Chem. Acta*, 1989, **62** 401
155. K Uekama, F Hirayama, S Yamasaki, et al. *Chem. Lett.*, 1977, (12) 1389
156. J M Bowen, N Purdie *Anal. Chem.*, 1981, **53** 2249
157. M Chéron-Francke *Minutes of the 5th International Symposium on Cyclodextrins*, Edition de Santé, Paris, 1990, p. 192
158. H A Benesi, J H Hildebrand *J. Am. Chem. Soc.*, 1949, **71** 2703
159. L Andrews, R Keefer *Molecular Complexes in Organic Chemistry* (Translated into Russian from English), Mir, Moscow, 1967, 206 pp
160. R L Scott *Recl. Trav. Chim. Pays-Bas*, 1956, **75** 787
161. N J Rose, R S Drago *J. Am. Chem. Soc.*, 1959, **81** 6138
162. M P Mack, R R Hendrixson, R A Palmer, et al. *J. Am. Chem. Soc.*, 1976, **98** 7830
163. C B Monk *Electrolytic Dissociation*, Academic Press, New York, 1961, p. 186
164. J L Hoffman, R M Bock *Biochemistry*, 1970, **9** 3542
165. F C Hawkins *The Absolute Configuration of Metal Complexes* (Translated into Russian from English), Mir, Moscow, 1974, 347 pp
166. W Kuhn *Ann. Rev. Phys. Chem.*, 1958, **9** 417
167. W Kauzmann, F B Clough, I Tobias *Tetrahedron*, 1961, **13** 57
168. J G Kirkwood *J. Chem. Phys.*, 1937, **5** 479
169. P E Schipper *J. Am. Chem. Soc.*, 1978, **100** 1433
170. C C Bott, T Kurucsev *J. Chem. Soc., Faraday Trans. 2*, 1975, **71** 749
171. W G Hill, S F Mason, R D Peacock *J. Chem. Soc., Perkin Trans. 2*, 1977, (10) 1262
172. *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry* (Translated into Russian), Mir, Moscow, 1970, 440 pp
173. P Krabbe *The Use of Chiroptical Methods in Organic Chemistry* (Translated into Russian), Mir, Moscow, 1974, 168 pp
174. M Legrand, M J Rougier *Stereochemistry, Fundamentals and Methods* (Edited by H B Kagan), Georg Thieme, Stuttgart, 1977, Vol. 2, p. 33
175. P E Schipper, A Podger *J. Am. Chem. Soc.*, 1983, **105** 4541
176. P E Schipper *J. Am. Chem. Soc.*, 1978, **100** 3658
177. J A Schellman *Acc. Chem. Res.*, 1968, **1** 144
178. H Eyring, H-C Liu, D H Caldwell *Chem. Rev.*, 1968, **68** 525
179. P Atkins *Quanta. Handbook of Concepts* (Translated into Russian from English), Mir, Moscow, 1977, p. 427
180. N Harada, K Nakanishi *Circular Dichroism Spectroscopy. Exciton Coupling in Organic Stereochemistry*, University Science Books, California, 1983, 460 pp
181. K Nishida, Y Ando, H Nomura *Colloid Polym. Sci.*, 1979, **257** 603
182. K Nishida, A Iwasaki *Kolloid-Z. und. Z. Polymere*, 1978, **251** 136
183. Yu A Zhdanov, Yu E Alexeev, V A Tjumenev *Eurocarb V. Fifth European Symposium on Carbohydrates 1989, Aug. 21–25*, Prague, p. 67
184. J P Riehl, F S Richardson *Chem. Rev.*, 1986, **86** 1
185. F S Richardson, J P Riehl *Chem. Rev.*, 1977, **77** 773
186. F Cramer, W Dietsche *Chem. Ber.*, 1959, **92** 378
187. M Mikolaiczyk, J Drabowicz *J. Am. Chem. Soc.*, 1978, **100** 2510
188. A F Drake *Eur. Spectros. News.*, 1986, **69** 10

Translated from *Uspekhi Khimii* 61 1047–1060 (1992) U.D.C. 541.1; 535.37; 535.376

Crystal phosphors for storage luminescent screens

A M Gurvich, V V Mikhailin
Scientific-Research X-Ray Radiological Institute, Moscow
M V Lomonosov State University, Moscow

ABSTRACT. A review is given of the work on photostimulated crystal phosphors as materials of storage luminescent screens used in digital radiography. The properties of barium fluorohalides, particularly of BaFBr:Eu, important in these applications are considered. Much attention is given to the influence of conditions during preparation on these properties, to physicochemical relationships describing the processes of formation and interaction of crystal lattice defects, and to the current ideas on the mechanism of photostimulated luminescence.

The bibliography contains 94 references.

Contents

I. Introduction. Storage luminescent screens as alternatives to silver-halide photographic materials 576
II. Selection of crystal phosphors for storage screens 576
III. Structure and principal properties of barium fluorohalides 577
IV. Dependences of properties of BaFBr:Eu phosphor on the conditions during its preparation 578
V. Crystal lattice defects in BaFBr:Eu phosphor and photostimulated luminescence mechanism 579
VI. Excitation spectra of steady-state luminescence, phosphorescence, and photostimulated luminescence of barium fluorohalides 580
VII. Some applications of storage luminescent screens 581

I. Introduction. Storage luminescent screens as alternatives to silver-halide photographic materials

Inorganic (crystal) phosphors, storing energy and liberating it in the form of light—photostimulated luminescence excited by infrared or visible radiation—have been known for a long time. They are used in dosimetry and in visualisation of infrared radiation.[1–4] The development of computers and lasers has opened up new opportunities for the applications of these materials and this has led to the development of luminescent digital (computer) radiography.[5,6] This method differs from conventional radiography because instead of a photographic (radiographic) film or its combination with amplifying screens, use is made of an image-storing crystal phosphor (we shall use just the word phosphor) screen capable of emitting luminescence.

The latent image is developed by scanning such a screen with a sharply focused beam of a helium–neon laser. The light flashes (scintillations) generated are converted in a photomultiplier into a series of electrical signals and then, after discretisation, they are made up into a digital code. The data digitalised in this way are stored in an optical disk or on a magnetic tape, and—after computer processing—are converted back into analog signals, modulating the intensity of an electron beam used in a display or modulating radiation from a second laser which scans a photographic film†.

Luminescent digital radiography has a number of advantages over conventional (film) radiography,[7] the main of these is a wide dynamic range.[8,9] This makes it possible, for example, to attain a high-contrast resolution of parts of an object which differ greatly in respect of the absorption of ionising radiation, and also to reduce the risk of obtaining a poor-quality image because of an incorrect selection of the exposure conditions.

The idea of luminescent digital radiography has long been in the "air" (see, for example, Ref. 10), but it has been realised only after the development of phosphors satisfying the full range of the necessary requirements.

II. Selection of crystal phosphors for storage screens

Phosphors used in luminescent screens should satisfy the following requirements:[7,11] 1) a high energy efficiency of the room-temperature photostimulated luminescence in order to reduce the noise associated with fluctuations of the photon flux; 2) luminescence and excitation bands sufficiently far apart for spectral separation of the laser radiation from the photostimulated luminescence; 3) a rapid decay of the laser-excited light flashes, so as to ensure the necessary speed of image readout (reconstruction) and prevent superposition of signals due to different parts of the image; 4) long-term retention of the stored energy (weak fading); 5) a linear dependence of the photostimulated luminescence intensity on the exciting-radiation dose, which is the precondition for the attainment of a wide dynamic range; 6) efficient absorption of ionizing radiation in order to minimize the quantum noise and reduce the dose necessary to obtain a high-quality image.

These requirements were taken as the basis of an investigation of the feasibility of using a large number of phosphors capable of the photostimulated luminescence. These phosphors included zinc and alkaline-earth sulphides, for example SrS:Ce:Sm and SrS:Eu:Sm;[1,17] alkali halides,[10,13] particularly RbBr:Tl;[9,11] oxides (ThO_2:Er) and oxysulphides (La_2O_2S:Eu:Sm);[12] alkaline-earth fluorohalides;[5,14] some sulphates, borates, and silicates;[11,13,15] haloborates, halosilicates, halophosphates, and halogermanates of alkaline-earth metals, particularly $Ba_5SiO_4Br_6$:Eu.[11,16] In the case of luminescent digital radiography the best of these phosphors have proved to be barium fluorohalides activated with europium (BaFHal:Eu), the ability of which to emit the photostimulated luminescence had been investigated early,[5,14] as well as later on a large number of occasions. A particularly favourable combination

† In the latest systems made by Fuji the same laser is used to scan a storage screen and a photographic film.

of properties is exhibited by the BaFBr:Eu phosphor,[12,17–19] used in storage screens manufactured on a commercial scale.[17] The energy efficiency of its photostimulated luminescence can reach 5%[19] and the luminescence (λ_{max} = 390 nm) and excitation (λ_{max} = 590–600 nm) bands are far apart, the photostimulated luminescence decay time is τ = 0.8 μs,[8] the fading does not exceed 25% in 8 h,[17] and the presence of barium in the phosphor base ensures a strong absorption of X-rays.[20] It should be pointed out that unsuccessful attempts had been made and are still being made to improve some properties of BaFBr:Eu by partial replacement of Br with Cl or I.[13]

III. Structure and principal properties of barium fluorohalides

The first barium fluorohalide to attract attention was BaFCl as an object of investigations of colour centres[21–24] and (when activated with europium) as an efficient phosphor for amplifying X-ray screens.[25,26] The high efficiency of the photoluminescence and cathodoluminescence of MFHal:Eu^{2+} phosphors (M = Sr, Ba; Hal = Cl, Br) was mentioned in Ref. 27.

Barium and strontium fluorohalides have a layer tetragonal structure of the PbFCl type,[28,29] which can be represented by a sequence of layers F_2MHalHalM..., oriented along the [001] direction (Fig. 1). The subscript 2 of fluorine indicates that the number of ions in an F^- layer is twice as high as in Hal or M layers. The distances between the F^- ions are $\sqrt{2}$ times less than the distances between the Br^- and Ba^{2+} in the relevant layers.

The presence of anions of two types in barium fluorohalide crystals facilitates the formation of two different types of the colour (F) centres, for example, fluorine‡ (V_F) and chlorine (V_{Cl}) vacancies in BaFCl, and of fluorine and bromine (V_{Br}) vacancies in BaFBr, when these vacancies have captured electrons. The appearance of the corresponding bands in the absorption spectra of crystals had been confirmed experimentally, and an investigation of the ESR spectrum[22] and a theoretical analysis[23] have resulted in an attribution of the short-wavelength band to the V_F centres, which are frequently denoted also by the symbol $F(F^-)$. It has also been shown that additive colouring produces only the F centres of the V_F type.[30] This can be explained by the fact that an excess of Ba penetrates deeper into crystals along dislocations, which are formed at the edge between two adjacent F_2 and Ba layers that terminate inside the crystal (at the edges of BrBrBa layers the formation of dislocations is less probable for steric reasons).

We investigated earlier[14] the characteristics of the luminescence emitted by the $BaCl_2-BaF_2$ system and showed that an excess of BaF_2 formed a solid solution in BaFCl. This implied that some of the Cl^- ions were replaced with F^- giving rise to antisite defects F_{Cl}.[19] The presence of similar defects was postulated also for BaFBr.[33] The association of these defects§ with $V_{Cl}^{\cdot}$ ($V_{Br}^{\cdot}$) gave rise to F centres with parameters differing somewhat from those of non-associated centres of this type.[19]

‡The subscript of the symbol for a defect identifies the lattice sites at which this defect is formed or an interstitial position (i), as is usual in the literature on the physical chemistry of solids.[31,32]

§Here and later a dot (bullet) is used to denote an effective positive charge of a defect relative to the surrounding lattice and a prime is used for an effective negative charge (the number of the primes indicates the magnitude of the charge).

Barium fluorohalides are capable of emitting luminescence unrelated to the presence of impurities. As in the case of other halide phosphors,[34] it can be explained by the recombination of electrons with V_k centres (molecular Hal_2 centres, formed by the capture of a hole shared by two adjacent halogen ions).[35,36] The presence of two different halogens in a crystal facilitates the formation of at least two types of V_k centres, for example F_2^- and Cl_2^- in BaFCl. The F_2^- ions are taken to be responsible for a short-wavelength luminescence band observed only at low temperatures for all the fluorohalides and for BaF_2.[35] The room-temperature luminescence of nonactivated BaFCl and BaFBr has been attributed to the recombination of electrons with the Cl_2^- and Br_2^- centres, respectively. They are formed by Hal^- ions located at the shortest distance from one another in adjacent layers. In view of the lower electronegativity of Br, compared with Cl, it is found that the V_k centres of the Br_2^- type predominate in mixed $BaFCl_xBr_{1-x}$ crystals.[35] The presence of V''_{Ba} barium vacancies may have a stabilising influence on the adjoining V_k centres.

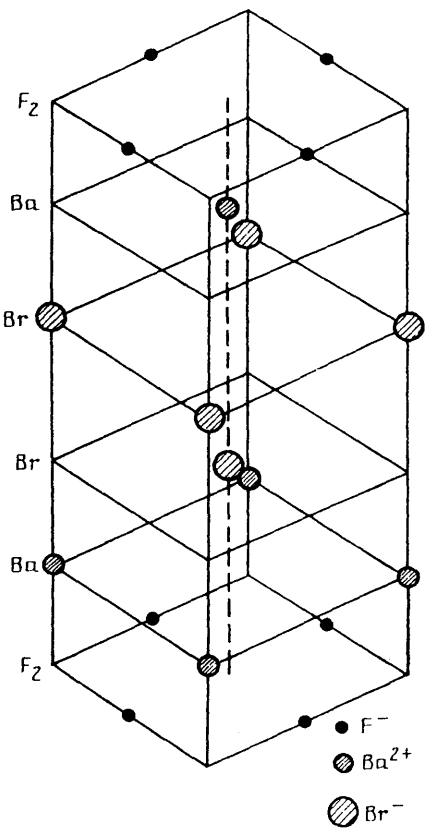


Figure 1. Positions of ions in the crystal lattice of BaFBr. The symbols F_2, Ba, and Br identify the layers formed by the F^-, Ba^{2+}, and Br^- ions, respectively.

Barium and strontium fluorohalides are readily activated by divalent rare-earth ions such as Eu^{2+} [5,25,37,38] and Sm^{2+},[39,40] because such activation does not require charge compensation. The

luminescence spectrum of Eu^{2+}, characterised by a strong room-temperature band with a maximum at 385 nm for BaFCl and at 390 nm for BaFBr, is very suitable for luminescent digital radiography, because this spectrum corresponds to the maximum sensitivity region of ordinary photocathodes and at the same time is shifted significantly relative to the excitation bands,[5] as demonstrated in Fig. 2 using the example¶ of BaFBr: 10^{-4} Eu.[41]

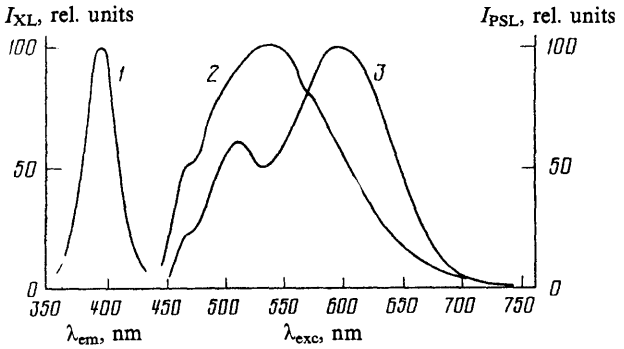


Figure 2. The luminescence (*1*) and excitation (*2*, *3*) spectra of BaFBr: 10^{-4} Eu phosphor prepared by heating a charge at 800 °C without further annealing (*2*) and after annealing at 550 °C (*3*). The spectra were recorded at 20 °C. The abscissa gives the wavelengths of the emitted luminescence (λ_{em}) and of the exciting (λ_{exc}) light and the ordinate gives the intensities of the X-ray luminescence (I_{XL}) and of the photostimulated luminescence (I_{PSL}). The spectra distribution of the photostimulated luminescence of BaFBr: Eu phosphor is identical with its X-ray luminescence spectrum. The curves are normalised to the maximum.[41]

In addition to the luminescence band due to the $4f^6 5d \rightarrow 4f^7$ transition in the Eu^{2+} ion, there may be a line 363 nm due to the $4f^7 \rightarrow 4f^7 ({}^6P_{7/2} \rightarrow {}^8S_{7/2})$ transition.[37] This transition becomes possible because, due to the relatively weak splitting of the 5*d* state into ^2e_g and $^2t_{2g}$, the lowest excited 4*f* level lies somewhat below the ^2e_g levels. The line at 363 nm becomes weaker, compared with the above-mentioend luminescence band, when Sr is replaced with Ba and when Cl is replaced with Br or I, and it also becomes weaker with increase in temperature,[37] so that in the case of BaFBr: Eu and BaFI: Eu this band is no longer observed at room temperature.

When the BaFCl: Eu phosphor is used in the preparation of amplifying screens, one of the most difficult tasks is to suppress a weak but very persistent afterglow,[26,38,42] indicating the presence of deep traps. It is an investigation of this effect, manifested more clearly in the case of BaFBr: Eu,[25] that has led to the discovery of the ability of fluorohalides to store a large amount of light energy and to liberate this as a result of optical stimulation. Charge separation, which is the condition for storing the energy, is due to a strong capture of holes by the Eu^{2+} centres and of electrons by the anion vacancies. The participation of the $V_F^{\cdot}$ and $V_{Hal}^{\cdot}$ in this process is confirmed by a comparison of the stimulation and absorption spectra of the *F* centres, which are formed by the capture of electrons.[43] The energy efficiency of the photostimulated luminescence of BaFBr: Eu excited by X-ray radiation can reach 5%.[19] Moreover, a rapid decay of the photostimulated luminescence flashes is important: it is due to the fact that the rate-limiting stage of the process is the allowed intracentre $4f^6 5d \rightarrow 4f^7$ transition. In the case of continuous optical stimulation, the rate of emptying of traps τ_{em}^{-1} is proportional to the maximum photostimulated luminescence intensity I_{PSL}, which in turn is governed by the intensity of the exciting (stimulating) light I_{st} and by the initial concentration of electrons n_F captured by the *F* centres:

$$I_{PSL} = \sigma I_{st} n_F. \quad (1)$$

Here, τ_{em} is the time during which the photostimulated luminescence intensity decreases by a factor *e* under the conditions of continuous excitation and σ is the cross section of the optical excitation process.[44]

IV. Dependences of properties of BaFBr: Eu phosphor on the conditions during its preparation

Among the many known methods for the preparation of barium fluorohalides,[20,25,29,45] three have been found suitable for the preparation of BaFBr: Eu phosphors. One of them, mentioned in the majority of the investigations (see, for example, Refs. 12, 18, and 44), is a solid-phase reaction involving heating of a charge composed of a mixture of BaF_2 and $BaBr_2$, containing europium bromide[12] or fluoride.[42] The second method differs from the first because the initial stage of the process occurs in an aqueous suspension of fine grained BaF_2 in a solution of $BaBr_2$.[25,46,47] After evaporation of the suspension and addition of $EuBr_3$, the resultant charge is heated usually in a reducing atmosphere. A special feature of the third method is that the source of fluorine is NH_4F,[19,41,48,49] interacting with $BaBr_2$ first in the solution and then (after evaporation) in the solid phase.

The properties of BaFBr: Eu depend very strongly on the conditions during its preparation.[10,41,50,51] The highest photostimulated luminescence efficiency is usually obtained when the concentration of europium is less than that needed to ensure the strongest steady-state luminescence.[41] If NH_4F is used as a fluorinating agent, this concentration is almost an order of magnitude less than for the interaction of $BaBr_2$ with BaF_2, and it amounts to 10^{-4} g-atom/mol.[52] The fluorinating effect of NH_4F favours also the incorporation of other rare-earth activators in the lattice and removal of oxygen† from it, which increases the phosphorescence intensity and reduces the photostimulated luminescence intensity, obviously due to the formation of defects of the $O'_{Br}V_{Br}^{\cdot}$ type.[19] Although the activation of BaFBr by divalent europium is quite efficient when a charge is heated together with NH_4F and with a flux (the flux may be, for example, KBr—see Ref. 41) in air, it is preferable to use a weakly reducing medium such as nitrogen containing an admixture of hydrogen[12,44] or of CO.[19,26,53] Even in this case we cannot prevent the formation of the

¶ The number in front of the activator symbol is its concentration in gramme-atoms per mole in the charge from which the phosphor was prepared.

† The source of oxygen can be water of crystallisation with which barium halides readily interact.[21]

O'_{Hal} centres.[54] The nature of the flux has a considerable influence on the excitation spectrum[52] and its concentration—and the temperature to which it is heated—affects the grain size.[45] In selecting the method for removal of the flux we must bear in mind that the hygroscopic nature of MFHal compounds and their tendency to hydrolyse increases on reduction in the size of the M^{2+} cation and on increase in the size of the Hal^- anion;[29] in the case of BaFBr it is considerably greater than in BaFCl.

An important aspect is the choice of the temperature at which a charge is heated[41] and of the ratio of the components forming the base of a phosphor. This ratio influences the completeness of the solid-phase reaction,[29,57] as well as the excitation spectrum and fading.[12] The changes in the properties of BaFBr:Eu with the rate of its cooling and the conditions during annealing are particularly striking.[41,55,56] It is found that if the excess of $BaBr_2$ is reduced before annealing,[52] the subsequent annealing of the phosphor at 450–650 °C shifts the maximum in the excitation spectrum (Fig. 2) from the yellow–green region (520–540 nm) and orange–red (595–600 nm). This reduces the intensity of the steady-state X-ray luminescence, weakens greatly the room-temperature phosphorescence, and lowers the total light (liberated due to thermal excitation) by at least an order of magnitude; the high-temperature peaks on the thermoluminescence curve are much stronger than the low-temperature peaks. On the other hand, the photostimulated luminescence efficiency sometimes even rises. The determination of the excitation spectra at liquid nitrogen temperature during the subsequent annealing of the thermally stimulated luminescence (thermoluminescence) peaks provides additional support for the conclusion that there is no direct relationship between the characteristics of thermally and optically stimulated luminescence.[41] This follows from the fact that optical de-excitation of the investigated phosphor does not suppress the thermoluminescence or phosphorescence.[50,52]

V. Crystal lattice defects in BaFBr:Eu phosphor and photostimulated luminescence mechanism

If we assume that thermal disordering of the BaFBr lattice can produce both the Frenkel and the Schottky defects, and that the antisite defects can also be present, we have to allow for the formation of the following point defects in BaFBr:Eu phosphors:[19,33,57,58] V''_{Ba}, $V_{\dot{F}}$, $V_{\dot{Br}}$, F'_i, Br'_i, F_{Br}, and Eu_{Ba}. Computer modelling of defects in crystals[59] has made it possible to calculate the enthalpy and entropy of the processes of disordering of the BaFBr lattice.[33] A thermodynamic analysis based on these data shows[58] that among the effectively charged point defects in a regular lattice at the temperatures of formation and annealing of these phosphors the $V_{\dot{Br}}$ and F'_i defects shoud predominate (at 550 °C their concentration should be an order of magnitude less than at 800 °C). The following approximate equation corresponds to equilibrium:

$$[F'_i] \approx [V^*_{\dot{Br}}]. \qquad (2)$$

A comparison of the excitation spectra with the action spectra for attenuation of the ESR signal under the influence of exciting light[8] leads to the conclusion that the vacancies $V_{\dot{Br}}$ are responsible only for the long-wavelength part of the excitation spectrum with its maximum at 595–600 nm, whereas the short-wavelength region, which predominates in the case of the nonannealed phosphor (Fig. 2), is associated with $V_{\dot{F}}$.

This apparent disagreement between the theoretical calculations and experiments is removed if we allow for the data on the influence of annealing BaFBr:Eu given in the preceding section on the thermally stimulated luminescence and the photostimulated luminescence.[41,58] Obviously, annealing (like slow cooling) in the preparation of ZnS:Cu electroluminescent phosphors[32,60] results in segregation of point defects, so that they concentrate near dislocations and block boundaries. As pointed out already (see Section III), dislocations are more likely to form at the edges between two adjacent F_2 and Ba layers. Such dislocations can generate $V_{\dot{F}}$ and V''_{Ba}) vacancies, but these remain in the region of a crystal adjoining an extended defect. Annealing a phosphor causes the $V_{\dot{Br}}$ vacancies, which predominate in the bulk of a crystal, as well as interstitial F'_i ions and the Eu_{Ba} impurity defects to migrate towards dislocations and block boundaries. This process is accompanied by the interaction of F_i with $V_{\dot{F}}$,

$$F'_i + V^*_{\dot{F}} = F_F, \qquad (3)$$

which increases the concentration ratio $[V_{\dot{Br}}]/[V_{\dot{F}}]$. If we now assume that the photostimulated luminescence is generated mainly near linear and surface defects, whereas the thermally stimulated luminescence is primarily due to the processes that occur in a regular lattice, we can account for all the reported data on the influence of annealing: the enhancement of the photostimulated luminescence in the long-wavelength part of the excitation spectrum, which corresponds to $V_{\dot{Br}}$, the absence of a direct relationship between the thermally stimulated luminescence, which is weakened by annealing, and the photoluminescence which is then even enhanced, as well as the reduction in the afterglow and in the energy efficiency of steady-stage luminescence caused by annealing. Moreover, we can also account for the results of a number of investigations supporting the tunnel mechanism of the photostimulated luminescence. These include a weak temperature dependence of the decay time of the photostimulated luminescence when excitation is in the form of short light pulses[18] (this is also true of KI:Tl-type phosphors[10]) and the absence of photoconductivity when excitation occurs under conditions such that the photostimulated luminescence is generated with the participation of effectively only the V_F centres.[61] From this point of view, the possibility of tunnel transitions of electrons is the result of the following: segregation of point defects near linear and surface defects brings close together the luminescence centres (Eu_{Ba}) and the anion vacancies.[41] The fact that the photostimulated luminescence involving the V_{Br} centres is accompanied by photoconductivity, whose excitation spectrum is similar to the luminescence excitation spectrum,[43,61] should be regarded as evidence of the coexistence of the tunnel mechanism of optical excitation with photostimulated luminescence occurring due to transitions of electrons via the conduction band,[41] although the former mechanism clearly predominates. On the other hand, the thermally stimulated luminescence and the room-temperature phosphorescence are emitted in all cases with involvement of the conduction band and are primarily due to defects located in the regular lattice.

In the course of determination of the excitation spectra of BaFBr:Eu phosphors at liquid nitrogen temperature, following successive annealing of the thermally stimulated luminescence peaks, it has been established that such annealing increases considerably the energy efficiency of the photostimulated luminescence and the contribution of the short-wavelength components in the excitation spectrum.[41] This can be explained by the transfer of electrons from traps, responsible mainly for the thermally stimulated luminescence, to traps which are the most active in the photostimulated

luminescence process. Exactly the same explanation has been applied to the partial recovery of the photostimulated luminescence after complete optical de-excitation of a phosphor.[52] The kinetics of this process, described by the equation

$$I_{PSL} = k\sqrt{t} \quad (4)$$

(where t is the storage time of a phosphor after the de-excitation and k is a coefficient), is evidence of the diffusive nature of the transfer of electrons. It should be pointed out that a model allowing for the tunnel mechanism of the photostimulated luminescence and based on the hypothesis of radiative formation of the F centres as a result of formation of $F-H$ pairs on decay of excitons located near activators[18,36] fails to account for all the observations, particularly for the strong influence of the conditions during cooling and annealing of a phosphor on the excitation spectrum and on the photostimulated luminescence energy efficiency.

A careful investigation of the excitation spectrum reveals its complex structure, which cannot be reduced to the presence of two bands.[19,41] This can be explained by the fact that the F-centres governing the form of the spectrum differ from one another not only by the nature of the anion vacancy (V_F, V_{Br}), but also in respect of its environment, particularly because of the already mentioned association with other defects, primarily with antisite defects of the F_{Br} type.[19,62] Some role may be played here also by the distribution of the excited p-state of the F-centres.[22,63]

In investigations of phosphors based on BaFCl and activated with Eu^{2+} and Sm^{2+} it has been found that their properties change greatly, and the changes include enhancement of the phosphorescence, in the presence of an excess of BaF_2.[38,39,45] There are indications that an excess of BaF_2 influences also the properties of BaFBr:Eu by increasing the proportion of the bands associated with V_{Br} in the excitation spectrum.[12] This can be attributed to intercrystalline reactions of the type

$$F_{Br} = V^{\bullet}_{Br} + F'_i, \quad (5)$$

$$F_{Br} + V^{\bullet}_{F} = F_F + V^{\bullet}_{Br}. \quad (6)$$

The first of these can be called the antisite Frenkel disordering.[52] It obviously plays a specially important role, because it involves participation of the $V^{\bullet}_{Br}$ and F'_i defects which dominate in the regular lattice. It therefore follows that it is necessary to control rigorously the conditions during preparation, which influence the excess of BaF_2, particularly during the stage of washing away the flux and annealing of BaFBr:Eu phosphors[52,64] (hydrolysis during washing of BaFBr can remove a certain amount of $BaBr_2$).

VI. Excitation spectra of steady-state luminescence, phosphorescence, and photostimulated luminescence of barium fluorohalides

The excitation spectra of steady-state luminescence, phosphorescence and photostimulated luminescence of barium and strontium fluorohalides, which are of interest from the purely scientific and utilitarian points of view, had been investigated in a wide range of energies on a number of occasions.[14,36,38–40,50,64–70] The long-wavelength edge of the main (strongest) band in the excitation spectrum of the phosphorescence, which is obviously associated with interband transitions, has been used to estimate the band gap E_g of BaFCl.[14] This band gap is 8.5–9 eV. The corresponding band gap of BaFBr is 8–8.5 eV.[40,43,71]

In the range $E < E_g$ the excitation spectra of the steady-state luminescence depend on the nature of the luminescence centres and, therefore, they are different for nonactivated phosphors and for phosphors containing Eu^{2+} and Sm^{2+}.[39,40] They depend at least in the case of activation with europium, also on the oxidation—reduction properties of the medium in which a phosphor is heated during preparation.[38] For example, the excitation spectrum of BaFCl:2×10^{-2} Eu, prepared in a CO medium, includes a strong activator band extending from 3.3 to 5.4 eV with a barely detectable splitting into two bands due to the $5d(^2e_g)$ and $5d(^2t_{2g})$ states of the Eu^{2+} ion. Howevever, heating of this phosphor in air at 650–700 °C weakens strongly the Eu^{2+} band (although the intensity of the steady-state X-ray luminescence even rises somewhat[26]). Then, a weak peak at 318 nm remains in the long-wavelength part of the excitation band whereas a structure appears in the short-wavelength part corresponding to the t_{2g} state and this structure is due to transitions of electrons from the $4f^7(^8S)$ level to the levels of the $4f^6(^7F_J)5d(^2t_{2g})$ state split by the spin–orbit interaction. Heating in CO smears out this structure because of reduction of europium on the phosphor surface, where the Eu^{2+} ions may be in a different environment.[38] The structure of the part of the spectrum located between the band corresponding to the intracentre transitions and the energy E_g is attributed to the ionisation of Eu^{2+} and the presence of the edge Γ excitons [at 8.4 eV in the case of BaFCl and at 7.4 and 7.9 eV in the case of BaFBr [39,66,71]] associated with the $4p$-states of the Cl^- and Br^- ions.

The nature of the excitation spectra of the steady-state luminescence recorded in the range $E > E_g$ is practically independent of the activator and there is a considerable qualitative similarity of the BaFCl and BaFBr spectra (Fig. 3). The most remarkable feature of the spectra in the range 9–30 eV is the presence of a two-hump maximum at 16–20 eV in the case of BaFCl and 15–19.5 eV in the case of BaFBr. It can be attributed to the simultaneous influence of the formation of a plasmon and a core exciton,[40] due to the excitation of electrons in the $5p$-shell of the Ba^{2+} ions. The formation of an exciton increases the absorption coefficient and thus enhances the surface losses and gives rise to a narrow dip in the spectrum at 18.1–18.3 eV. The photon multiplication is manifested largely by a tendency to establish a constant energy efficiency η of the luminescence rather than by an abrupt increase in the quantum efficiency η_q.[39,40] Already in the range 20–30 eV the value of η becomes approximately equal to the energy efficiency of X-ray luminescence: 11–12% for BaFCl:10^{-2} Eu and 16–18% for BaFBr:Eu.[40,41] In the case of BaFBr:Eu the constancy of η is supported by measurements in the range from 10 to 1000 eV.[70] The annealing of BaFBr:Eu at 550 ± 100 °C reduces the energy efficiency of the steady-state luminescence at $E > 11$ eV by a factor of about 2; on the other hand, at 10 eV a strong excitation band is observed (Fig. 4 *a*) and this band is difficult to detect in the case of nonannealed phosphors. It is possibly due to the formation of F_{Br} clusters (10 eV is the initial energy of the appearance of excitons, bound to the $2p$-states of the F^- ions[36]).

The excitation spectrum of the photostimulated luminescence of BaFBr:Eu had been determined under somewhat different conditions by two research teams independently.[36,50,64–66] We can see from Fig. 4 that in the range $E > 11$ eV this spectrum is basically similar to the excitation spectrum of the steady-state luminescence. On the other hand in the range $E < 11$ eV of the two spectra are very different. For example, at 10 eV instead of a maximum, observed in the excitation spectrum of the steady-state

luminescence of the annealed phosphors, the corresponding photostimulated luminescence spectrum has a dip. A narrow intense peak at 7 eV is very typical of the excitation spectrum of the photostimulated luminescence. Following the two concepts of the mechanism of the photostimulated luminescence mentioned above, this peak is attributed to a transition of an electron from Eu^{2+} to an adjacent vacancy or to an exciton, the dissociation of which forms a $F-H$ pair.[36,50] It is important to stress that the phosphorescence of BaFBr:Eu begins to be excited effectively at higher energies of about 8 eV.[50]

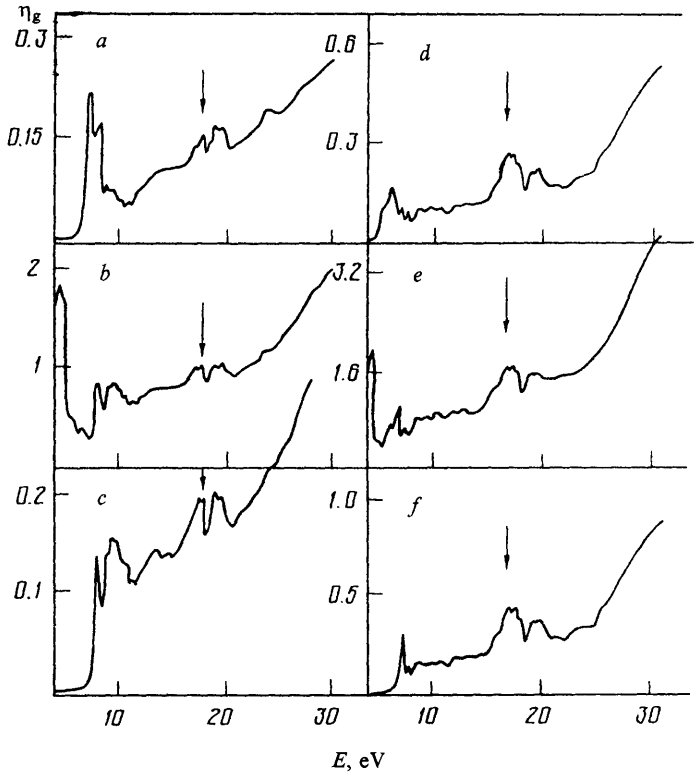


Figure 3. Excitation spectra of steady-state luminescence of nonactivated BaFCl (*a*), BaFCl:2×10^{-2}Eu (*b*), BaFCl:10^{-2}Sm (*c*), nonactivated BaFBr (*d*), BaFBr:10^{-3}Eu (*e*), and BaFBr:10^{-2}Sm (*f*). The ordinate represents the quantum efficiency relative to sodium salicylate. The arrows identify the calculated values of the plasmon energy.[40]

VII. Some applications of storage luminescent screens

The development of storage luminescence screens and of the luminescent digital radiography based on them has opened up new opportunities in X-ray diagnostics. This is based on the combination of computer techniques with the large area of the images required in medicine, a relatively high spatial resolution, and a wide dynamic range. There have been several reports on the application of luminescent digital radiography in examination of lungs, breasts, and other organs,[72–77] and in checking the position of a radiation beam as well as in obtaining information on the distribution of the dose in a body being irradiated by radiotherapy.[56,78,79] Technical difficulties and cost are hindering the extension of a wider use of the method in medicine.[7,80]

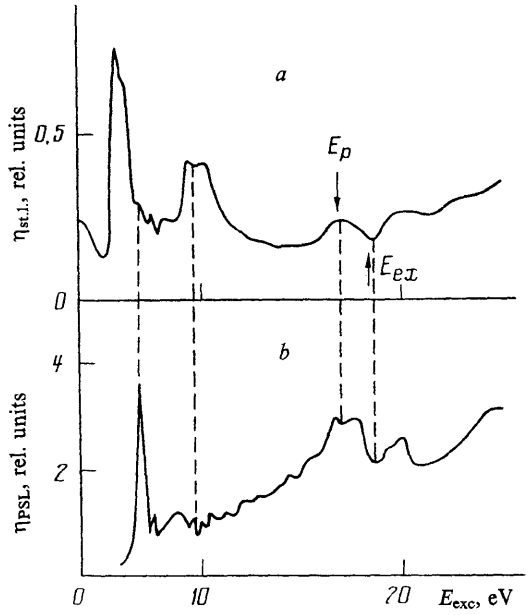


Figure 4. Excitation spectra of the steady-state luminescence (*a*) and of the photostimulated luminescence (*b*) of BaFBr:10^{-4}Eu phosphor annealed at 550 °C. The arrows identify the calculated values of the plasmon energy (E_p) and of the energy of the core exciton (E_{ex}), formed on excitation of electrons from the 5*p*-shell of the Ba^{2-} ion.[50]

There have been several descriptions of the application of luminescent digital radiography in obtaining diffractograms,[81,87] particularly in studies of biological objects with the aid of synchroton radiaiton. This method can be used to obtain high-quality records after exposures tens of times shorter than usual.[81,84,85] There have been suggestions of the use of luminescent digital raidography in transmission electron microscopy[88] and in recording various radiations both electromagnetic—from the VUV range[40,89] to the bremsstrahlung emitted by electron accelerators[56]—and the corpuscular,[89] including determination of the natural background. One should bear in mind that barium salts employed as phosphors usually contain a small amount of radium.[17,20] Obviously, luminescent digital radiography can be used also in astrophysics research, including X-ray astronomy, where a wide dynamic range of energy storing luminescent screens can be particularly valuable.

The different applications of these screens have led to studies of the parameters governing the quality of the images obtained by luminescent digital radiography and of threshold values of the flux

of the radiation being detected.[6,81,90–92] As usual, a dominant role is played by the efficiency of energy conversion of the radiation which excites the emitted luminescence, by the noise, by the frequency–contrast characteristic, by the dynamic range, and by the kinetic parameters.[93] On the other hand, these screen quality factors and systems as a whole are influenced by a number of factors specific to luminescent digital radiography.[7,90] These factors depend on the properties of the phosphors and screens employed and include the scattering of exciting light,[11] fading,[13,94] and fluctuations of photon fluxes (luminescence noise).[87] The last of these factors is particularly important as a component of the general noise in the case of a low energy efficiency of the photostimulated luminescence and high light losses between a screen and a photomultiplier.

We can thus see that the development of efficient crystal phosphors or image-storing screens and of the luminescent digital radiography method based on these screens has laid the foundation stone for a new branch of research, which is now developing rapidly in various directions.

References

1. V V Antonov-Romanovskii, V L Levshin Z L Morgenshtern, Z A Trapeznikova *Dokl. Akad. Nauk SSSR*, 1946, **54** 19
2. V L Levshin N V Mitrofanova, Yu P Timofeev, et al. *Tr. Fiz. Inst. Akad. Nauk SSSR*, 1972, **59** 64
3. S W S McKeever *Thermoluminescence of Solids*, Cambridge University Press, 1985
4. Yu P Timofeev, S A Fridman, M V Fok *Preobrazovanie Sveta* (Conversion of Light), Nauka, Moscow, 1985, 176 pp.
5. M Sonoda, M Takano, J Miyahara, H Kato *Radiology*, 1983, **148** 833
6. J D Newell, C A Kelsey (Editors) *Digital Imaging in Diagnostic Radiology*, Churchill Livingstone, New York, 1990, 163 pp
7. A M Gurvič, M G Myagkova, Yu Ryudiger *Med. Tekh.*, 1990, (3) 27
8. K Takahashi, J Miyahara, V Shibahara *J. Electrochem. Soc.*, 1985, **132** 1492
9. H von Seggern, T Voigt, K Schwarzmichel *Siemens Forsch.-Entwicklungsber.*, 1988, **17**B(3) 125
10. G I Vlasov, R A Kalnyn'sh, L E Nagli, et al. *Avtometriya*, 1980, (1) 66
11. A Meijernink *Luminescence of New X-Ray Storage Phosphors*, Drukkerij Elinkwijk, Utrecht, 1990, 175 pp
12. K Takahashi, T Nakamura, US P. 4 535 237, 13 Dec. 1983/13 Aug. 1985
13. H Degenhardt, German P. DE 3 347 207 A1, 27 Dec. 1983/11 July 1985
14. A M Gurvich, M A Il'ina, V P Kavtorova, et al. *Zh. Prikl. Spektrosk.*, 1983, **38** 765
15. A Meijering, G Blasse, M Glasbeek *J. Phys. Condens. Matter*, 1990, **2** 6303
16. A Meijering, G Blasse *Mater. Chem. Phys.*, 1989, **21** 261
17. J Miyahara *Computed Radiography* (Edited by Y Tateno, T Linuma, M Takano), Springer Verlag, Berlin, 1987, p. 7
18. H von Seggern, T Voigt, W Knüpfer, G Lange *J. Appl. Phys.*, 1988, **64** 1405
19. A M Gurvič, W P Kavtorova, M G Mjagkova, et al. *Proc. Second Intern. Meeting on Luminescence—35 Years Luminescence in Greifswald*, Ernst-Moritz-Arndt-Universität, Greifswald, 1989, p. 114
20. A M Gurvič *Röntgenleuchtstoffe und Röntegenlumineszenz-bildwandler*, Akademie Verlag, Leipzig, 1988, 164 pp
21. E Nicklaus, F Fischer *Phys. Status Solidi, B* 1972, **52** 453
22. M Yuste, L Taurel, M Rahmani, D Lemiyne *J. Phys. Chem. Solids*, 1976, **37** 961
23. S Lefrant, A H Harker *Solid State Commun.*, 1975, **19** 853
24. K Somaiah, P Veeresham, K L N Prasad, V Hari Babu *Phys. Status Solidi, A*, 1979, **56** 737
25. A L Stevels, F Pingault *Philips Res. Rep.*, 1975, **30** 737
26. A M Gurvič, R V Katomina, N P Soshchin *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1977, **41** 1372
27. J L Sommerdijk, J M P J Verstegen, A Bril *J. Lumin.*, 1974, **8** 502
28. M Sauvage *Acta Crystallogr., Sect. B*, 1974, **30** 2786
29. H P Beck *J. Solid State Chem.*, 1976, **17** 275
30. D Lemoyne, J Duran, M Yuste, M Brillardon *J. Phys. C*, 1975, **8** 1455
31. F A Kröger *The Chemistry of Imperfect Crystals*, North-Holland, Amsterdam, 1974
32. A M Gurvič *Vvedenie v Fizicheskuyu Teoriyu Kristallofosforov* (Introduction to Physical Theory of Crystal Phosphors), Vysshaya Shkola, Moscow, 1971, 366 pp; 1982, 376 pp
33. R C Baetzold *Phys. Rev. B*, 1987, **36** 9182
34. K A Kalder *Elektronnye Vozbuzhdeniya Kristallov $A^{II}B^{VII}$: Diss. Kand. Fiz.-Mat. Nauk* (Electronic Excitations of II–VII Crystals: Thesis for Candidate's Degree of Physico-Mathematical Sciences), Tartu, 1972
35. M K Crawford, L H Brixner, K Somaiah *J. Appl. Phys.*, 1989, **66** 3758
36. H Rütter, H von Seggern, R Reininger, V Saile *Phys. Rev. Lett.*, 1990, **65** 2438
37. J L Sommerdijk, J M P J Verstegen, A Bril *J. Lumin.*, 1974, **8** 502
38. A M Gurvič, V B Gutan, M A Il'ina, et al. *Opt. Spektrosk.*, 1982, **52** 289
39. A M Gurvič, M A Il'ina, V V Mikhailin, et al. *Zh. Prikl. Spektrosk.*, 1988, **49** 246
40. A M Gurvič, V V Mikhailin, M G Myagkova, M A Terekhin *Vestn. Mosk. Univ. Fiz. Astron.*, 1990, **31** 44
41. A M Gurvič, M G Myagkova, Yu Ryudiger, V P Kavtorova *Zh. Prikl. Spektrosk.*, 1990, **53** 56
42. L H Brixner *Mater. Chem. Phys.*, 1987, **16** 253
43. K Takahashi, K Kohda, J Miyahara, et al. *J. Lumin.*, 1984, **31**(32) 266
44. D M De Leeuw, T Kovats, S P Herko *J. Electrochem. Soc.*, 1987, **134** 491
45. *Research Disclosure*, 1978, (165) 17
46. A N Campball, A J R Campball *Trans. Faraday Soc.*, 1939, **35** 241
47. A L N Stevels, A D M Schrama-de Pauw, F Pingault, US P. 4 157 981, 3 April 1978/12 June 1979
48. Su Mian-Zeng, Xu Xiao-Lin, Ruan Shen-Kang, Gong Man-Lin *J. Less-Common Met.*, 1983, **93** 361
49. A M Gurvič, S I Golovkova, M A Il'ina, et al. *Lyuminestsentnye Priemniki i Preobrazovateli Ioniziruyushchego Izlucheniya* (Luminescent Detectors and Converters of Ionising Radiation), Nauka, Novosibirsk, 1985, p. 72
50. A N Belskiy, A M Gurvich, I A Kamenskikh, et al. *Nucl. Instrum. Methods Phys. Res. A*, 1991 **308** 190

51. D Starick, A M Gurvič, M G Miagkova, et al. *Abstracts of Papers Presented at the Third Intern. Meeting on Luminescence*, Trassenheide, 1991, p. 16
52. A M Gurvič, M G Mjagkova, J Rüdiger, V P Kavtorova *Proc. Intern. Symposium on Luminescent Detectors and Transformers of Ionising Radiation*, University of Latvia, Riga, 1991, D1
53. Y Biao, Nin Jian-Hua, Su Miang-Zeng *J. Lumin.*, 1988, **40**(41) 323
54. J-M Spaeth *Proc. Intern. Symposium on Luminescent Detectors and Transformers of Ionising Radiation*, University of Latvia, Riga, 1991, p. 13
55. A M Gurvič, V P Kavtorova, M G Mjagkova, et al. *Abstracts of Papers Presented at Intern. Symposium on Luminescent X-Ray Screens*, Moscow, 1989, p. 29
56. A M Gurvic, R S Milshtejn, M G Myakhova, et al. *Radiat. Prot. Dosim.*, 1990, **34** 265
57. R C Baetzold *J. Phys. Chem. Solids*, 1989, **50** 915
58. A M Gurvič *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1992, **56** 139
59. C R A Catlow, M Dixon, W C Mackrodt *Computed Simulation of Solids*, Springer Verlag, Berlin, 1982
60. O N Kazankin *Sb. Tr. Gos. Inst. Prikl. Khim. Leningr.*, 1966, **53** 12
61. Y Imabuchi, Ch Umemoto, K Takahashi, S Shionoya *Abstracts of Papers Presented at Intern. Conf. on Luminescence*, Lisbon, 1990, p. 158
62. A M Gurvič, V P Kavtorova, M G Myagkova, et al. *Abstracts of Papers Presented at Intern. Symposium on Imaging Systems—150 Years of Photography*, Dresden, 1989, p. 179
63. Sun Xiao-Ping, Su Mian-Zeng *J. Lumin.*, 1988, **40**(41) 171
64. A M Gurvič, M G Myagkova, Ju Rudiger, et al. *Proc. Second Intern. Conf. on Rare Earths, Development, and Applications*, Beijing in *J. Rare Earths* (Spc. issue), 1991, **2** 730
65. H H Rüter, H von Seggern, R Reininger, V Saile *HASYLAB Jahresber.*, 1989, p. 149
66. H-H Rüter, H von Seggern, R Reininger, V Saile *Abstracts of Papers Presented at Inter. Conf. on Luminescence*, Lisbon, 1990, p. 629
67. V I Alekseev, A N Vasil'ev, A M Gurvič, et al. *Preprint*, No. 20, P N Lebedev Physics Institute, Academy of Sciences of the USSR, Moscow, 1986
68. I M Ternov, V V Mikhailin *Sinkhrotronpoe Izluchenie. Teoriya i Eksperiment* (Synchrotron Radiation: Theory and Experiment), Energoatomizdat, Moscow, 1986, 296 pp
69. V V Mikhailin, M A Terekhin *Nucl. Instrum. Methods Phys. Res. A*, 1989, **282** 607
70. H H Rüter *Erzeugung Photostimulierbarer Zentren im VUV und XUV Spektralbereich*, HASYLAB, Hamburg, 1991, 169 pp
71. E Nicklaus *Phys. Satus Solidi A*, 1979, **53** 217
72. R D Müller, V John, M Voss, E Löhr, et al. *Abstracts of Papers Presented at Intern. Symposium on Luminescent X-Ray Screens*, Moscow, 1989, p. 27
73. L R Goodman, C R Wilson, W D Foley *Am. J. Roentgenol.*, 1988, **150** 1241
74. B Schwermer, G Witte, R P Spielman, et al. *Fortschr. Röntgenstr.*, 1990, **153** 161
75. E Boijen *Book of Abstracts Charite-Symposium on CT and MR Medicine*, Berlin, 1988, p. 130
76. B Bergh, W Döhring *Digital Radiographie: Referate und Vorträge*, Schnetztor Verlag, Konstanz, 1989, p. 117
77. K F Neufang, B Krug, R Lorenz, N Steinbrich *Fortschr. Röntgenstr.*, 1990, **152** 501
78. R M Wilenzick, C R B Merritt, S Balter *Med. Phys.*, 1987, **14** 389
79. D Gur, M Deutsch, C R Fuhrmann, et al. *Med. Phys.*, 1989, **16** 132
80. R Schittenhelm *Electromedica*, 1986, **54** 72
81. J Miyahara, K Takahashi, Y Amemiya, N Kamiya, et al. *Nucl. Instrum. Methods Phys. Res. A*, 1986, **246** 572
82. Y Amemiya, N Kamiya, J Miyahara *Oyo Buturi*, 1986, **55** 978
83. N Kamiya, Y Amemiya, J Miyahara *J. Crystallogr. Soc. Jpn.*, 1986, **28** 350
84. Y Amemiya, T Matsushita, A Nakagawa, Y Satow, et al. *Nucl. Instrum. Methods Phys. Res. A*, 1988, **266** 645
85. Y Amemiya, K Wakabayashi, H Tanaka, Y Ueno, et al. *Science*, 1987, **237** 164
86. R B Whiting, J F Owen, B H Rubin *Nucl. Instrum. Methods Phys. Res. A*, 1988, **266** 628
87. D Bilderbeck, K Moffat, J Owen, et al. *Nucl. Instrum. Methods Phys. Res. A*, 1988, **266** 636
88. N Mori, T Oikawa, T Katoh, et al. *Ultramicroscopy*, 1988, **25** 195
89. J Miyahara *J. Soc. Instrum. Control. Eng.*, 1987, **26** 657
90. W Hillen, U Schiebel, T Zaengel *Med. Phys.*, 1987, **14** 744
91. H Fujita, K Ueda, J Morishita, T Fujikawa, et al. *Med. Phys.*, 1989, **16** 52
92. K Klingenbeck, B Conrad *Siemens Forsch.-Entwicklungsber.*, 1987, **16** 192
93. A M Gurvič *Fizicheskie Osnovy Radiatsionnogo Kontrolya i Diagnostiki* (Physical Basis of Radiation Monitoring and Diagnostics), Energoatomizdat, Moscow, 1989, 168 pp
94. H von Seggern *Cryst. Lattice Defects Amorphous Mater.*, 1989, **18** 399

Translated from *Uspekhi Khimii* 61 1061–1090 (1992) U.D.C. 547.233+541.27+546.110.23

Current approach to the problem of nitrenium ions

T P Simonova, V D Nefedov, M A Toropova, N F Kirillov
Perm State University
St. Petersburg State University

ABSTRACT. This review is devoted to the chemistry of nitrenium ions, which are highly reactive species whose bivalent nitrogen atom has an incomplete (sextet) electron shell and bears a formal positive charge. All known methods for generating these ions, including a nuclear chemical method developed by the authors, their reactions, structure, and also the role of nitrenium ions in the chemistry of nitrogen-containing compounds are examined.

The bibliography includes 159 references.

Contents

I.	Introduction	584
II.	General characteristics and electronic structure of nitrenium ions	584
III.	Methods of generation	586
IV.	Reactions of nitrenium ions	594

I. Introduction

The idea that it is possible to form charged species containing bivalent nitrogen (nitrenium cations) was first put forward at the beginning of this century in the studies of Stieglitz et al.[1–3]

Up to the 1970s the publications devoted to studies on these species were not only limited but also contradictory. Different schemes for the same reaction of nitrogen-containing compounds were put forward, assuming and excluding the formation of nitrenium ions as intermediates. It is sufficient to say that an unequivocal affirmation of the fact that nitrenium ions are actually formed only became possible as a result of studies during the last 20–25 years.

The first attempt to correlate the available information on nitrenium ions was made in 1970.[4] However, an extensive series of studies by Gassman marked the beginning in the development of the chemistry of these reactive nitrogen-containing intermediates. The results of Gassman's studies, which were published in a review article,[5] contained fundamental data that demonstrated the possibility of such cations existing as independent species. Gassman produced convincing data on the electronic structure of nitrenium ions and evidence for their possible existence both in a singlet and triplet state.

Subsequent experimental studies[6–8] and quantum-mechanical calculations[9–25] confirmed the basic conclusions of Gassman. It was shown that nitrenium ions containing alkyl groups occur mainly in a triplet ground state while those containing aryl groups occur mainly in a singlet ground state.

In the 1970s and 1980s physicochemical[26–27] and nuclear chemical[28–32] methods for generating nitrenium ions were developed. It should be noted that with nuclear chemical methods it is possible to obtain these species in a free state and to study their reactions.

During the last ten years research on nitrenium ions and their reactions has been conducted with particular intensity.[28–48] The increased interest in this problem is mainly due to the important role of these species in carcinogenetic processes. Nitrenium ions are known to constitute the active form of strong chemical carcinogens, such as arylamines, *N*-arylhydroxylamines, and arylnitroso and arylnitro compounds.[24,49–53] It has been established that the active forms of chemical carcinogens are strong electrophilic reagents that are covalently bonded with the nucleophilic forms of nucleic acids and proteins. One of the main problems is to obtain information about the macromolecularly bonded products for each carcinogen. This is important in determining the relative role of each adduct in the carcinogenetic process.[49]

Furthermore, reactions of nitrenium ions open up exceptional opportunities for direct amination and on this basis the development of novel synthetic methods for preparing nitrogen-containing compounds.[54]

II. General characteristics and electronic structure of nitrenium ions

Nitrenium ions are nitrogen-containing organic compounds in which the nitrogen atom has an incomplete (sextet) electron shell and bears a formal positive charge (+1).

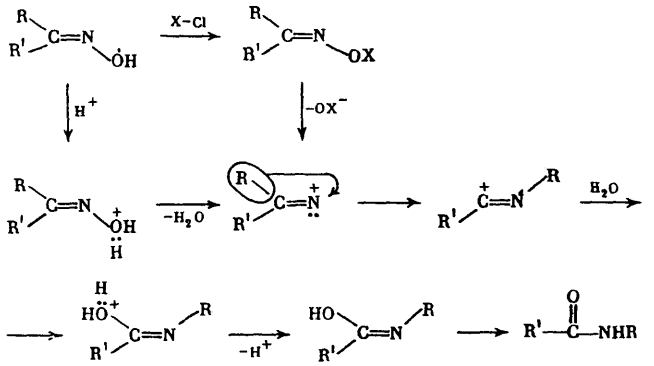
Nitrenium ions are formed as a result of the heterolytic elimination of a substituent from amines of two structural types:[55]

$$R_3N \xrightarrow[-R^-]{} R_2\overset{+}{N}: \qquad \text{(A)}$$

$$R^1R^2C{=}NX \xrightarrow[-X^-]{} R^1R^2C{=}\overset{+}{N}: \qquad \text{(B)}$$

Nitrenium ions of type (A) form the subject of our investigation.

An example of a reaction in which cations of type (B) are formed as an intermediate is provided by the Beckmann rearrangement (see the study of Donaruma and Heldt).[56] The mechanism by which this rearrangement occurs is described by Saik.[57]



X = $R''CO^-$; $R''SO_2^-$ etc.

In this case the synchronous cleavage of the N–O bond and migration of the group without formation of a nitrenium ion also cannot be excluded (possibly via a three-centred transition state), which is supported by the stereoselectivity of the reaction.

Nitrenium ions resemble carbocations in their behaviour. However, a number of significant differences in their behaviour caused by the nature of the heteroatom should be noted. Because of the presence of a positive charge on the more electronegative nitrogen atom compared to a carbon atom, the stability of nitrenium ions is expected to be lower than that of carbocations. By analogy with carbocations, nitrenium ions have a sextet of electrons and a vacant *p* orbital, but in contrast to carbocations there is a free electron pair on the nitrogen atom. The presence of the latter is responsible for several characteristics of the chemical behaviour of nitrenium ions that distinguish them from carbocations—the possibility of these species occurring in singlet (A) and triplet (B) states.[58]

(A) (B)

The singlet nitrene cation differs from triplet biradical species by virtue of its chemical behaviour and it displays a similarity to carbocations.

Quantum-chemical calculations carried out for the parent nitrenium ion $\overset{+}{N}H_2$,[9–13,16–19,23] its alkyl homologues $MeNH$,[11,14,21,23] Me_2N,[14,21,23] and others[15,23] and also for phenylnitrenium ions[24,25] demonstrated that the difference in energy between the singlet and triplet states is 20–40 kcal mol^{-1} in certain cases. For the unsubstituted $\overset{+}{N}H_2$ and the simplest alkyl homologues the ground state is the radical-like triplet state.†

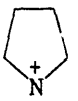
Arylnitrenium ions occur preferentially in a singlet ground state.[24] Both forms (singlet and triplet) in the case of arylnitrenium ions are stabilised through transfer of electron density from the phenyl substituent to the nitrogen atom, but for the triplet form this transfer, and hence the magnitude of the stabilising effect, is less than for the singlet, since the *p* orbital in the triplet state is partly filled[24] (Fig. 1).

The calculated heats of formation of certain nitrenium ions (ΔH_f) and their relative stabilisation energies (ΔE) are given in Table 1.

S T

Figure 1. Mesomeric stabilisation of singlet and triplet nitrenium ions.

Table 1. Heats of formation (ΔH_f) and relative stabilisation energies (ΔE) of the singlet and triplet states of certain nitrenium ions (MNDO method).

Ion	ΔH_f, kcal mol^{-1} (Ref.24)		(S_0-T_1), kcal mol^{-1}	ΔE^*, kcal mol^{-1} (Ref.24)	
	S_0	T_1		S_0	T_1
$\overset{+}{N}H_2$	313.4	292.2	21.2	0	0
$MeNH$	277.9	271.7	6.2	-37**	-22
Me_2N	259.1	251.1	8.0	-57	-44
	240.4	250.9	-10.5	-70	-38
$PhNH$	241.5	267.6	-26.1	-106**	-59

*Values of the stabilisation energies given relative to $\overset{+}{N}H_2$.

**The corresponding stabilisation energies of $MeCH_2$ and $PhCH_2$ relative to CH_3 are −37 and −56 kcal mol^{-1}.

The data shown are in good agreement with the results of experimental studies by Japanese research workers.[45,48] In the case of the reactions between alkyl- and phenyl-nitrenium ions with different aromatic nucleophiles it is possible to establish a trend for the decrease in energy of singlet nitrenium ions:

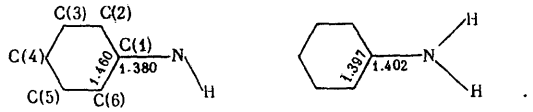
$$\overset{+}{N}H_2 > Alk\overset{+}{N}H > Ph\overset{+}{N}H.$$

It can be seen from Table 1 that aromatic nitrenium ions have a higher stabilisation energy than the aliphatic ions.[5]

Quantum-chemical calculations of the energy, geometry, and electronic structure of phenylnitrenium ions were made in two studies.[24,25] Calculation of electron density by the MNDO method

† At the same time it was established[58] that solvents containing heavy atoms can catalyse spin inversion. This effect has been observed in three studies.[41,43,59]

for phenylnitrenium ions[24] assumes an optimum geometry for planarity of the cation.‡ From the calculations of Krylov[25] the following optimum geometry of the phenylnitrenium ion was established (the geometry of aniline is shown for comparison):



It should be noted that the C–N bond in phenylnitrenium ions is considerably shorter than in alkylnitrenium ions. As expected, the results of calculation of the electronic structure of phenylnitrenium ions suggest that a partial positive charge occurs on the second (0.112), sixth (0.112), and fourth (0.169) carbon atoms of the benzene ring. At the same time the charge on the carbon atom at the *para* position exceeds the positive charge on the nitrogen atom (0.123) (Table 2).

Table 2. Charges on the electrophilic sites of phenylnitrenium ions.

Atom	MNDO method (Ref.24)		CNDO/2 method (Ref.25)
	LUMO	*q* (total)	*q* (total)
N	0.444	0.001	0.123
C(1)	-0.087	-0.065	—
C(2)	-0.459	0.346	0.112
C(3)	0.043	-0.010	—
C(4)	0.590	0.384	0.169
C(5)	-0.004	-0.041	—
C(6)	-0.496	0.233	0.112

Krylov[25] concluded from the charge distribution data that there is a considerable contribution from mesomeric carbocation structures in phenylnitrenium ions.

(I) (II) (III) (IV)

The values of the LUMO coefficients§ shown in Table 2 also show that four electrophilic sites occur in phenylnitrenium ions.

‡ Similar calculations[63,64] give a nonplanar structure for aniline.

§ According to general multielectron perturbation theory, a donor-acceptor interaction may be charge-controlled (type I) or (frontier) orbital-controlled (type II). Electrophilic aromatic substitution (benzene as a mild nucleophile) is a "frontier orbital-controlled" reaction. The reaction sites of the electrophile will be atoms having the highest charge density on their lowest unoccupied molecular orbital (LUMO).[65]

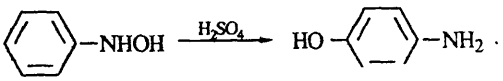
The experimental data (see Section IV) suggest that nitrenium ions with aromatic substituents do in fact behave both strictly as nitrenium ions (I) and as carbocations (II)–(IV).

III. Methods of generation

1. Bamberger and Stieglitz rearrangements

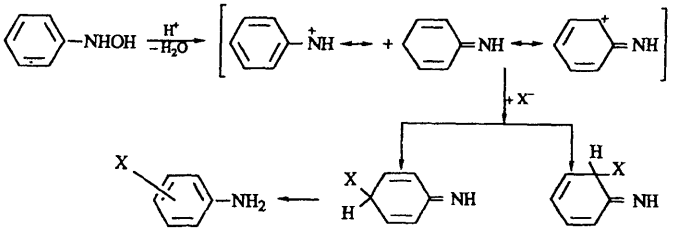
The original ideas about the existence of unstable bivalent nitrogen intermediates developed as a result of studies on the rearrangements of *N*-arylhydroxylamines — the so-called Bamberger and Stieglitz rearrangements.

The Bamberger rearrangements takes place on treatment of *N*-phenylhydroxylamine with aqueous mineral acid, resulting in the formation of *p*-aminophenol.[66–68]



Bamberger assumed that arylhydroxylamines are dehydrated to nitrenes, which react with nucleophilic reagents to give rearrangement products.

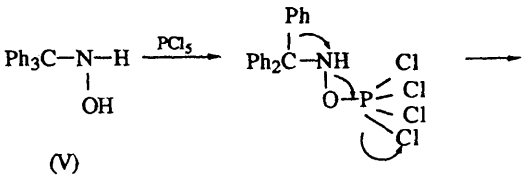
Subsequent studies of this reaction[69–72] demonstrated that a nitrenium ion is formed at an intermediate stage. In an investigation of the acid catalyst trifluoromethanesulphonic acid (TFMSA), *ortho*- and *para*-substituted anilines were obtained.[72]



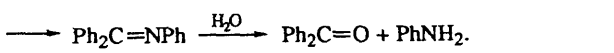
X = HO, PhO, MeO, Cl, Ph etc.

It could be assumed from kinetic studies that the nitrenium ion is formed in a slow stage and then rapidly adds a nucleophile molecule.[73]

Stieglitz et al.[1,2] initially studied the rearrangement of *N*-monoalkylhydroxylamines in which the carbon atom adjacent to the nitrogen was fully substituted, such as in tritylhydroxylamine (V).



(V)

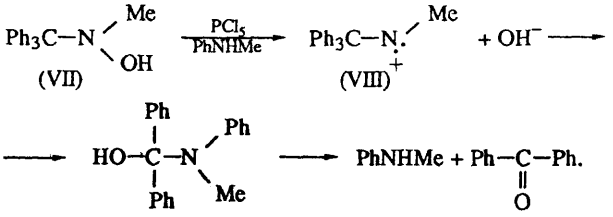


(VI)

Treatment of (V) with phosphorus pentachloride causes one of the phenyl groups to migrate to the nitrogen atom with the formation of the imine (VI), and after hydrolysis benzophenone and aniline are formed. At the same time migration was thought to be an

intramolecular process. Stieglitz et al. put forward the suggestion that species with a univalent nitrogen atom (nitrene as interpreted at the present time) were formed as an intermediate.

This interpretation of substituted hydroxylamines as originally proposed by Stieglitz encounters difficulties when attempts are made to distinguish between nitrenium ions and nitrenes in *N*-monosubstituted hydroxylamines. In order to exclude the formation of nitrene, Stieglitz et al.[3] studied the rearrangement of a dialkyl-substituted hydroxylamine, namely, triphenylmethyl-*N*-methylhydroxylamine (VII) under similar conditions (with PCl_5), as a result of which only triphenylchloromethane was formed. However, when the reaction was carried out in the presence of small quantities of *N*-methylaniline, the rearrangement products—benzophenone and *N*-methylaniline—were isolated in low yield together with triphenylchloromethane. In this case it is impossible to depict the formation of nitrene, and the authors put forward another reaction scheme, which actually features the nitrenium ion (VIII):



Later studies[5] supported the conclusion of Stieglitz, by demonstrating that under certain conditions the rearrangement of disubstituted hydroxylamines actually occurs via the formation of a nitrenium ion.

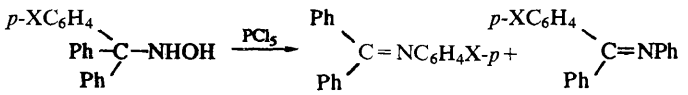
Research on the rearrangements of Stieglitz and Bamberger assisted in the development of different methods for the synthesis of nitrenium ions. For a long time the most widely studied of the reactions that occur via intermediate nitrenium ions were the reactions of hydroxylamine and *N*-haloamine derivatives.

Other methods of generating nitrenium ions are reactions involving organic azides and hydrazine derivatives and the photolysis and thermolysis of pyridinium and sulphonium salts and other salts. At the present time nitrenium ions may also be obtained by physicochemical and nuclear chemical methods. Let us examine these methods in greater detail.

2. Generation of nitrenium ions at intermediate stages of organic reactions

a) Reactions of hydroxylamines. It was possible to conclude from an examination of the rearrangements of Stieglitz and Bamberger that the formation of nitrenium ions is affected both by the nature of the actual nitrogen-containing organic compounds (sources of nitrenium ions) and by the medium in which these reactions occur.

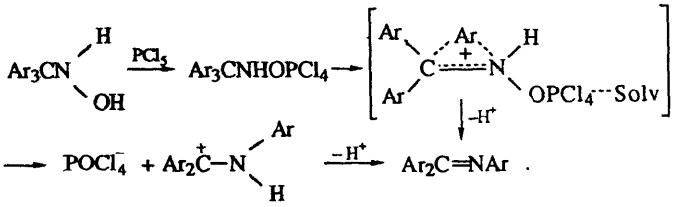
Studies by Newman and Hay[74] also provide evidence for the formation of nitrenium ions in the Stieglitz rearrangement. In a study of the effect of substituents in the aromatic ring on the migrating ability of the ring in the rearrangement of triarylhydroxylamines on treatment with PCl_5



X = OMe, Cl, NO_2 ,

it was established that a decrease in the electron-donating properties of the substituents leads to a reduction in the migrating ability of the corresponding group: 9.10 (C_6H_4OMe), 0.55 (C_6H_4Cl), and 0.38–0.18 ($C_6H_4NO_2$). The authors concluded that, by analogy with the pinacol rearrangement (a typically ionic process), the Stieglitz rearrangement is also accompanied by the formation of ionic species.

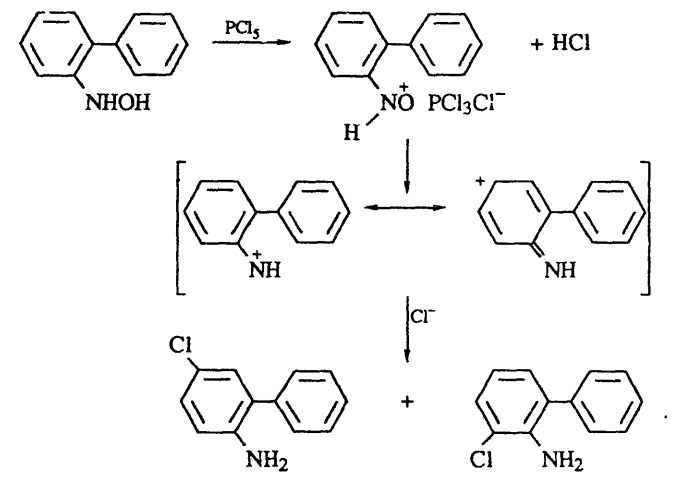
We should not that this rearrangement is interpreted by Krylov[25] as the synchronised cleavage of the N–O bond and migration of a group to the nitrogen atom



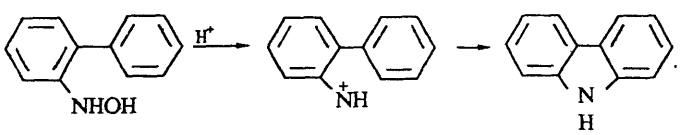
However, the possibility of nitrenium ions being formed in very polar media (in polyphosphoric acid, for example) cannot be excluded.

It should be noted that the mechanism of the Stieglitz rearrangement by treatment with various Lewis acids[75–77] depends on the electrophilicity of the reagent used. The probability of a nitrenium ion being formed increases with an increase in the electrophilicity of the reagent and is reduced to zero in the case of weak electrophiles (*o*-isopropyl methylphosphonochloridate, for example).[78]

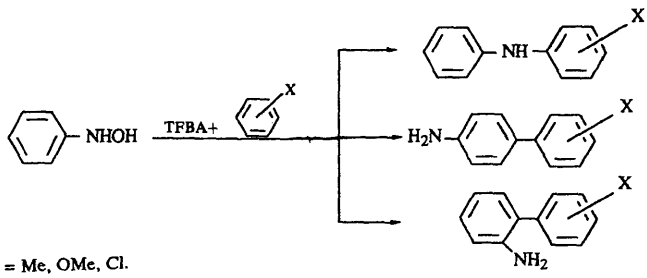
For the rearrangement of 2-hydroxylamino-1,1′-biphenyl, which takes place on treatment with PCl_5, a scheme involving the formation of an intermediate nitrenium ion was proposed by Potts et al.[79]



A similar process, but one that occurs on treatment with strong proton acids, gives carbazole which is formed from a nitrenium ion.[80]



Considerable attention has been given recently to intermolecular reactions involving the introduction of aminophenyl groups into an aromatic ring. On treatment of phenylhydroxylamine with tetrafluoroboroic acid (TFBA) in aromatic hydrocabons, the arylamination products were isolated in 20–50% yield:[81]

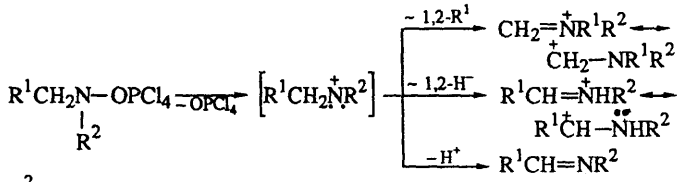


X = Me, OMe, Cl.

It was assumed in this case that initially a phenylnitrenium ion is formed, which subsequently reacts with an aromatic ring.

Further studies in this area showed that other acids, such as acetic acid (AA),[33,34,36] trifluoroacetic acid (TFAA),[35,37,40,41,43] and trifluoromethanesulphonic acid (TFMSA)[39,43,72,82] can act as catalysts of arylamination occurring via the formation of a nitrenium ion. It was found, moreover, that the nature of the acid has an effect on the ratio of the final products.

Four studies by Krylov et al.[6–8,25] investigated the rearrangements of *N*-alkyl- and *N,N*-dialkylhydroxylamines and also their salts with phosphorus pentachloride involving migration of hydrogen and alkyl groups:



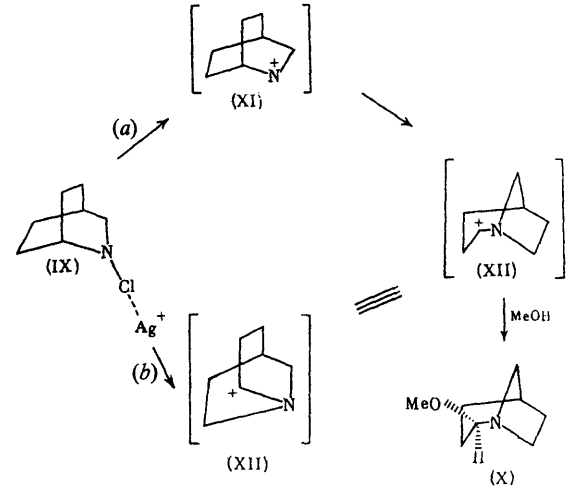
R^2 = H, CH_2R.

The authors assumed that the primary and secondary amines were formed as a result of the rearrangement of nitrenium ions, accompanying migration of a group to the electron-deficient nitrogen atom.

b) Reactions of *N*-haloamines. The first, rather contradictory, studies on the preparation of nitrenium ions as a result of the cleavage of the N–Hal bond in *N*-haloamines were published in the mid-1960s.[83–85] Because of the large number of studies in this area, it has been shown at the present time that many of the compounds that contain an N–Hal bond are very convenient substrates for the preparation of nitrenium ions.[5,59,86–108] Such compounds include azabicyclic compounds, haloamines with cyclic groups (cyclopropane and cyclobutane) and aromatic groups (anilines), etc.

Scheme 1 illustrates the formation of nitrenium ions by solvolysis of *N*-chloroisoquinuclidine (IX) in a methanol solution of silver nitrate.[5]

Scheme 1

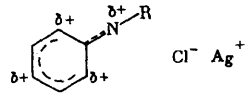


The conversion of (IX) to (X) can occur by two routes: route (*a*)—the heterolytic cleavage of a chloride anion resulting in the formation of nitrenium ion (XI): route (*b*)—simultaneous loss of a chloride anion and migration of an alkyl group with its pair of bonding electrons, giving product (XII). Regardless of which of the two routes is followed in this rearrangement, the species (XI) with a deficiency of electrons on the nitrogen atom participates in this process.

In studying the reaction depicted in Scheme 1, Gassman and Cryberg[59] conducted an experiment on the conversion of nitrenium ions from a singlet to a triplet state. By using solvents containing heavy atoms, it was possible to control the conversion of singlet to triplet states according to a previously established method.[109–110] The authors[59] believe that this constitutes evidence for the existence of nitrenium ions.

A series of studies[90,94,97,101,102,105] is concerned with the formation of nitrenium ions in nucleophilic aromatic substitution in anilines. Thus, on solvolysis of *N*-chloroanilines, products that were similar to those of the Bamberger rearrangement[72] were isolated, as illustrated by Scheme 2. It is clear from Scheme 2 that, at the initial stage of the reaction, ionisation of (XIII) occurs with the formation of arylnitrenium ions with various resonance structures [(XIVa) ⟷ (XIVb) ⟷ (XIVc)].

Even though an excess of silver ions is present in the reaction mixture, chloro derivatives are formed. Gassman et al.[101] attribute this phenomenon to the formation of an intimate ion pair at an intermediate stage of the reaction.



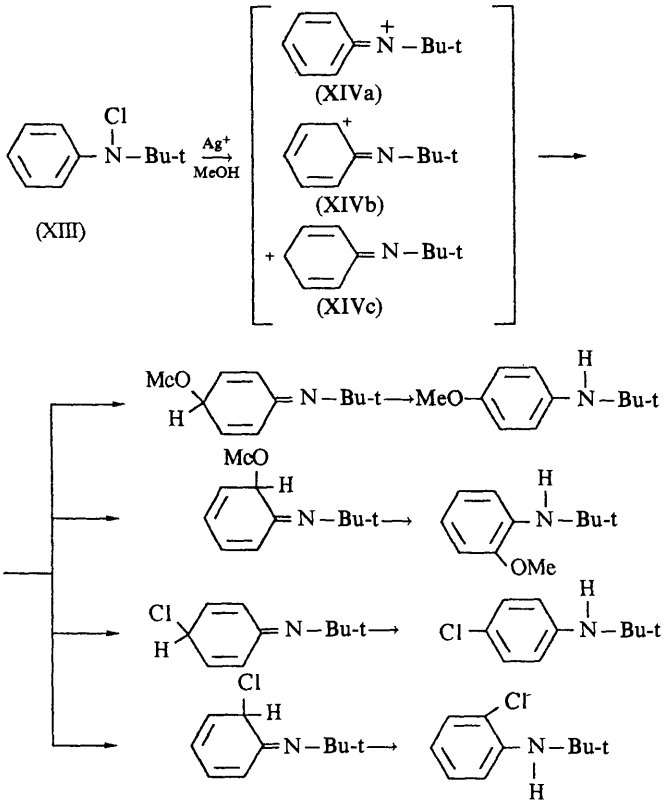
Similar results were obtained from the thermal rearrangement of *N*-chloroanilines.[102]

The formation of nitrenium ions as intermediate species was also detected in the solvolysis of *N*-chloroamines containing a multiple bond.[89,96,111–115] It should be noted that in the solvolysis of *N*-haloamines, cleavage of the N–Hal bond can take place both heterolytically and homolytically, depending on the structure of the

initial compound and the reaction conditions. The presence of rearrangement products in the reaction mixture may be regarded as an important argument in favour of heterolytic cleavage of the bond.

It has been shown in a number of studies[116–123] that the rearrangements of *N*-haloamines on treatment with Lewis acids also occur via the formation of nitrenium ions.

Scheme 2



c) Reactions of organic azides. It was shown in studies in the 1950s and then particularly in research carried out in the 1980s that organic azides represent convenient sources of nitrenium ions. The majority of organic azides are unstable compounds. They readily decompose with the elimination of molecular nitrogen on exposure to heat, light, and various chemical reagents. Reactions involving the acid-catalysed decomposition of azides and their possible conversions through reaction of the latter with carbocations (Schmidt reaction) are of interest in relation to the problem of nitrenium ions

$$RNN_2 + X^+ \longrightarrow \left[R-\underset{\displaystyle X}{\underset{|}{N}}-N_2\right]^+ \longrightarrow R-\overset{+}{\underset{\cdot\cdot}{N}}-X + N_2$$

X = H, R etc.

Despite the considerable quantity of experimental data, the question as to whether nitrenium ions are formed during acid-catalysed decomposition of azides and in the Schmidt rearrangement remains open. In a number of studies[124–129] the concept of the intermediate formation of nitrenium ions was introduced to explain the acid-catalysed rearrangement of azides. However, the alternative possibility of synchronous migration of a group to the nitrogen atom and the elimination of a nitrogen molecule generally cannot be excluded. In three review articles devoted to the rearrangement of azides[130–132] it is noted that despite the concept of nitrenium ions being introduced to explain a number of azide reactions, it has not been possible to date to provide significant evidence for their formation at an intermediate stage of the reaction.

It was shown in four studies[133–136] that rearrangements similar to the Schmidt reaction occur by interaction of azides with a nitrosonium cation. Doyle et al.[134] assumed that nitrosonitrenium ions are formed at an intermediate stage of the reaction. However, in two subsequent studies[135,136] another reaction scheme was put forward:

$$Ph_2CH-N_3 + NO_2^+ \longrightarrow Ph_2CH^+ + N_2 + N_2O,$$

$$Ph_2CH-N_3 + Ph_2CH^+ \longrightarrow Ph_2CHN(N_2^+)CHPh_2 \xrightarrow{-N_2} PhCH=\overset{+}{N}(Ph)CHPh_2 \xrightarrow{-Ph} Ph_2CH-\overset{+}{N}-CHPh_2$$

$$PhCH=\overset{+}{N}(Ph)CHPh_2 \xrightarrow{H_2O} PhCHO + PhNHCHPh_2 .$$

The constant ratio of unsubstituted to substituted benzaldehydes for reactions of phenylarylazidomethanes with nitrosonium tetrafluoroborate or $PhAr\overset{+}{C}H\ BF_4^-$ whatever the reagent used was regarded[135,136] as evidence for the participation of dialkylnitrenium ions in these reactions.

A group of Japanese scientists directed by H Takeuchi[33–48] studied the photolysis and thermolysis of azides, pyridinium and sulphonium salts, and other products in the presence of proton acids, which result in the formation of nitrenium ions. They generate nitrenium ions with various structures: $\overset{+}{N}H_2$ and its alkyl homologues,[45,46,48] ethoxycarbonylnitrenium ions,[33,35,40] unsubstituted phenylnitrenium ions,[34,37,39,41,46] and phenyl-substituted[42–44,46] and naphthyl-substituted[39] nitrenium ions with different substituents.

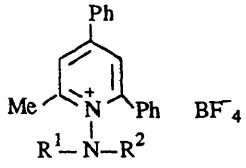
It was found that in proton acids such as acetic acid, trifluoroacetic acid (TFAA), and trifluoromethanesulphonic acid (TFMSA), phenyl azide completely decomposes after a few minutes at 25 °C,[43] whereas in aromatic solvents azides decompose at temperatures above 130 °C.[43] Furthermore, Takeuchi et al. studied the decomposition of azides in a mixture of an aromatic solvent and a proton acid. For example, in a mixture of benzene (70%) and trifluoroacetic acid (30%) at 25 °C, phenyl azides decompose over a period of 10 h. In the opinion of Takeuchi et al.[43] photolysis (thermolysis) of azides yields a nitrene, which is protonated by the acid to form its conjugate base and a nitrenium ion.

For example, in the thermolysis of ethyl azidoformate in acetic acid, nitrene (XV) is first formed, then the ion pair (XVI) is formed:[33,34]

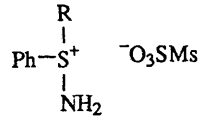
Scheme 3

$$N_3CO_2Et \xrightarrow{h\nu \text{ or } \Delta T} :\ddot{N}CO_2Et \xrightarrow{MeCOOH} [MeCOO^- \ ^+NH_2CO_2Et].$$
(XV) (XVI)

d) Photolysis (thermolysis) of pyridinium and sulphonium salts. In addition to azides, Takeuchi et al.[45,47,48] proposed the use of sulphonium and pyridinium salts as sources of nitrenium ions. The photolysis or thermolysis of pyridinium tetrafluoroborate (XVII) or *S*-aminosulphonium salts (XVIII) in the presence of TFAA



(XVII)



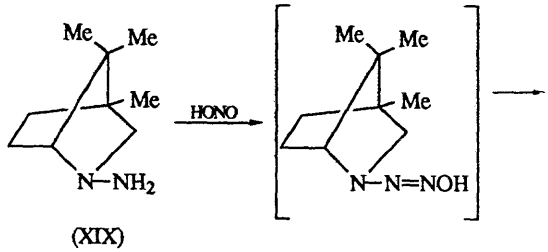
(XVIII)

$R^1 = R^2 = H$; $R^1 = H$, $R^2 = Ph$;
$R^1 = R^2 = Alk$.

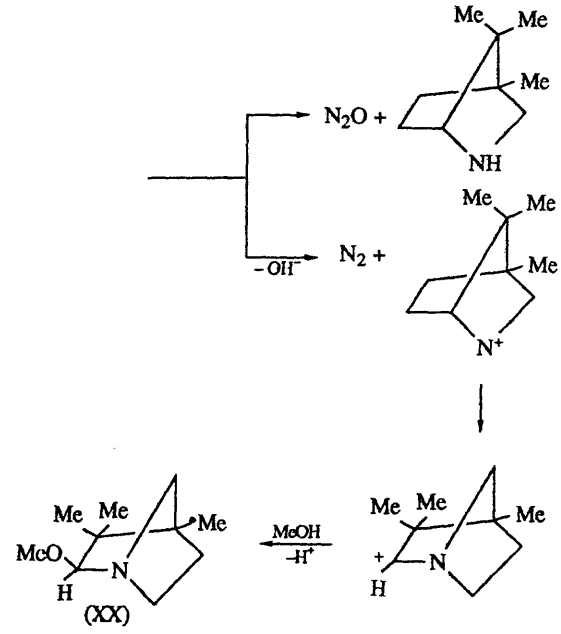
generates nitrenium ions in both singlet and triplet states. These studies are of particular interest because quantum-chemical calculations showed that for the simplest nitrenium ion and its alkyl homologues the ground state is triplet (see Section II).

e) Other reactions that occur via the formation of nitrenium ions. Together with the previously studied solvolysis reactions of *N*-haloamines, where the formation of intermediate nitrenium ions was established, reactions of hydrazines with a similar structure were also studied.[98] On nitrosation of the hydrazine (XIX) with isoamyl nitrite, the product (XX) was isolated (21% yield), derived from a hypothetical rearranged nitrenium ion (Scheme 4). Unfortunately, in this study there was no analysis of the gaseous products that was necessary to establish the actual pathway for formation of the secondary amine.

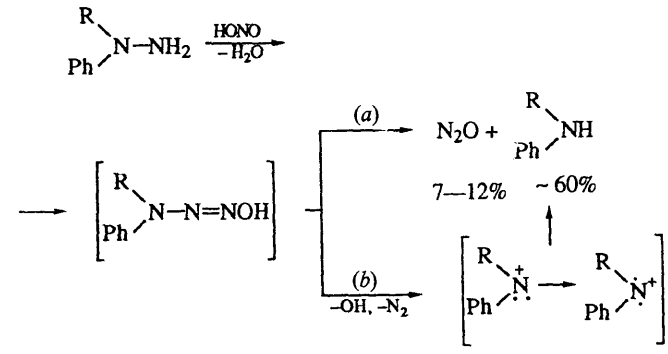
Scheme 4



(XIX)



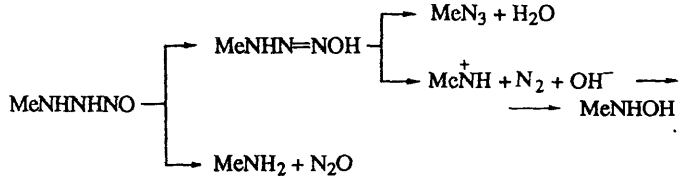
The reactions of 1,1-alkylarylhydrazines with nitrosating agents were studied in greater detail by De Rosa,[137] who put forward the following reaction scheme:



Analysis of the products showed that the yield of secondary amine was much higher than that of nitrous oxide. This phenomenon, in the opinion of De Rosa,[137] demonstrates the possibility that the secondary amine is formed via the conversion of a nitrenium ion from a singlet to a triplet state [route (*b*)].

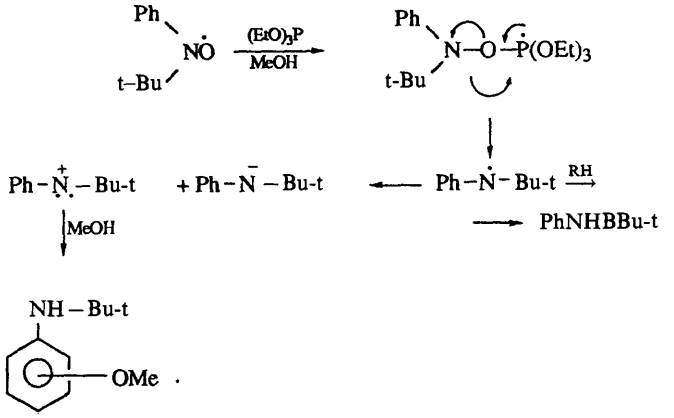
The possible formation of monosubstituted alkylnitrenium ions was also noted by Perrott et al.[138] A study of the kinetics of the nitrosation of hydrazines suggested the possibility of this reaction occurring by two routes (Scheme 5)

Scheme 5

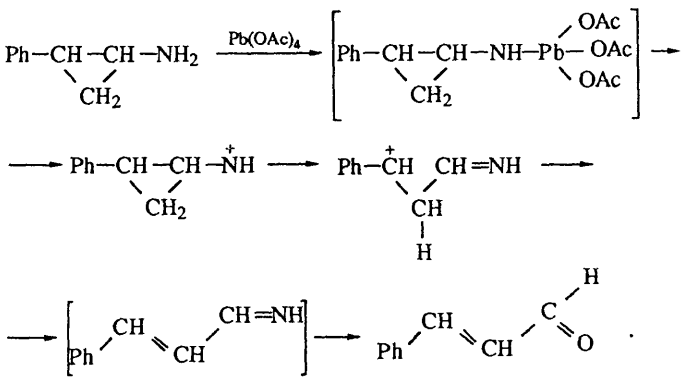


It is clear from Scheme 5 that nitrosation on the unsubstituted atom can result in the formation of a nitrenium ion.

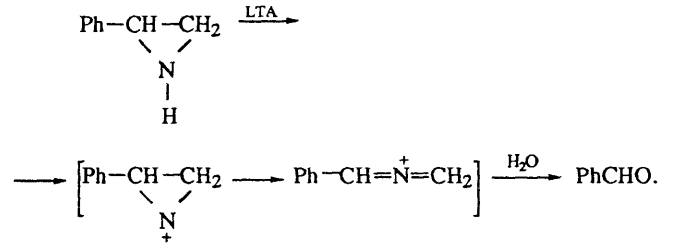
A further route for the generation of nitrenium ions was investigated by Cadogan and Rowley:[139]



It is assumed that the oxidation of the *trans*- and *cis*-isomers of 2-phenylcyclopropylamine with lead tetraacetate (LTA) to the *trans*-isomer of cinnamaldehyde also occurs via the formation of an intermediate nitrenium ion.[140]

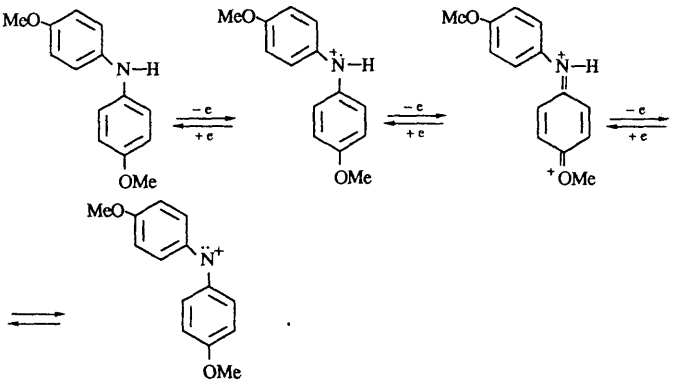


Isomerisation of an intermediate nitrenium ion to an azaallyl ion also occurs on oxidation of aziridines with ring opening:[140]



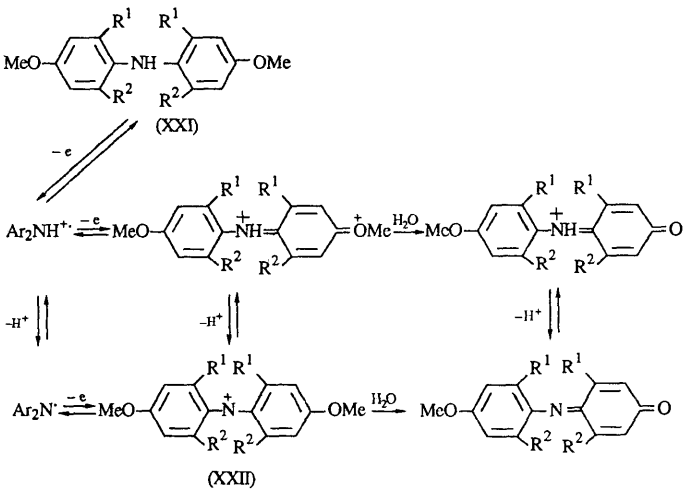
3. Physicochemical methods of generating nitrenium ions.

Electrochemical methods have been used to generate and study the behaviour of nitrenium ions.[26,27,141,142] It was through the use of electrochemical research methods such as polarography and different forms of voltammetry that the first direct evidence for the existence of nitrenium ions was obtained.[26] Cyclic voltammetry was used to study the oxidation of dianisylamine and to establish the lifetime of the dication formed by two-electron oxidation of dianisylamine (~1 s). In acetonitrile the equilibrium is probably shifted towards the unprotonated form—a nitrenium ion.



Similar studies were carried out for a number of other diarylamines:[141]

Scheme 6



$R^1 = R^2 = OMe$(a); $R^1 = OMe$, $R^2 = H$ (b); $R^1 = R^2 = H$ (c).

Table 3. Half-wave potentials for oxidation of diphenylamines (XXI) in MeCN and absorption spectra of amines (XXI) and nitrenium ions (XXII).[141]

Amine	$E^{ox}_{1/2}$, V	λ_{max} of (XXI), nm; (lg ε), neutr. MeCN	λ_{max} of (XXII), nm; (lg ε), MeCN with 2,6-lutidine
(a)	0.035; 0.570	345(4.19); 373(4.02); 796(4,23)	364 (4.36); 535 (3.43); 723(4.39)
(b)	0.180; 0.725	259(3.66); 377(4.34); 798(4,46)	378(4.27); 675(4.58)
(c)	0.295; 0.850	294(3.98); 360(4.23); 762(4,50)	660

* Values of $E_{1/2}$ given relative to Ag/10^{-2} M Ag^+.

Solutions of nitrenium ions (XXII) were obtained by controlled-potential electrolysis of amines (XXI). Values of λ_{max} for amines (XXI) and for cations (XXII) are given in Table 3. The spectra of the initial amine and radical cation differ considerably from the values given for the nitrenium ion.

Electrolysis was also employed subsequently in the oxidation of different substituted pyrroles[142] and the UV spectra of the corresponding nitrenium ions were obtained.

It has been reported[143] that nitrenium ions are also formed by electron bombardment of a mixtures of methane and ammonia, but the reactions investigated only apply to the gas phase.

$$CD_3^+ + NH_3 \longrightarrow [CD_3NH_3^+]^* \begin{cases} \longrightarrow (CD_2{=}NH_2^+)^* + HD \quad 70\% \\ \longrightarrow CD_3{-}NH^+ + H_2 \quad 30\% \end{cases}$$

4. Nuclear chemical method for generating nitrenium ions

The nuclear chemical method of obtaining reactive species is based on the chemical consequences of the β^--decay of atoms forming part of the different molecules.[28,144,145]

β^--Decay is known to be the spontaneous conversion of the nuclei that accompanies the emission of a nuclear electron and antineutrino. At the same time changes occur in the nucleus in accordance with the following scheme:

$$^0_1n \rightarrow {}^1_1p + e^- + \tilde{\nu},$$

where n and p are nuclear particles (neutron and proton); e^- and $\tilde{\nu}$ are an electron and antineutrino. Such a conversion signifies the formation of the nucleus of an atom of a new element that lies one square to the right relative to the mother (initial) element in the Periodic Table. This process occurs within about $10^{-22}-10^{-21}$ s. The electron formed in the nucleus leaves the atom after about 10^{-18} s.

Since the process of β^--decay is accompanied by an increase in the number of protons (nuclear charge) by one and the electron shell is inherited from the mother atom, there is a deficit of electrons in the latter in relation to the new (daughter) nucleus. Thus, the charge state of the daughter atom increases by one. If the decaying atom forms part of a molecule, the composition and charge state of the new chemical structure—the primary molecular ion (PMI)—is given by the general scheme

$$\left[{}^A_ZXY\right]^q \xrightarrow{\beta^-} \left[{}^A_{Z+1}XY\right]^{q+1},$$

where ${}^A_ZX$ is the atom undergoing β^--decay and Y is the normal state of the molecular system. For example,

$$^{14}CH_4 \xrightarrow{\beta^-} [^{14}NH_4]^+,$$

$$NH_2{}^3H \xrightarrow{\beta^-} [NH_2He]^+ \rightarrow NH_2^+ + He.$$

It is quite clear that there is continuity between the electronic structure of the initial molecule and the primary molecular ion formed as a result of β^--conversion of one of the atoms. The number and nature of the ligands also remains unchanged. Thus, the initial and final molecular forms are isoelectronic, isostructural, and have the same number of ligands.

Furthermore, there is a definite correlation between the free energy in the initial molecule and in the primary molecular ion. Will the PMI be stable? In the examples shown the resulting NH_4^+ ion is the familiar stable ammonium ion while NH_2He^+ is an unstable ion which fragments to form a nitrenium ion and helium.

Theoretical calculations and numerous experimental results suggest that in the vast majority of cases β^--decay of the atoms in molecules results in the formation of stable PMIs in high yield.[28]¶ Only in the β^--conversions of tritium (and the lightest halogens) does the formation of unstable ions occur.[145]

The instability of helium-containing organic primary molecular ions is primarily due to the migration of positive charge from the helium atom to the organic group:

$$[RHe^+] \rightarrow [R^+He].$$

This redistribution of charge occurs because the ionisation potential of the helium atom is higher than that of the organic groups. At the next stage the species $[R^+He]$ decomposes to form positively charged ions (carbenium, nitrenium, etc.) and helium atoms (the energy of the C–He bond is close to zero):[146,147]

$$[R^+He] \rightarrow R^+ + He.$$

The time required for such processes to occur is 10^{-13} s, which is considerably less than the time between collisions of two interacting particles. Therefore, the resulting reactive species will interact with molecules of the surrounding medium as free particles.

The nuclear chemical method of obtaining intermediate reactive species has a number of advantages over known methods, in particular classical methods. It follows from the above description that the nuclear chemical method provides the possibility of obtaining reactive charged species in a free state (without counterions or solvent cage),† with a strictly defined structure and a given initial charge localisation.

The rate of generation of reactive species using the nuclear chemical method is determined solely by the rate of radioactive decay of tritium [$T_{1/2}(^3H)$ = 12.2 years] and does not depend on external conditions (temperature, pressure, state of aggregation, composition of reaction mixture, etc.).

The number of molecular ions (N_{R^+}) formed after a given time t from N_{R-^3H} mother molecules can be calculated from the equation

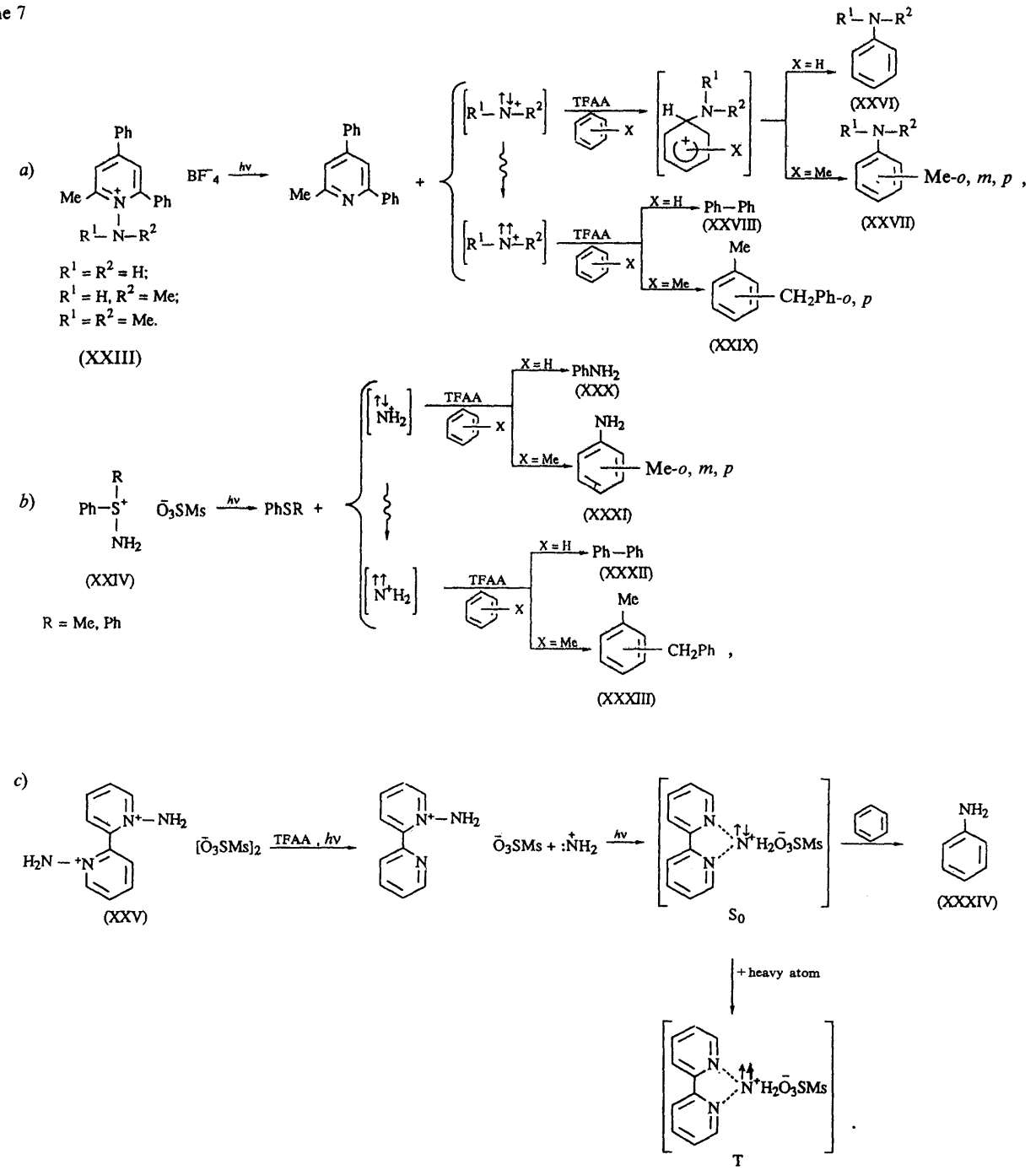
$$N_{R^+} = kN_{R-^3H}\cdot(1-e^{-\lambda t}) \approx k\lambda N_{R-^3H}t \quad \text{when} \quad t \ll T_{1/2},$$

where N_{R-^3H} is the number of molecules of hydrocarbon labelled with tritium; λ is the radioactive decay constant of tritium; k is the coefficient of probability of particle formation; $k = ng$ (n is the number of tritium atoms in the mother molecule; g is the proportion of β^--emissions resulting in the formation of unexcited primary molecular ions).

¶ We have deliberately not considered processes involving the excitation and ionisation of the electron shells of daughter atoms which result in decomposition of PMIs, since the proportion of such β^--conversions does not exceed 30%.

† The β^--particle (nuclear electron) emitted in the process of decay cannot serve as a counterion since it escapes to a distance at which the interaction energy between the ion and the nuclear electron is very low.

Scheme 7



Let us consider the decay of tritium in PhN^3H_2 as an example. If the activity of aniline in this series is 3.7×10^{10} Bq, the total number of nitrenium ions formed in 24 hours is 4.8×10^5.

An undoubted merit of the nuclear chemical method is its potential for studying the reactions of free reactive species with pure compounds and their mixtures in the gas, liquid, and solid states. Considerable experience in the generation of carbocations[28,144,145,148–151] and silicenium[152] ions using the nuclear chemical method has been gained to data. This method has also been used during the last ten years to generate nitrenium ions. The nuclear chemical method has been successfully used by Nefedov et al.[29–32] for the synthesis of free phenylnitrenium ions and to study their reactions with aromatic hydrocarbons.

The formation of phenylnitrenium ions occurs as a result of the β^--decay of tritium in aniline that has doubly tritiated amino group according to the following scheme

$$PhN^3H_2 \xrightarrow{\beta^-} [PhN^3HHe]^+ \rightarrow [PhN^3H^+Hc] \rightarrow PhN^3H^+ + He.$$

IV. Reactions of nitrenium ions

As indicated above, nitrenium ions are reactive species having a positive charge and free *p* orbital. With these characteristics they can be classified as species with well-defined electrophilic properties. The large heats of formation[23] (for example, for phenylnitrenium ions in singlet and triplet states these are 241.5 and 267.5 kcal mol^{-1} respectively)[24] and the presence of a charge and free orbital govern not only the reactivity but also the strictly controlled interaction pathway of these species. These species interact with residues with high electron density in substrate molecules. These reaction characteristics of nitrenium ions also govern the nature of the resulting intermediate complexes and reaction products.

1. Reaction of alkylnitrenium ions

The simplest nitrenium ion $:\overset{+}{N}H_2$ and its alkyl homologues have a triplet ground state[23] and are not capable of causing direct aromatic amination.[48]

Takeuchi et al.[48] carried out the direct amination of benzenes in arene–TFAA (30%) mixtures with singlet alkylnitrenium ions generated by photolysis of pyridinium (XXIII), sulphonium (XXIV), and bipyridinium (XXV) salts (Scheme 7) containing an amino substitutent on the nitrogen or sulphur atoms. The reactions depicted in Scheme 7 indicate that the products (XXVI), (XXVII), (XXX), (XXXI), and (XXXIV) are typical examples of the aromatic substitution of hydrogen in benzene or toluene by a singlet nitrenium ion. Products (XXVIII), (XXIX), (XXXII), and (XXXIII) are characteristic of the reaction of triplet nitrenium ions. It was noted that S → T conversion is more favourable in toluene. Takeuchi et al. established the following pattern of change in energy of the singlet state on going from an unsubstituted to an aliphatic and aryl nitrenium ion:

$$\overset{+}{N}H_2 > Alk\overset{+}{N}H > Ph\overset{+}{N}H,$$

which is supported by the fact that aromatic amination with singlet alkylnitrenium ions, in contrast to aryl ions, has both low substrate and positional selectivity.[40,42,46,48]

It was established[48] that the reactivity of the simplest nitrenium ion generated from *N*-aminopyridinium salt (XXIII) is governed by the nature of the substituent in the pyridine ring of salt (XXIII) and by the nature of the counterion. An electron-withdrawing group (for example, CN) in the pyridine ring and a counterion capable of forming an H-bond with the nitrenium ion increase the selectivity factor. It is assumed that the unsubstituted nitrenium ion which is generated at the first stage is not free but interacts with both the unshared electron pair of the pyridine and with the counterion (Fig. 2).

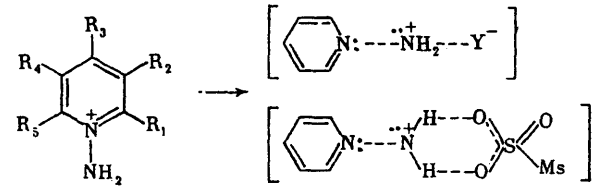
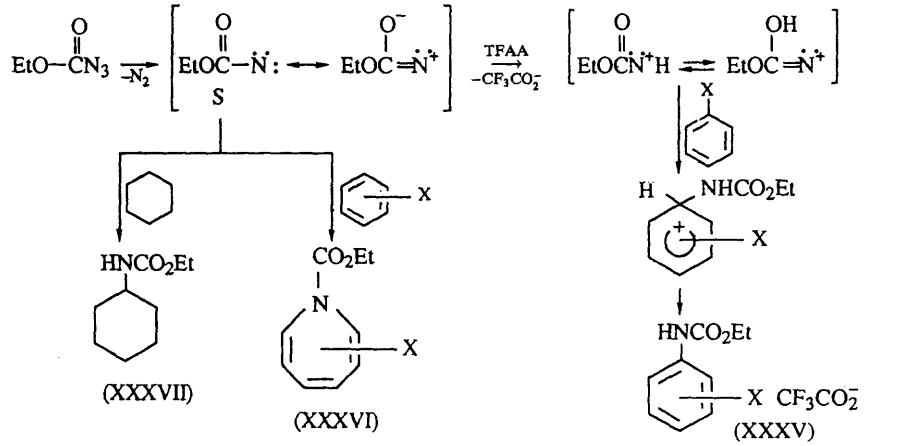


Figure 2. Interaction of an unsubstituted nitrenium ion with an electron pair and hydrogen bonding.[48]

This type of interaction assumes a favourable singlet reaction. A similar interaction of the unshared electron pairs of heteroatoms was predicted in the chemistry of nitrenes.[153–155]

By comparing pyridinium (XXIII) and sulphonium (XXIV) salts (Scheme 7) as sources of nitrenium ions, Takeuchi et al.[48] established that for (XXIII) for nitrenim ions were predominantly in the singlet state while for (XXIV) they were mainly in the triplet state. The explanation for this is that the electron pair of sulphur interacts with the nitrenium more weakly than the electron pair of nitrogen in pyridine, since sulphides are less electrophilic then pyridine. Thus, it may be concluded that interaction of nitrenium ions with a free electron pair plays an important part in stabilisation of the singlet

Scheme 8



X = H (a), Me (b).

X = H (a), *o*-Me (b), *p*-Me (c) *o*-NO_2 (d), *m*-NO_2 (e).

state. A weakening of this interaction assists a more rapid S → T triplet conversion.

In the photolysis of pyridinium or sulphonium salts in solvents containing heavy atoms (for example, dichloromethane, dibromomethane, an oxygen molecule, etc.), the yields of singlet products are considerably reduced.

Stabilisation of the singlet state through hydrogen bonding between the nitrenium ion and counterion is currently being investigated.[48]

Takeuchi et al.[33,35,40] studied the electrophilic substitution reaction between the ethoxycarbonylnitrenium ion generated from the corresponding azide and certain aromatic compounds (benzene, toluene, nitrobenzene) in different media that affect the nature of the intermediate (Scheme 8).

Product (XXXV) in Scheme 8 results from the reaction of ethoxycarbonylnitrenium ion with substituted benzenes. In the absence of TFAA, products (XXXVI) and (XXXVII) are obtained, resulting from the reaction between the intermediate nitrene in a singlet state and benzene (toluene) or cyclohexane. The subsequent addition of TFAA to (XXXVI) and (XXXVII) gives products (XXXVa)–(XXXVc).

The reactions of ethoxycarbonylnitrenium ions with aromatic substrates having electron-donating and electron-withdrawing substituents, as shown in Scheme 8, suggest that this nitrenium ion has low substrate selectivity and high positional selectivity. The latter relates to the selective attack at the *ortho* and *para* positions in toluene and the *ortho* and *meta* positions in nitrobenzene. This phenomenon is in good agreement with the assumption that the transition state with the highest energy, which governs substrate selectivity, depends on the nature of the π-complex, and the resulting σ-complex governs the positional selectivity.[156,157] The activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for thermolysis of azide do not differ in TFAA and benzene. This demonstrates that thermolysis of the azide in TFASA does not occur via the azide–acid conjugate but via a nitrene. Thus, the keto and enol forms of the nitrenium ion occur on transfer of a proton from TFAA to nitrene.

This review of the above classical studies on the reactions of alkylnitrenium ions indicates that a considerable number of factors influence the chemical behaviour of these species. These are primarily the methods and conditions of their generation, the nature of the source of nitrenium ions, the nature and concentration of the components of the media in which these reactions occur, etc. This introduces certain difficulties in the interpretation of the chemical nature of these reactive species.

2. Reactions of phenylnitrenium ions

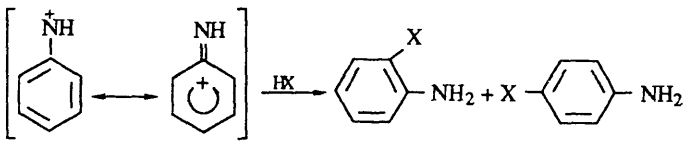
As indicated above, arylnitrenium ions are reactive metabolites of carcinogenic amines and act as intermediates in many organic syntheses. This accounts for the fact that the greatest number of studies have been devoted to the reactions of these species.

The qualitative composition of the products of the ion-molecule reactions between phenylnitrenium ions and different nucleophilic reagents can be predicted from the structural characteristics of these species. The occurrence of four mesomeric structures of the phenylnitrenium ion with an almost equal contribution from each to the actual hybrid structure (see Section II) suggests that these cation sites interact with nucleophilic reagents and that various aminophenylation products of the latter are formed.

Despite the results of quantum-chemical calculations[24,25] which indicate the preference for attack on the carbon atoms of the benzene ring in the phenylnitrenium ion, the experimental data, with a few exceptions,[81] suggest that reactions on the nitrogen cation site of arylnitrenium ions are preferred.

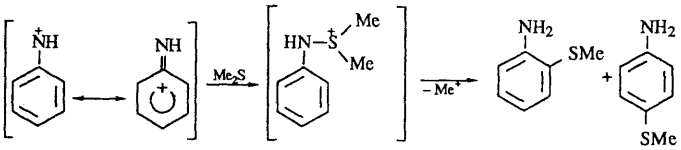
It is shown in a number of studies[37,39,41,43,46,72,81,124–126] that arylnitrenium ions are usually formed at the intermediate stages of reactions in strong proton acids. The chemical behaviour of phenylnitrenium ions usually does not depend on their source of generation (phenyl azides or phenylhydroxylamines) but is dependent on the specific nature of the media in which this ion is formed.

a) Interaction of phenylnitrenium ions with the unshared electron pair of a nucleophile. When nucleophiles containing atoms with an unshared electron pair (alcohols, phenols, acids, water) are treated with phenylnitrenium ions generated from phenylhydroxylamine in the presence of TFMSA, *ortho*- and *para*-substituted anilines are formed in significant yield.[72,124–126]



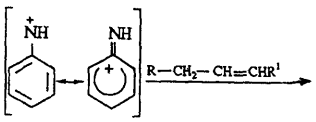
X = OH, PhO, MeO, Cl.

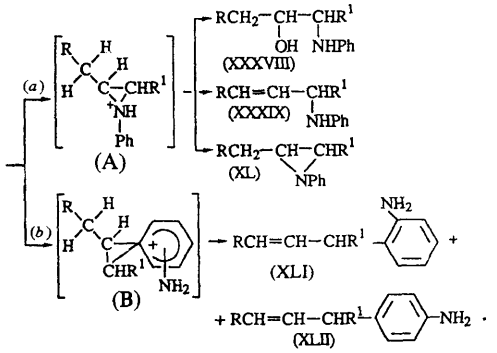
The reaction of phenylnitrenium ions with dimethyl sulphide results in the formation of similar products.[47]



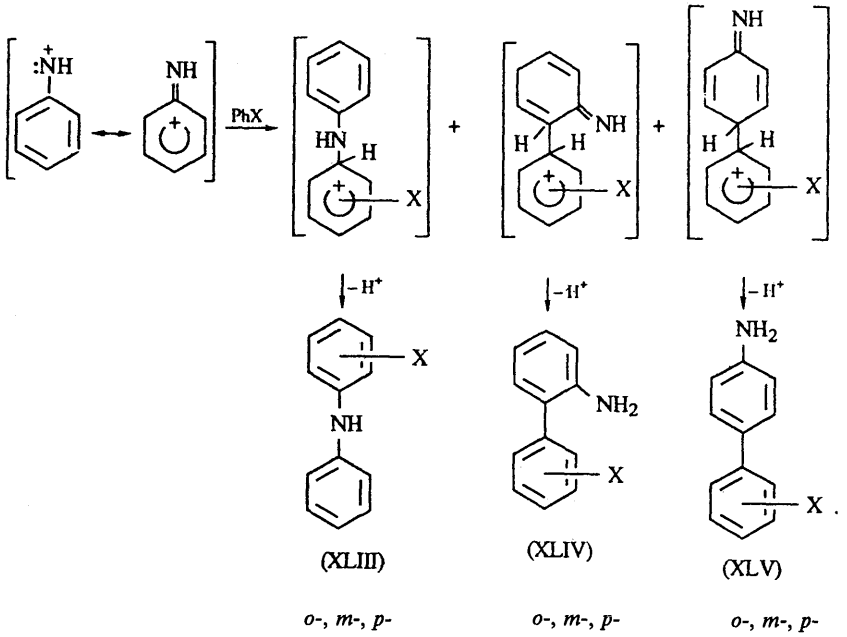
b) Reactions of phenylnitrenium ions with olefins. The reaction of phenylnitrenium ions obtained from azides in the presence of TFAA with aliphatic and cyclic olefins on their double bond results in the formation of addition products both on the N-cation [route (a)] and C-cation [route (b)] sites of the phenylnitrenium ions according to Scheme 9.[41]

Scheme 9





Scheme 10



In the absence of steric hindrance a mixture of products (XXXVIII)–(XLII) is always formed through reaction of the phenylnitrenium ion with aliphatic olefins as shown above. Only their ratio varies according to the reaction conditions. The reaction of a phenylnitrenium ion by route (*a*) occurs via the substituted aziridine cation (A) as an intermediate. The yields of reaction products depend on both the structure of the olefins and the concentration of TFAA. The main reaction product is the *N*-phenyl-β-hydroxylamine (XXXVIII). As the concentration of TFAA is increased, the yield of main product usually decreases, which is due to a side reaction involving polymerisation of the initial alkene.

With cyclohexene the reaction is stereospecific and the *trans* isomer is formed. The unsaturated compounds (XXXIX), (XLI), and (XLII) are isolated as by-products in the reaction with cyclohexene. Product (XXXIX) results from the addition of phenylnitrenium ion to the nitrogen site, while products (XLI) and (XLII) are formed as a result of the reaction of phenylnitrenium ion on a carbon site of the benzene ring. In the latter case the reaction occurs via the cation complex (B).

Products of C-substitution are not formed in the reaction of *cis*- and *trans*-4-methyl-2-pentene with the phenylnitrenium ion. Takeuchi et al.[41] assume that intermediate complex (B) is not formed because of steric hindrance.

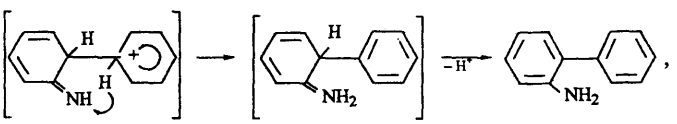
In the reaction of the phenylnitrenium ion with *cis*-4-methyl-2-pentene not only product (XXXIX) but also (XL) is isolated, which corroborates the mechanism put forward by the authors.

The by-product (XXXIX) is not formed at all with methyl acrylate.

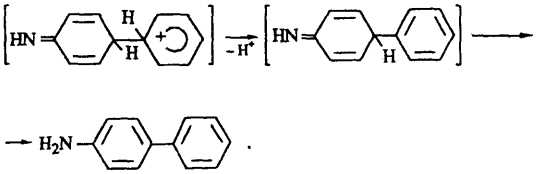
c) Reactions of phenylnitrenium ions with aromatic hydrocarbons. The reactions of phenylnitrenium ions with aromatic compounds have been studied in the greatest detail. These are reactions involving the electrophilic substitution of hydrogen in a benzene ring (S_E) which are complicated by the presence of four cation sites in phenylnitrenium ions.

Reaction of the latter with benzene, depending on the nature of the medium, leads either exclusively to N-substitution products[47,158] or to preferential attack on the carbon atoms of the phenylnitrenium ion,[81] and more frequently to both products with preferential substitution on nitrogen.[37,39,72,159] In this case the *ortho*- and *para*-isomers of aminobiphenyls (C-substitution products) are formed in almost equal proportion.

It is interesting to compare the results of the reactions of benzene and phenylnitrenium ions obtained by classical methods with the reactions of free phenylnitrenium ions generated by the nuclear chemical method.[30] In the absence of specific media that are capable of suppressing the nitrogen or carbon cation sites of the phenylnitrenium ions, the free nitrenium ion on reacting with benzene behaves to an almost equal extent as a nitrenium ion (55%) and a carbocation (45%). At the same time the ratio of *ortho*- to *para*-isomers—the C-substitution products (XLIV) and (XLV) in Scheme 10—was 8 : 1, which is probably due to a difference in the rate of proton transfer in the intermediate σ-complexes. In the case of the *ortho*-isomers this is a rapid direct intramolecular process



while for the *para*-isomer intermolcular deprotonation occurs:



In the reaction of phenylnitrenium ions with toluene, the formation of six products (XLIII, *o*, *p*-), (XLIV, *o*, *p*-), and (XLV, *o*-, *p*-) is possible, according to the classical orientation rules (see Scheme 10). However, Takeuchi et al.[37,39,47] detected only the N-substitution products (XLIII, *o*-, *p*-) and the ratio of *ortho*- to *para*-isomers varied in relation to the method of generating the phenylnitrenium ion (from pyridinium salts or azides) in TFAA. On conducting this reaction, Parish and Whiting[81] isolated all six isomers with a twofold or greater excess of C-substitution products. Differences in the reaction conditions may account for these findings.

In the reaction of toluene with free phenylnitrenium ion generated by the nuclear chemical method, the sole product was 4-methyldiphenylamine (XLIII, *p*-) (Scheme 10).[31] The results of other studies[82] also show that the reaction mainly occurs on nitrogen.

In the reactions of nitrenium ions with other substituted benzenes (RPh, where R = Pr, Cl, Ph) and with naphthalene there is a tendency for preferential substitution on the nitrogen atom to occur.[37,39] Only when special media are used, as demonstrated by Parish and Whiting,[81] is there a marked increase in the yields of C-substitution products.

On reaction of phenylnitrenium ions in TFMSA with a substrate having an electron-withdrawing substituent (for example, nitrobenzene), products of the aminophenylation of nitrobenzene were not detected.[39]

The reactions of *para*-substituted phenylnitrenium ions (p-$RC_6H_4\overset{+}{N}H$, where R = Me, OMe, CN, NO_2) with benzene and toluene have been studied by Takeuchi et al.[43] It was established that the phenylnitrenium ions with electron-withdrawing groups (CN, NO_2) solely undergo aromatic N-substitution. On the other hand, the positive charge of phenylnitrenium ions with electron-donating groups is preferentially delocalised on the carbon atoms of the ring as a result of the positive mesomeric effect of the substituent. Prolongation of the lifetime in this type of resonance effect can lead to the coexistence of both the triplet and singlet states, which results in an increase in the yields of products of hydrogen removal.

Studies were carried out by Takeuchi et al.[39] on the reactions of naphthylnitrenium ions obtained from 1-azidonaphthalenes in the presence of TFMSA with benzene. 1-Amino-4-phenylnaphthalene—a C-substitution product—is formed as a result of this reaction. No N-substitution products were detected. This results from the preferential localisation of positive charge in the naphthylnitrenium ion at the *para* position of the ring rather than on the nitrogen atom.

Thus it may be concluded from the above information that in the organic reactions of nitrogen-containing compounds monitoring the behaviour of nitrenium ions meets with certain difficulties. The fact that these species are formed at intermediate stages has usually been established from the final reaction products. However, the ratio of final products depends on the nature of the specific media in which these reactions are occurring.

It is evident that the most reliable data on the chemical nature and properties of the intermediate species may be obtained when there is the possibility of generating them in a free state and studying their reactions in the absence of extraneous substances (counterions, catalysts, etc.). The nuclear chemical method of generating nitrenium ions opens up considerable possibilities in this respect. This non-traditional approach to the study of reactive intermediate species can assist in the interpretation of the mechanisms of classical organic reactions.

---o0o---

The review of studies on the properties and reactions of nitrenium ions presented here indicates the increased interest shown in these species by scientists from different countries. This is mainly because a study of these reactive intermediate species is closely related to the development of general theoretical problems in organic chemistry. In particular, a study of the properties and reactions of nitrenium ions is necessary for an understanding of the reaction mechanisms and development of synthetic methods for organonitrogen compounds. In this respect the new methods for obtaining and studying the reactions of free nitrenium ions that have been developed during the last ten years are of particular significance.

It follows from several original publications[49–53] that an important part is played by these species in carcinogenetic and mutagenetic processes. Therefore, a study of nitrenium ions is of paramount importance in finding a solution to specific problems in oncology, genetics, and ecology.

References

1. J Stieglitz, P N Leech *Chem. Ber.*, 1913, **46** 2147
2. J Stieglitz, P N Leech *J Am. Chem. Soc.*, 1914, **36** 272
3. J Stieglitz, B A Stagner *J. Am. Chem. Soc.*, 1916, **38** 2046
4. P T Lansbury *Nitrenes* (Edited by W Lwowsky), Interscience, New York 1970, p. 457
5. P G Gassman *Acc. Chem. Res.*, 1970, **3** 26
6. B V Stolyarov, A I Krylov *Zh. Org. Khim.*, 1980, **16** 1802
7. A I Krylov, B V Stolyarov *Zh. Org. Khim.*, 1978, **14** 2224
8. A I Krylov, B V Stolyarov *Vestn. Leningr. Univ.*, 1978, 144
9. S T Lee, K Morokuta *J. Am. Chem. Soc.*, 1971, **93** 6863
10. S Y Chu, A K Q Siu, E F Hayes *J. Am. Chem. Soc.*, 1972, **94** 2969
11. W A Lathan, L A Curtiss, W Hehre, et al. *Prog. Phys. Org. Chem.*, 1974, **11** 175
12. J F Harrison, C W Eakers *J. Am. Chem. Soc.*, 1973, **95** 3467
13. M J S Dewar, R C Haddon, W K Li, et al. *J. Am. Chem. Soc.*, 1975, **97** 4540
14. G F Kosser *J. Chem. Soc., Chem. Commun.*, 1973, 461
15. A B Cornford, D C Frost, F G Herring, C A McDowell *J. Chem. Phys.*, 971, **54** 1872
16. C F Bender, J H Meadows, H F Schaefer *Faraday Discuss. Chem. Soc.*, 1977, **62** 58
17. S D Peyerimhoff, R J Ruenker *J. Chem. Phys.*, 1979, **42** 167
18. S A Pope, I H Hillier, M F Guest *Faraday Symp. Chem. Soc.*, 1984, **19** 109
19. J A Pople, P v R Schleyer *Chem. Phys. Lett.*, 1986, **129** 279
20. J A Pople, L A Curtiss *J. Phys. Chem.*, 1987, **91** 155
21. R Gunde, A Z Azman *Z. Naturforsch., A*, 1974, **29** 832
22. G D Hartman, H B Schlegel *Chem.-Biol. Interact.*, 1981, **36** 319
23. G P Ford, P S Herman *J. Am. Chem. Soc.*, 1989, **111** 3987
24. G P Ford, J D Schribner *J. Am. Chem. Soc.*, 1981, **103** 4281
25. A I Krylov, Candidate's Thesis in Chemical Sciences, Leningrad State University, Leningrad, 1978, 124 pp
26. U Svanholm, V D Parker *J. Chem. Soc., Perkin Trans. 1*, 1972, 1978
27. U Svanholm, V D Parker *J. Am. Chem. Soc.*, 1974, **96** 1234
28. V D Nefedov, E N Sinotova, M A Toropova *Khimicheskie Posledstviya Radioaktivnogo Raspada* (The Chemical Consequences of Radioactive Decay), Energoizdat, Moscow, 1981, p. 78

29. V D Nefedov, M A Toropova, T P Simonova, V E Zhuravlev *Radiokhimiya*, 1990, **32**(1) 61
30. V D Nefedov, M A Toropova, T P Simonova, et al. *Zh. Org. Khim.*, 1989, **25** 156
31. V D Nefedov, M A Toropova, T P Simonova, et al. *Zh. Org. Khim.*, 1990, **26** 1133
32. USSR P. 1 219 585; *Byull. Izobret.*, 1986, (11) 129
33. H Takeuchi, T Takahashi, T Mashuda, et al. *J. Chem. Soc., Perkin Trans. 2*, 1979, 1321
34. H Takeuchi, K Koyama *J. Chem. Soc., Chem. Commun.*, 1981, 202
35. H Takeuchi *J. Chem. Soc., Chem. Commun.*, 1982, 226
36. H Takeuchi, K Koyama *J. Chem. Soc., Perkin Trans. 1*, 1982, 1269
37. H Takeuchi, K Takano, K Koyama *J. Chem. Soc., Chem. Commun.*, 1982, 1254
38. H Takeuchi, R Ihara *J. Chem. Soc., Chem. Commun.*, 1983, 175
39. H Takeuchi, K Takano *J. Chem. Soc., Chem. Commun.*, 1983, 447
40. H. Takeuchi, E Halsubara *J. Chem. Soc., Perkin. Trans. 1*, 1984, 981
41. H Takeuchi, M Macda *J. Chem. Soc., Perkin Trans. 1*, 1985, 677
42. H Takeuchi, M Macda, M Mitani *J. Chem. Soc., Chem. Commun.*, 1985, 287
43. H Takeuchi, K Takano *J. Chem. Soc., Perkin Trans. 1*, 1986, 611
44. H Takeuchi, M Macda, M Mitani, et al. *J. Chem. Soc., Perkin Trans. 1*, 1987, 57
45. H Takeuchi, *J. Chem. Soc., Chem. Commun.*, 1987, 961
46. H Takeuchi, S Hirayama, M Mitani, et al. *J. Chem. Soc., Perkin Trans. 1*, 1988, 521
47. H Takeuchi, K Koyama *J. Chem. Soc., Perkin Trans. 1*, 1988, 2277
48. H Takeuchi, S Hayakawa, H Murci *J. Chem. Soc., Chem. Commun.*, 1988, 1287
49. J A Miller *Cancer Res.*, 1978, **38** 1479
50. J A Miller *Cancer Res.*, 1970, **30** 559
51. C Heidelberger *Annu. Rev. Biochem.*, 1975, **44** 79
52. P G Gassman, I E Granrud *J. Am. Chem. Soc.*, 1984, **106** 1498
53. E C Miller, J A Miller *Cancer*, 1981, **77** 2327
54. R R Abramovitch, R Jeyaraman *Azides and Nitrenes: Reactivity and Utility* (Edited by E F V Scriven), Academic Press, 1984, p. 297
55. N K Kochetkov (Editor) *Obshchaya Organicheskaya Khimiya, T. 3* (General Organic Chemistry. Vol. 3), Khimiya, Moscow, 1982, p. 334
56. L G Donaruma, W Z Heldt *Org. React. (N. Y.)*, 1960, **11** 1
57. P Saik *Mekhanizmy Reaktsii v Organicheskoi Khimii* (Reaction Mechanisms in Organic Chemistry) (Edited by Ya M Varshavskii), Khimiya, Moscow, 1973, p. 134
58. A G Anastassion *J. Am. Chem. Soc.*, 1966, **88** 2322
59. P G Gassman, R L Cryberg *J. Am. Chem. Soc.*, 1969, **91** 5176
60. G A Olah, D J Donovan *J. Org. Chem.*, 1978, **43** 1743
61. J C Traeger, R G McLoughlin *J. Am. Chem. Soc.*, 1981, **103** 3649
62. J C Schultz, F A Houle, J L Beauchamp *J. Am. Chem. Soc.*, 1984, **106** 3921
63. D G Lister, J K Tyler *J. Mol. Struct.*, 1974, **23** 253
64. P Scharfenberg *Z. Chem.*, 1979, **19** 198
65. G Klopman (Editor) *Reactivity and Reaction Routes* (Translated into Russian), Mir, Moscow, 1977, 383 pp
66. E Bamberger, J Lagutt *Chem. Ber.*, 1898, **31** 1500
67. E Bamberger *Chem. Ber.*, 1894, **27** 1548
68. E Bamberger *Liebigs Ann. Chem.*, 1925, **441** 297
69. H E Heller, E D Hughes, C K Ingold *Nature (London)*, 1951, **166** 909
70. Y Yukawa *J. Chem. Soc. Jpn.*, 1950, **71** 547
71. I I Kukhtenko *Zh. Org. Khim.*, 1971, **7** 330
72. T Okamoto, K Shudo, T Ohta *J. Am. Chem. Soc.*, 1975, **97** 7184
73. S Hashimoto *Proc. Faculty Eng. Keigijuku Univ.*, 1948, **1** 32; *Chem. Abs.*, 1950, **44** 5831
74. M S Newman, P N Hay *J. Am. Chem. Soc.*, 1953, **75** 2322
75. E R Ayres, C R Hauser *J. Org. Chem.*, 1948, **13** 116
76. M N Rerick, C H Frottier, R Daignault, et al. *Tetrahedron Lett.*, 1963, 629
77. H J Barber, E Lunt *J. Chem. Soc.*, 1960, 1187
78. R E Plapinger, O O Owens *J. Org. Chem.*, 1956, **21** 1186
79. K T Potts, A A Kutz, F C Nachod *Tetrahedron*, 1975, **31** 2171
80. T B Patrik, T A Shield *Tetrahedron Lett.*, 1973, 445
81. J H Parish, M C Whiting *J. Chem. Soc.*, 1964, 4713
82. K Shudo, T Okamoto *Tetrahedron Lett.*, 1973, 1839
83. O E Edwards, D Vocelle, J W Ap Simon, et al. *Tetrahedron Lett.*, 1965, **87** 678
84. O E Edwards *Synthesis, Structure and Properties of Heterocyclic Compounds, Poznan*, Poxnan, 1975, p. 9
85. O E Edwards, D Vocelle, J W Ap Simon *Can. J. Chem.*, 1972, **50** 1167
86. P G Gassman, B L Fox *J. Chem. Soc., Chem. Commun.*, 1966, 153
87. P G Gassman, B L Fox *J. Am. Chem. Soc.*, 1967, **89** 338
88. P G Gassman, R L Gryberg *J. Am. Chem. Soc.*, 1968, **90** 1355
89. P G Gassman, F Hoyda, J Dygos *J. Am. Chem. Soc.*, 1968, **90** 2716
90. P G Gassman, G Campbell, R Frederick *J. Am. Chem. Soc.*, 1968, **90** 7377
91. P G Gassman, D K Dygos *J. Am. Chem. Soc.*, 1969, **91** 1543
92. P G Gassman, R L Gryberg *J. Am. Chem. Soc.*, 1969, **91** 2047
93. P G Gassman, A Carrasguillo *J. Chem. Soc., Chem. Commun.*, 1969, 495
94. P G Cassman, G A Campbell *J. Chem. Soc., Chem. Commun*, 1970, 427
95. P G Gassman *Tetrahedron Lett.*, 1970, 4149
96. P G Gassman, G Dygoes *Tetrahedron Lett.*, 1970, 4745
97. P G Gassman, G A Campbell *J. Am. Chem. Soc.*, 1971, **93** 2567
98. P G Gassman, K Shudo *J. Am. Chem. Soc.*, 1971, **93** 5899
99. P G Gassman, G A Campbell *J. Chem. Soc., Dalton Trans.*, 1971, 1437
100. P G Gassman *Tetrahedron Lett.*, 1971, 109
101. P G Gassman, G A Campbell, R C Frederick *J. Am. Chem. Soc.*, 1972, **94** 3884
102. P G Gassman, G A Campbell *J. Am. Chem. Soc.*, 1972, **94** 3891
103. P G Gassman, R L Gryberg, K Shudo *J. Am. Chem. Soc.*, 1972, **94** 7600
104. P G Gassman, G Gruetzmacher, R H Smith *Tetrahedron Lett.*, 1972, 497
105. P G Gassman, K Shudo, R L Gryberg, et al. *Tetrahedron Lett.*, 1972, 875
106. P G Gassman, G Hartman *J. Am. Chem. Soc.*, 1973, **95** 449

107. P G Gassman, J Nichiguchi, H Yamamoto *J. Am. Chem. Soc.*, 1975, **97** 1600
108. P G Gassman, K Uneyama, J L Hahnfeld *J. Am. Chem. Soc.*, 1977, **99** 647
109. A G Anastassion *J. Am. Chem. Soc.*, 1966, **88** 2322
110. A G Anastassion *J. Am. Chem. Soc.*, 1967, **89** 3184
111. M Mokotoff, R F Sprecher *Tetrahedron*, 1974, **30** 2623
112. J W Bastable, J D Hobson, W D Riddell *J. Chem. Soc., Perkin Trans. 1*, 1972, 2205
113. O E Edwards, G Bernath, J Dixon, et al. *Can. J. Chem.*, 1974, **52** 2123
114. O E Edwards, D H Paskovich, A H Reddoch *Can. J. Chem.*, 1973, **51** 978
115. R Furstoss, R Tadayoni, B Waegell *Nouv. J. Chim.*, 1977, **1** 167
116. P Kovacic, M K Lawery, K W Field *Chem. Rev.*, 1970, **70** 639
117. P Kovacic, M K Lawery, P D Roskos *Tetrahedron*, 1970, **26** 529
118. P Kovacic, J H Liu, P D Roskos, et al. *J. Chem. Soc., Chem. Commun.*, 1970, **16** 1034
119. P Kovacic, J H Liu, E M Levi, et al. *J. Am. Chem. Soc.*, 1971, **93** 5801
120. S J Padegimas, P Kovacic *J. Org. Chem.*, 1972, **37** 2672
121. R D Fisher, T D Bogard, P Kovacic *J. Am. Chem. Soc.*, 1972, **94** 7599
122. T Kling, M B Nazareno, P Kovacic *J. Am. Chem. Soc.*, 1972, **94** 2157
123. T A Kling, R E White, P Kovacic *J. Am. Chem. Soc.*, 1972, **94** 7416
124. R A Abramovitch, B Davis *Chem. Rev.*, 1964, **64** 149
125. C K Ingold *Structure and Mechanism in Organic Chemistry, 2nd Edition*, Cornell University Press, Ithaca, 1969, p. 906
126. R A Abramovitch, E P Kyba *The Chemistry of the Azide Group* (Edited by S Patai), Interscience, New York, 1971, p. 234
127. C H Gudmundsen, W E McEwen *J. Am. Chem. Soc.*, 1957, **79** 329
128. W Pritzkow, G Pohl *J. Prakt. Chem.*, 1963, **20** 132
129. W Pritzkow, G Mahler *J. Prakt. Chem.*, 1959, **8** 314
130. P A S Smith *Molecular Rearrangement* (Edited by P de Mayo), Interscience, New York, 1963, Vol. 1, p. 479
131. G L'Abbé *Chem. Rev.*, 1969, **69** 345
132. D V Banthorpe *The Chemistry of the Azide Group* (Edited by S Patai), Wiley, 1971, p. 398
133. M P Doyle, W Wierenga *J. Am. Chem. Soc.*, 1970, **92** 4999
134. M P Doyle, W Wierenga *J. Am. Chem. Soc.*, 1972, **94** 3896
135. R H McGirk, E H White *J. Am. Chem. Soc.*, 1973, **95** 3804
136. M P Doyle, D M Hedastrand, S C Busman, et al. *J. Am. Chem. Soc.*, 1975, **97** 5554
137. M De Rosa, Ph D Thesis, City University, New York, 1974, p. 99
138. J R Perrott, G Stedman, N Uysal *J. Chem. Soc., Perkin Trans. 2*, 1977, 274
139. J I G Cadogan, A G Rowley *J. Chem. Soc., Chem. Commun.*, 1974, 179
140. T Hiyama, H Koide, H Nozaki *Tetrahedron Lett.*, 1973, 2143
141. D Serve *J. Am. Chem. Soc.*, 1975, **97** 432
142. P-I Grossi, L Marchetti, R Ramassene, et al. *J. Electronanalyt. Chem.*, 1978, **87** 353
143. W T Huntress, D D Elleman *J. Am. Chem. Soc.*, 1970, **92** 3565
144. V D Nefedov, V M Zaitsev, M A Toropova *Usp. Khim.*, 1963, **32**(11) 1367 [English translation in *Russ. Chem. Rev.*, 1963(11)]
145. V D Nefedov, E N Sinotova, M A Toropova *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1980, 35
146. V Ya Bespalov, N A Korobochko *Zh. Strukt. Khim.*, 1977, **18** 1381
147. S Ikuta, S Iwata, M Inamura *J. Chem. Phys.*, 1977, **66** 4671
148. V D Nefedov, E N Sinotova, R K Bermudes *Radiokhimiya*, 1983, **25** 72
149. V D Nefedov, E N Sinotova, V A Shishkunov *Zh. Org. Khim.*, 1976, **12** 1351
150. V D Nefedov, E N Sinotova, V A Shishkunov *Zh. Org. Khim.*, 1976, **12** 1495
151. V D Nefedov, E N Sinotova, L P Kuzhelev, et al. *Radiokhimiya*, 1985, **27** 690
152. V D Nefedov, N P Kharitonov, E N Sinotova *Khimiya i Prakticheskoe Primenenie Si- i P-Organicheskikh Soedinenii* (The Chemistry and Practical Application of Organosilicon and Organophosphorus Compounds), High School Symposium of Scientific Transactions, Leningrad, 1980, p. 135
153. R Gleiter, R Hoffman *Tetrahedron*, 1968, **24** 5899
154. D S Breslow, E J Edwards *Tetrahedron Lett.*, 1972, 2041
155. G R Felt, S Linke, W Lwowski *J. Org. Chem.*, 1974, **39** 2128
156. G A Olah, H C Lin *J. Am. Chem. Soc.*, 1974, **96** 549
157. G A Olah, S J Kuhn, S H Food *J. Am. Chem. Soc.*, 1961, **83** 4581
158. W Borsche *Chem. Ber.*, 1942, **75** 1312
159. B Iddon, O Meth-Cohn *Angew. Chem.*, 1979, **18** 900

Translated from *Uspekhi Khimii* 61 1092–1113 (1992) U.D.C. 541.65:547.1'3

Conjunction in organic compounds of silicon-subgroup elements

A N Egorochkin
Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhnii

ABSTRACT. The existing theoretical ideas concerning the intramolecular interactions in organic compounds of silicon-subgroup elements are examined in relation to the results of experimental studies. It is shown that the overall resonance effect of organoelement substituents includes acceptor (joint influence of unoccupied *nd* and antibonding σ^* orbitals) and donor (σ,π conjugation, σ,π^* conjugation, and σ,n conjugation) components. The relative contributions of these components to the resonance effect are analysed as a function of the type of central element, the organic groups linked to it, and the reaction centre.

The bibliography includes 161 references.

Contents

I. Introduction 600
II. Theoretical ideas concerning conjugation 600
III. Comparison of theoretical ideas with experiments 604
IV. Conclusion 609

I. Introduction

The problem of intramolecular interactions is of key importance in theoretical and applied organoelemental chemistry. A steady trend in recent years has involved the appearance of new ideas and improvement of the methods of study of this still inadequately elucidated problem (see, for example, Refs. 1–10). The aim of the present review is to analyse the experimental data and the existing theoretical ideas about the intermolecular interactions and especially about the effects of conjugation in silicon-subgroup compounds.

Group IVB organoelemental compounds constitute unusual model systems in the chemistry of non-transition [main Group] elements.[3,11,12] Typical difficulties, arising in the solution of the problem of intramolecular interactions where alternative but inadequately supported views are put forward about a number of its important aspects, are manifested clearly for the given compounds. Under the conditions of a growing stream of information, which requires the development of a general theoretical standpoint for its consideration, one has to adopt a critical attitude to extreme views claiming universality—not only to attractively simple ideas but also to hypotheses seemingly disproving them which are applicable in reality only to a limited number of facts. The overall concept must, firstly, include these polar ideas as special limiting cases and, secondly, must be based on large sets of correct experimental data, must explain them without contradictions, and must possess predictive power, at least in principle.

Unfortunately this entirely evident methodology has been frequently infringed in the study of conjugation in compounds of silicon-subgroup elements despite the availability in the literature of a constructive basis for the avoidance of such errors.[13] Since the available data on the subject of the review are contradictory, the reivew has been constructed in accordance with the following scheme to elucidate the causes of the contradictions and to seek ways for their elimination: the choice of a general theoretical concept most consistent with the available set of experimental data and intramolecular interactions: the elucidation on its basis of "score" points in the literature data; comparison of the possibilities of the concept employed and of alternative ideas for the explanation of experimental facts; establishment of the limits of applicability of the chosen concept.

In the present review, preference is given to the consideration of (1) studies of fundamental importance for the elucidation of the given subject and (2) the most thoroughly investigated compound of tetracoordinate silicon-subgroup elements. The review does not deal with data, which are of specialised interest, concerning the relationship between intramolecular interactions and reactivity (see, for example, Refs. 2, 11, 12 and 14) and also compounds of pentacoordinate elments.[12,15–19]

II. Theoretical ideas concerning conjugation

1. Separation of the inductive, resonance and steric effects

In the first place, it is necessary to make a series of general remarks which will explain the approaches used in the review to the analysis of literature data. The absolute majority of publications on the subject of the review presuppose the use in an explicit or implicit form of two important principles of physical organic chemistry: the linear relation between free energy changes (LFE) and the independence and additivity of the influences of the inductive, resonance, and steric effects on the free energy change. An enormous number of studies have been devoted to the verification of these semiempirical principles (see, for example, Refs. 6, 20, and 21), which indicate a high degree of their generality. At the same time, a number of difficulties arise in the theoretical justification and practical use of these principles. These have been analysed in greater detail in a number of other communications.[6,20,21] We shall consider briefly the essential features of the above principles.

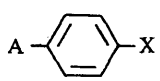
The most concise formulation of the LFE principle is the familiar Hammett equation $\lg K - \lg K_0 = \rho\sigma$,[22] which relates the rate or equilibrium constants K (a spectroscopic or other physical parameter having the significance of the Gibbs free energy can also be used as $\lg K$ [20,23]) for substituted and unsubstituted compounds to σ constants characterising the substituent. The reaction constant ρ characterises the sensitivity of the reaction centre (for chemical

reactions) or the indicator centre (for physical parameters) to the electronic effects of the substituents. The quantity σ is a constant only for constant properties of the medium (temperature, solvent, etc.).[6,22] For compounds of the type $A-B-ER_3$, the value of σ for an organoelement substitutent ER_3 (here and henceforth E is a silicon subgroup element, i.e. Si, Ge, Sn, or Pb) can generally speaking depend on the nature of the conducting fragment B of the molecule and on the type of the reaction (indicator) centre A.[6,24,25] The latter factor necessitates, on the one hand, a cautious approach to the use of σ constants as universal characteristics of the electronic effects of organoelement substituents, but, on the other hand, it can be used in the study of the dependence of intramolecular substituent–reaction centre and substituent–conducting fragment interactions on the nature of the varied A and B.[6,24,25]

In practice, when the LFE principle is used it is necessary in the majority of cases to take into account yet another principle, whose essential feature consists in the possibility of representing the Gibbs free energy change ΔG (in chemical processes or in the correlation of physical properties) by the sum of independent and additive components, i.e. $\Delta G = \Delta G_I + \Delta G_R + \Delta G_S$, determined by the influence of the inductive, resonance, and steric effects. The LFE principle must then be applied not to the overall quantity ΔG but to each of the three components separately.[20,22] The development of the LFE principle on this basis leads to three new σ constants: σ_I, σ_R, and E_S (there are also other designations), characterising the above effects. We shall mention briefly the problems arising in attempts at a theoretical justification of the principle of independence and additivity and of its practical application.[20–22]

Among the three components of ΔG, only the inductive component can be characterised with an adequate degree of approximation by a set of universal constants σ_I of the substituents.[20] The nature of the inductive effect (the field and/or bond polarisation effect) remains controversial.[26–28] Both factors are apparently significant for substituents EX_3 with electronegative groups X.[6] In highly excited electronic states, where there is appreciable charge separation under the influence of the inductive effect, the universality of the constants σ_I may break down.[29]

The constants σ_R of organic and organoelement substituents are used to characterise the change in ΔG under the influence of the resonance effect. The values of σ_R depend on the type of reaction centre.[6,20,21] Thus the constants σ_R^+ *and* σ_R^- have been widely used[6,22] as a quantitative measure of the resonance effect of substituents X (organic and organoelement) in the systems



in the presence of positive and negative charges on the reaction centre A respectively.

The resonance effects of two substitutents are not in general additive, which follows from theoretical analysis,[20,30,31] quantum-chemical calculations,[32] and experiment (for example, a wide variety of spectroscopic studies).[5,25,33,34] It has been established[5,20,25,30–34] that the non-additivity makes an appreciable contribution only when there is a large difference between the donor– acceptor properties of the two substituents or when both substituents are typical resonance electron donors.

The problem of isolating the component ΔG_R due to the influence of conjugation effects is unduly complex only at first sight. Experiment shows that the successive application of methods of correlation analysis with adequately representative selections of objects makes it possible to convert the above complications into their opposite, i.e. into an instrument for the study of fine details of resonance interactions in organoelement compounds. In particular, the important role of hyperconjugation effects in organoelement compounds was established in this way. It will be considered in greater detail below.

The isolation of the steric component ΔG_S constitutes a complex problem, since the influence of steric effects cannot be characterised by a standard set of universal constants invariant in relation to the system investigated. Steric constants of the type E_S, v, and their derivatives[35] are of limited applicability, especially in the study of intermolecular and intramolecular interactions with participation of Group IVB organoelement compounds.[36] Furthermore, the electronic and steric aspects of intramolecular interactions are interrelated in many instances (the stereoelectronic effect—see, for example, Egorochkin[3,36]). Generally speaking, a dual approach to the elucidation of the presence or absence of a dependence of ΔG_S on the nature of the varied substituents is possible. Firstly, there are several versions of computational schemes estimating with different degrees of approximation the shielding of the reaction (indicator) centre by substituents.[37–40] Secondly, the role of the component ΔG_S can be estimated by carrying out a correlation analysis of representative sets of experimental data of the kind mentioned above for ΔG_R. The significance of steric factors then becomes evident if the impossibility of explaining the influence of substituents (at least bulky ones) by electronic effects alone is observed explicitly.

An independent and extremely important approach to the study of intramolelcular interactions, one which has as yet been inadequately developed for organoelement compounds, is based on quantum-chemical methods. The principal results will be examined below.

Thus fairly stable ideas have arisen in the literature concerning the possibilities and limitations of the experimental methods for the study of intramolecular interactions in organic and organoelement compounds. The principle of maximum consistency with these ideas has been the main criterion for the selection of correct literature data on intramolecular interactions in Group IVB organoelement compounds.

We shall now consider the problem of the selection of a general theoretical concept satisfying the experimental data to the greatest extent.

2. Characteristic features of conjugation in organoelement Group IVB compounds

The long trial and error procedure followed in the study of intramolecular interactions in compounds of the silicon-subgroup elements has still not reached completion. The evolution of views on conjugation, frequently reflected in review communications,[6,13,41–46] is especially contradictory. We shall consider briefly the main stages of this evolution.

The first stage was based on the idea that unoccupied $3d$ orbitals of the silicon atom may participate in the formation of multiple bonds ($d_\pi-p_\pi$ conjugation).[47] This idea was invoked to account for the small length of the silicon–oxygen and silicon–halogen bonds.[48] A series of symbols are used to designate the conjugation of the atoms E with π- and n-electron substituents, among which the most concise are d,π and d,n respectively.

The hypothesis of unoccupied nd orbitals was subsequently applied to the interpretation of an enormous number of experimental facts obtained in the study of virtually all types of organoelement Group IVB compounds with the aid of chemical and physical methods (see the relevant reviews[41,42,49–51]). This hypothesis proved

to be extremely effective for the explanation of a most important difference between compounds of the elements E and carbon—the existence of π-acceptor properties in the atoms of E. It was established that these properties weaken with increase in the atomic number of E and that there is a close analogy between them and the conjugation effects in organic chemistry.[42]

Although the *nd*-orbital hypothesis agrees qualitatively with general quantum-chemical ideas, numerous attempts to obtain quantitative information about the involvement of *d*,π orbitals by means of approximate semiempirical methods were always open to criticism, since they did not lead to unambiguous, correct conclusions.[42,46,52] Such dual role of the approximate quantum-chemical methods left a strong imprint on the second stage of the evolution of ideas about conjugation in silicon-subgroup compounds.

The second stage was prepared for by the vigorous development with the aid of various chemical and physical methods[3,10,54–56] of the initial idea of Nesmeyanov and co-workers[53] concerning the more important role of hyperconjugation in organoelemental compounds than in organic compounds. A study by Pitt,[57] in which the author concluded without adequate justification that only hyperconjugatin occurs in silylacetylenes and that there is no need to resort to the idea of *d*,π conjugation, can apparently be regarded as the start of the second stage. Although subsequently Pitt corrected his ideas signifcantly,[13] his initial study[57] actually stimulated a series of publications (see, for example, Ponec and Chvalovsky[58,59]), whose authors considered hyperconjugation as an alternative to *d*,π conjugation in α,β-unsaturated compounds of the elements E. Despite the erroneous nature of the initial postulate, these studies have also played a constructive role, because they promoted the recognition of the complexity of the overall effect of conjugation in organoelemental Group IVB compounds.

The next stage of the evolution of views on conjugation, which arose almost simultaneously with the second, was the attempt to explain the electron-accepting properties of the atoms E not by the presence in them of *nd* orbitals but by the involvement of the antibonding σ* orbitals of the E–X bond in hyperconjugation.[7,9,60–65] Different versions of hyperconjugation interactions were proposed as alternatives to the *d*-orbital hypothesis (and sometimes as an addition to it—see, for example, West and Wadsworth[66,67]): (1) the interaction of σ*(E–C) orbitals with the π-electrons of the substituents Y in the C–E–Y fragments, where Y = aryl,[68] ethenyl,[69] ethynyl,[69] furyl, or thienyl;[70] (2) the interaction of the σ*(Si–C) and σ*(Si–H) orbitals with the lone pairs (LP) of Y in the (H)C–Si–Y fragments, where Y = NR_2, OR, SR, SeR, or F (R = organic and organosilicon groups);[7,64,65,71] (3) the interaction of the σ*(Si–H) orbitals with the carbanionic centre in $H_3SiCH_2^-$.[61,72] The qualitative aspects of the hyperconjugation interactions involving the antibonding orbitals of the bonds formed by elements of the Second and Third Periods were examined in the study of the anomeric effect[7,9,64] and other stereoelectronic effects.[9,73–75] The general approach to the problem of the involvement of antibonding orbitals will be examined below. Here we may note the possibility of invoking the concept of antibonding orbitals in the study of hypervalent bonds[15] in atranes (see, for example, Arshinova[9]) and in certain other compounds,[76,77] especially SiH_5^-.[78]

It is noteworthy that none of the three systems of views on conjugation presented above contains rigorous evidence for the erroneous nature of alternative ideas. In the search for such evidence, fundamental difficulties apparently arise inevitably owing to the complexity of the conjugation effects in organoelemental Group IVB compounds. Therefore views constituting the basis of the general theoretical concept which satisfies best the experimental facts must not exclude but supplement one another.

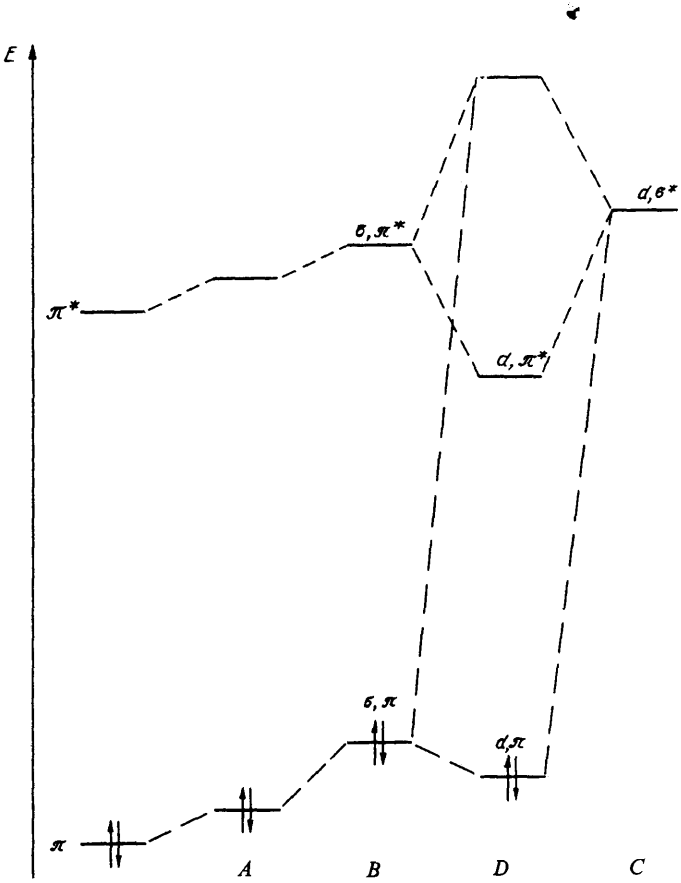


Figure 1. The influence of the substituents $E(CH_3)_3$ on the energies of the frontier orbitals π and π* of unsaturated hydrocarbons (according to Pitt's data[13]). Stage A—inductive +*I* effect of $E(CH_3)_3$; Stage B—σ,π and σ,π* conjugation; Stage C—mixing of σ*(E–C) orbitals of the substituent $E(CH_3)_3$ with the *nd* orbitals of the E atoms (a mixed *d*,σ* orbital with a lower energy is illustrated); Stage D—mixing of the *d*,σ* orbitals with σ,π* and σ,π; the formation of HOMO (*d*,π) and LUMO (*d*,π*) in the molecule.

Such a unifying concept was proposed by Pitt[13] in the fourth stage of the evolution of views on conjugation. Following Pitt, we shall consider this concept in relation to the change in the energy levels of frontier π and π* orbitals of substituted unsaturated hydrocarbons under the influence of the substituents $E(CH_3)_3$ (Fig. 1), i.e. as a result of the intramolecular interactions in compounds of the type $YE(CH_3)_3$, where Y = C_6H_5, $CH_2=CH$, etc. To facilitate the treatment, we shall represent arbitrarily the overall electronic effects of the substituents $E(CH_3)_3$ by several components.[13] In conformity with the ideas described in the first

part of Section II, the differentiation of the inductive and resonance components of the influence of the $E(CH_3)_3$ group then becomes entirely evident. As regards further subdivision of the overall resonance effect of $E(CH_3)_3$ into components, this problem is close in its significance to that solved in physical organic chemistry in estimations of the contributions of the hyperconjugation component to the overall conjugation effect of organic substituents.[20,22]

Stage A. The inductive effect. The inductive donor–acceptor properties of the substituents EX_3 depend on the nature of the groups X. The substituents $E(CH_3)_3$ have a positive inductive $+I$ effect (inductive electron donors), so that their influence results in an increase in the energy (destabilisation) of the orbitals π and π^*. On the other hand, if X are electronegative groups, then the substituent EX_3 is an inductive electron acceptor ($-I$ effect).

Stage B. Hyperconjugation of the σ,π and σ,π^* type [mixing of the $\sigma(E-C)$ orbitals of the substituent $E(CH_3)_3$ with the π and π^* orbitals of the fragment Y after taking into account the change in the energies of the initial orbtials under the influence of the inductive effect in stage A]. We may note certain key postulates and conclusions in Pitt's study.[13] From the linear combination of three $\sigma(E-C)$ orbitals, it is possible to obtain three wave functions, one of which, namely $\psi(\sigma)$, has π-type symmetry and can therefore interact with the $p_z(\pi)$ wave functions of the $Y-\psi(\pi)$ fragment. According to the perturbation molecular orbital theory,[13,30] the energy of the initial orbitals $E(\sigma)$ and $E(\pi)$ changes by the following amount after σ,π mixing:

$$\delta E(\sigma) = -\delta E(\pi) = \pm\sum[(4P^2(\pi\sigma) + \Delta E^2)^{1/2} - \Delta E] / 2, \quad (1)$$

where $P(\pi,\sigma)$ is the $\psi(\pi)P\psi(\sigma)d\tau$ perturbation operator and $\Delta E = E(\pi) - E(\sigma)$. If $\Delta E = 0$, then $\delta E = P(\pi\sigma)$ and if $\Delta E \gg P(\pi\sigma)$ (the case most often encountered), then Eqn. (1) becomes

$$\delta E = \pm P^2(\pi\sigma) / \Delta E. \quad (2)$$

Since $P(\pi\sigma) = a(\pi)a(\sigma)P$, where $a(\pi)$ and $a(\sigma)$ are respectively the p_z orbital coefficients of the carbon atom of the fragment Y and of the E atom in the σ orbital of the E–C bond while P is the perturbation integral of the $C(p_z)-E(p_z)$ bond, Eqn. (2) can be written in the form

$$\delta E = \pm a^2(\pi)a^2(\sigma)P^2 / \Delta E. \quad (3)$$

The perturbation integral in Eqn. (3) is related to the overlap integral $S(\sigma\pi)$ by the expression

$$P = -KS(\sigma\pi)[I(\sigma) + I(\pi)] / 2,$$

where I is the ionisation potential of the σ and π orbitals.

In hyperconjugation of the σ,π and σ,π^* types, the substituents $E(CH_3)_3$ behave as resonance electron donors in relation to the π system of the fragment Y, which results in further (in relation to that induced by the inductive effect) increase in the energy of the frontier orbitals, the latter acquiring a mixed character. It is significant that the degree of mixing of the σ,π^* type is smaller than that of the σ,π type owing to the smaller value of the overlap integral $S(\sigma, \pi^*)$ and the larger value of $\Delta E = E(\pi^*) - E(\sigma)$ compared with $\Delta E = E(\pi) - E(\sigma)$. Therefore conjugation of the type considered results in a greater destabilisation of the highest occupied molecular orbital (HOMO) compared with the lowest unoccupied molecular orbital (LUMO).

The ideas described above in connection with the consideration of stages A and B are sufficient, after slight modification, for the complete description of the electronic effects of the substituents in the benzyl derivatives $C_6H_5CH_2E(CH_3)_3$ and allyl derivatives $CH_2=CHCH_2E(CH_3)_3$, but are fundamentally inadequate for further analysis of compounds of the type $C_6H_5E(CH_3)_3$ and $CH_2=CHE(CH_3)_3$, since the electron-accepting properties of the substituents $E(CH_3)_3$ in relation to the π system cannot be explained on their basis. A constructive basis for the understanding of the causes of the above electron-accepting properties is the concept combining the hypotheses of the *nd* orbitals and antibonding σ^* orbitals. Using this concept as a guide, we shall consider stages C and D.

Stage C. The mixing of the $\sigma^*(E-C)$ orbitals of the substituent $E(CH_3)_3$ with the *nd* orbitals of the atom E. Although this stage was taken into account in the qualitative schemes for the consideration of the electron-accepting properties of $E(CH_3)_3$ as early as 20 years ago,[13,79] the authors of certain publications (see, for example, Giordan and Moore[68,69]) devoted to it unjustifiably little attention or actually neglected it. On the other hand, a number of considerations support the involvement of *nd* orbitals in conjugation. Thus it follows from Eqns. (1)–(3) that, in the absence of symmetry prohibition, the mixing of orbitals is greater, other conditions being equal, the smaller the difference between their energies. On the basis of this principle, Giordan and Moore[69] explained the electron-accepting properties of the substituents $E(CH_3)_3$ exclusively by the hyperconjugation interaction of the $\sigma^*(E-C)$ orbtials with the π^* orbitals of benzene, ethylene, and acetylene, whereas for thiophene and furan derivatives[70] the mixing of the $\sigma^*(E-C)$ and *nd* orbitals was not ruled out. Nevertheless, on the basis of the above principle, a real possibility of the mixing of the $\sigma^*(E-C)$ orbitals not only with the π^* orbitals of the fragment Y but also with the atomic *nd* orbitals of E for all the π systems enumerated follows from a simple consideration of the orbital energies.

Fig. 2 presents the experimental energies of the $\sigma^*(E-C)$ [68] and π^* [69,70] orbitals in the compounds YEX_3 determined by electronic transmittance spectroscopy. The energy of the unoccupied *nd* orbitals of the atom E (for the silicon atom as an example) was estimated by two procedures. Calcualtions by the Hartree–Fock self-consistent field method yield about –2 eV for the energy of the 3*d* orbitals of the silicon atom.[80–82] According to approximate estimates using a series of spectroscopic data for unsaturated compounds containing the $Si(CH_3)_3$ substituents, the 3*d* orbitals of silicon have a higher energy than the π^* orbitals of the fragment Y;[83] this view gained fairly wide currency (see, for example, Refs. 41, 50, and 79). Thus the orbitals $\sigma^*(E-C)$, *nd*, and π^* were found to have comparatively similar energies. There exists therefore a real possibility of the mixing of the $\sigma^*(E-C)$ orbitals with both π^* and *nd* orbitals. Following Pitt,[13] we shall arbitrarily select the mixing of $\sigma^*(E-C)$ and *nd* orbitals as the initial stage of the interaction between the three orbtials. This results in the formation of two mixed orbitals—with greater and smaller (presented in Fig. 1 and designated by *d*, σ^*) energies. Thus an unoccupied orbital arises in stage C with a lower energy than those of the $\sigma^*(E-C)$ and *nd* orbitals of the atoms E.

Certain comments must be made concerning the mixing of the orbitals in stage C. Fig. 2 presents only approximate energies of the orbitals $\sigma^*(E-C)$ and π^*. The exact energies of the initial orbitals

σ*(E−C) and π* could be obtained only after taking into account the influence of the inductive effect. Thus, for the calculation of the energy $E(\sigma^*)$, it is necessary to know the form of the dependence of $E(\sigma^*)$ for the fragment $E(CH_3)_3$ on the inductive effect of the substituent Y in $(CH_3)_3EY$ (Y = C_6H_5, $CH_2=CH$, etc.) while for the calculation of $E(\pi^*)$ account must be taken of the inductive effect of of $E(CH_3)_3$ and Y. Such calculations are so far lacking in the literature.

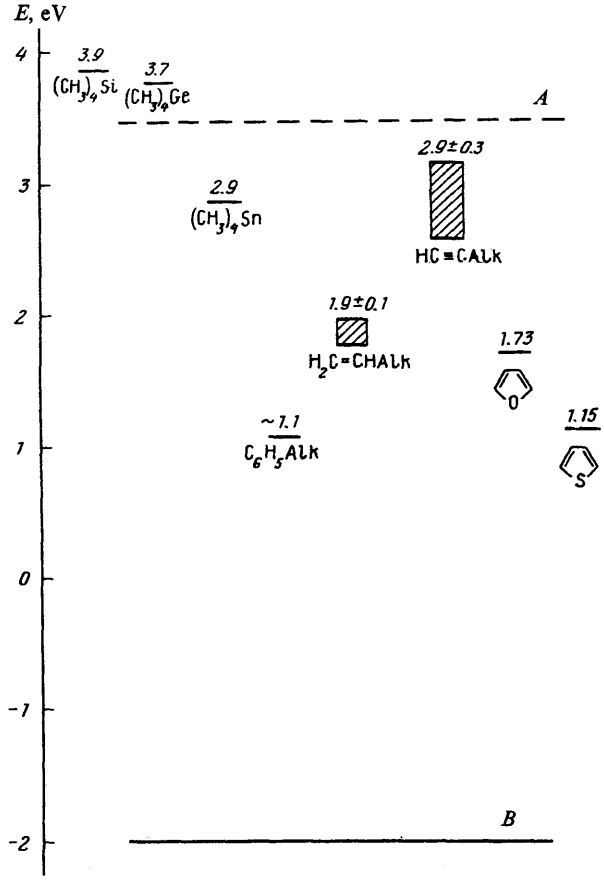


Figure 2. The energies of the σ*(E−C) orbitals in $E(CH_3)_4$,[68] the π* orbitals in certain unsaturated compounds,[69,70] and the unoccupied 3*d* orbtials of the silicon atom [(*A*) approximate estimate;[83] (*B*) calculated values[80−82]].

The problem of the exact energies of the *nd* orbitals *E*(*d*) is even more complex. This problem, as well as a number of others arising in the study of conjugation involving *nd* orbitals (their energy in isolated atoms E and molecules, the size and amplitude of *nd* orbtials, the charge on the atom E and the population, polarisation corrections in quantum-chemical calculations or real involvement of *nd* orbitals in bond formation) have been examined in a number of reviews.[41,42,46,49,51,84] Here we shall merely note yet again the absence of fundamental prohibition of the involvement of the *nd* orbitals of the atoms E in conjugation from the standpoint of quantum chemistry, but the results of even non-empirical calculations depend greatly on the choice of the basis set (see, for example, Res. 46, 85−88). Therefore, in estimating the correctness of such results, it is essential to exercise reasonable scepticism and caution.

One should also note that the π-bonds, formed with participation of the *nd* orbitals of the atoms E, are not analogous to those existing in unsaturated organic compounds.[84] As frequently mentioned in reviews,[3,6,36,42] the involvement of *nd* orbitals is only partial. Under these conditions, one cannot as yet estimate reliably the contributions of the atomic *nd* orbitals to the molecular orbitals. The self-evident nature of this assertion can be seen if only from the consideration of stage C above and the discussion of the data presented in Fig. 2.

Stage D. The mixing of the orbitals *d*,σ* and σ,π* formed in stages C and B, involving the formation of two new orbitals — with greater and lower (presented in Fig. 1 and designated by *d*,π*) energies. Similarly, on mixing of the *d*,π* and σ,π* orbitals, two orbitals are also produced [the orbital with a smaller energy (HOMO) is presented in Fig. 1 and is designated by *d*,π]. The orbital *d*,π* is stabilised i.e. its energy is reduced compared with the energy $E(\sigma,\pi^*)$ to a much greater extent than for the orbital *d*,π; this is caused by the sharp difference between the energies of the π* and π orbitals (10−15 eV [8,68−70]).

It follows from the foregoing that the orbtials σ*(E−C), *nd*, and π* are comparatively close to one another although they are not rigorously defined as regards energy. Therefore, the differentiation of stages C and D in the mixing of these three orbitals is purely arbitrary.

It follows from the consideration of stages C and D that attempts at an *a priori* quantum-chemical estimation of the relative role of each of them can at best claim to yield merely qualitative conclusions. At the same time, as quantum-chemical methods have improved, data have accumulated for the simplest organoelemental compounds, which can, on the one hand, be interpreted, at least in principle, on the basis of the scheme presented above and, on the other, they can serve as a justification of the individual stages (especially B) of this scheme. These data will be invoked in the third Section of the review together with the consideration of experimental studies in stages A−D and on conjugation as a whole.

III. Comparison of theoretical ideas with experiment

The consideration of the relevant data in this review is based predominantly on the methodology involving the separation of electronic effects adopted in physical organic chemistry, whose principles have been described in Section II. The separate stages of the intramolecular interactions with the substituents EX_3 and CH_2EX_3 as well as groups with a more complex structure having centres of not only π type but also *n* type are analysed. The arbitrary nature of the separation of the overall electronic effect of the above substituent into individual stages was considered in Section II.

1. The inductive effect

The differentiation of the inductive component ΔG_I from the overall electronic effect ΔG of organoelemental substituents constitutes, generally speaking, a standard procedure. Taking into

account certain limitations (see Section II as well as literature data[6,10]), the constants σ_I and their derivatives, tabulated, for example, by Egorochkin and Razuvaev[6] and Hansch et al.,[21] serve as a universal characteristic of the $\pm I$ effect. The possibile presence of a variable hyperconjugation component (σ,σ conjugation) constitutes in this connection a still inadequately elucidated problem. Although the contribution of this component is as a rule insignificant (except in special cases, for example, in compounds with chains of highly polarisable atoms E [3]), it can nevertheless depend on the type of centre to which the substituent is linked.[6]

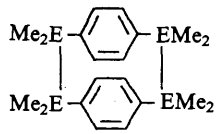
2. Hyperconjugation of the σ,π and σ,π^* type

This type of hyperconjugation has been studied in especially great detail (with the aid of physical and chemical methods) in the compounds YCH_2EX_3, where Y = phenyl, vinyl, ethynyl, furyl, thienyl, etc. In a number of reviews[3,6,10,55,89,90] and subsequent communications,[25,91–96] it was established that the substituents $CH_2E(CH_3)_3$ always behave as resonance electron donors in relation to the π systems of the fragment Y. This is indicated, in particular, by the negative values of their resonance constants σ_R^0, σ_R, and σ_R^+ as quantitative characteristics of conjugation respectively in the electronic ground state (NMR, IR spectroscopy), under the conditions of direct polar conjugation (IR spectroscopy of the hydrogen bond),[24] and in the presence of a positive charge on the π system (UV spectroscopy of charge-transfer complexes). The frontier orbitals formed on interaction of CH_2EX_3 with the π system of Y are of the σ,π and σ,π^* type. The HOMO energy increases (according to quantum-chemical calculations and photoelectron spectroscopic data) under the influence of the substituents $CH_2E(CH_3)_3$, while the LUMO energy is less sensitive to the effect of substituent.

With an increase in the atomic number of E (other conditions being equal), an enhancement of the σ,π conjugation is observed. Hyperconjugation also increases following the appearance of a positive charge on the π system. Thus the negative values of the resonance constants of the substituent $CH_2E(CH_3)_3$ increase in the sequence $\sigma_R^0 < \sigma_R < \sigma_R^+$. The magnitude of the effect of the σ,π conjugation depends on the nature of the groups X in CH_2EX_3 and on the substituent Z bound to the π system. The enhancement of the electron-accepting properties of X in CH_2EX_3 is accompanied by a weakening of the σ,π conjugation, whereas under conditions favouring direct polar conjugation between the substituents $CH_2E(CH_3)_3$ and Z via the π system [for example in the case of $(CH_3)_3SnCH_2C{\equiv}CSi(CH_3)_3$ [97]], σ,π conjugation intensifies with enhancement of the electron-accepting properties of Z.

In organotin and organolead compounds, especially in the presence of a positive charge on the π system, σ,π conjugation is a powerful resonance electron-donating effect, which exerts a strong influence on the reactivity of these compounds.[2,54]

Hyperconjugation of the σ,π and σ,π^* type depends significantly on stereoelectronic effects. The maximum σ,π conjugation therefore occurs only under favourable steric conditions, which has been considered in detail in a number of studies.[3,10,36,55,89,95] In σ,π conjugation with the π systems of a double bond, a triple bond, and benzene and naphthalene rings, substituents containing the E–E′ groups also participate. Here E and E′ represent different combinations of identical or different elements (Si, Ge, Sn).[3,55,98–101] Thus, as a consequence of the parallel disposition of the E–E bridges and the p_π ring orbitals, the σ,π conjugation in cyclophanes of the type



(E = Si, Ge)

is stronger than in the corresponding acylclic compounds.[102] On the other hand, the σ,π conjugation with participation of the groups $-Si-Si(CH_3)_3$ constitutes an appreciably weaker resonance electron-donating effect than the conjugation involving the substituent $CH_2Si(CH_3)_3$.[3] This finding can be explained by the existence in the disilyl substituent of two opposite resonance effects — the electron-donating effect [σ,π conjugation is apparently stronger than in the substituent $CH_2Si(CH_3)_3$ because of the greater polarisability of the Si–Si bond compared with Si–C [93]] and the electron-accepting effect [d,π conjugation, which is absent in the $CH_3Si(CH_3)_3$ group].[3]

According to the results obtained by different methods,[6,41,42,50,51] the substituents SiX_3 containing any organic groups X exert an overall resonance electron-accepting effect in relation to the π system, which follows, for example, from the positive resonance constants σ_R.[6,21] An alternative interpretation of the resonance effects of the substituents SiX_3 is formally permissible: either (a) these substituents manifest only electron-accepting properties or (b) the overall effect includes a weaker electron-donating component (σ,π conjugation) and a stronger electron-accepting component. Evidence in support of the second view, obtained in a general theoretical study (see Section II as well as the literature[103–105]) until recently had not received convincing experimental confirmation. Unambiguous proof of the presence of an electron-donating component (σ,π conjugation) in the overall resonance effect of the substituents EX_3 (E = Si, Ge, Sn, Pb) and $E'X_n$ (E′ = Hg, B, P, As, Sb, Bi) was obtained in the joint analysis of the constants σ_p abd σ_p^+ of phenyl derivatives with the above substituents and the benzyl derivatives $C_6H_5CH_{3-n}[E(CH_3)_3]_n$.[93] The principal factor determining the enhancement of the σ,π conjugation following the appearance of a positive charge on the aromatic ring in both phenyl and benzyl series is the polarisability of the chemical bonds of the substituent.[93] Under these conditions, the hyperconjugation is enhanced more the greater the atomic number of E in EX_3 and $CH_{3-n}[E(CH_3)_3]_n$.[93]

Yet another feature of the σ,π conjugation is its dependence on the type of the π system to which the organoelement fragment is linked. Thus systematic studies by different methods of benzene and acetylene derivatives with different substituents $EAlk_3$ [6,24,25,57,89,97,106] established, in particular, that the enhancement of the σ,π conjugation on passing from substituted benzenes to acetylenes is greater the higher the atomic number of the element E in the substituent $EAlk_3$ attached to the π system.[24] The idea that the σ,π conjugation between $E(CH_3)_3$ and π systems intensifies with increase in the atomic number E was also confirmed in other studies.[107–109]

Semiempirical quantum-chemical methods are used in the vast majority of cases in studies on σ,π conjugation, so that the conclusions reached with their aid are only qualitative. The existence of both electron-donating (σ,π conjugation) and electron-accepting effects in the substituents EX_3 and of only hyperconjugation in CH_2EX_3 has been established for benzene,[13,103,104,110] ethylene,[10,52,88,95,111,112] acetylene,[13,52,89,113,114] and furan[105,115]

derivatives and also for π systems of more complex structure.[116,117] Non-empirical calculations for vinylsilanes and their radical-cations,[118,119] silylacetylenes,[120,121] stannylacetylenes,[122] as well as the cyclopentadienyl[123] and naphthyl[101] derivatives of silicon provide better evidence. The joint application of modern quantum chemistry and photoelectron spectroscopy proved especially effective.[8,89]

3. Hyperconjugation of the σ,*n* type

The development of ideas about the dual nature of the overall resonance effect of substituents EX_3 in relation to π systems, which includes electron-donating (σ,π conjugation enhanced as E varies in the sequence Si < Ge < Sn) and electron-accepting components, was accompanied by the accumulation of facts concerning the effects of these substituents in relation to the groups Y comprising atoms with lone pairs in the α-position relative to the E atom. Pauling's initial concept,[48] according to which the substituents EX_3 exhibit exclusively an electron-accepting resonance effect in relation to Y ($d_\pi-p_\pi$ conjugation) was subsequently given a deeper content. This was based on numerous data obtained by various physical and chemical methods, which, although to a large extent indirect, nevertheless generated a consistent system of views concerning the presence of not only electron-accepting but also of electron-donating properties in the substituents $E(CH_3)_{3-n}X_n$ linked to Y.[3,124–128]

Initially (see, for exmaple, Egorochkin and co-workers[3,129]) the electron-donating properties of the substituents in the H–C–E–Y fragments were interpreted as the σ,σ conjugation of the H–C and E–Y bonds (like the conjugation of the E–C bonds in compounds with E–C–C–E atomic groups[130]). However, such interpretation is doubtful bearing in mind the weaker hyperconjugation in the H_3C-Si fragments than in H_3C-C.[131] On the basis of orbital approaches, the treatment of the resonance electron-donating properties of $E(CH_3)_3$ relative to Y as the σ,*n* mixing of the initial unperturbed σ orbitals of E–C with the *n* orbitals of the lone pairs of Y, which have a higher energy, appears more adequate.

The same procedures of the perturbation theory are applicable to the consideration of the σ,*n* conjugation as for σ,π conjugation. The rigorous allowance for the influence of the inductive effect on the energies of the initial orbitals gives rise to an appreciable complication under these conditions (see, for example, Baidin et al.[132]). Only qualitative estimates of the σ, *n* conjugation in the compounds $(CH_3)_3EX$ (X = OAlk, SAlk, Cl, Br) and $[(CH_3)_3E]_2X$ (X = O, S) are therefore available at the present time.[133–135] The effect of σ,*n* conjugation intensifies as E and X are varied in the sequences Si < Ge < Sn < Pb, S < O, and Br < Cl. On passing from the compounds $(CH_3)_3EX$ to $[(CH_3)_3E]_2X$, the σ,*n* conjugation is enhanced for X = O and is weakened for X = S, which is due to stereoelectronic factors determining the directions assumed in space by the interacting orbitals.[134]

Thus the effects of the σ,π and σ,*n* conjugation of the substituents $E(CH_3)_3$ linked to π or *n* systems intensify with increase in the atomic number of the E atom and depend on the type of each of the systems indicated. The effect of the σ,*n* conjugation in $(CH_3)_3EY$ intensifies as the atomic nubmer of the atoms with the lone pair in the α-position relative to the E atom diminishes. Within the framework of the phyiscal-organic chemical concept of the separation of the effects of substituents, adopted in this review, these facts have provided in recent years much evidence in support of the idea of the resonance effects of the groups $E(CH_3)_3$ as effects combining electron-donating and electron-accepting properties.

After the rigorous allowance for the inductive effects of the groups $E(CH_3)_3$, it was shown that the resonance electron-accepting effect of these groups is not enhanced but is actually weakened with increase in the atomic number of the E atoms, in contrast to σ,π and σ,*n* conjugation. On the other hand, both σ,*n* conjugation and the resonance electron-accepting effect weaken with increase in the atomic number of the Group VI or VII elements linked to E.[6,42,133,135] Thus the overall resonance effect of the groups $E(CH_3)_3$ relative to centres of the π and *n* type, representing the result of the combination of two opposed components, is a typical electron-accepting effect for organosilicon compound and a weak electron-accepting effect (and sometimes an electron-donating effect) for organotin compounds. In the case of organogermanium compounds and also in systems with weak resonance interactions, situations frequently arise which are difficult to predict. Therefore in the analysis of experimental data in early reviews[41,49–51] the interpretation of the overall resonance effect (traditionally given the term $d_\pi-p_\pi$ conjugation) on the assumption that $E(CH_3)_3$ has electron-accepting properties only encountered a number of difficulties. It is essential to note also the significantly different sensitivities of the research methods and indicator centres to the influence of resonance effects to which special attention has been drawn recently.[10]

The idea of dual donor–acceptor resonance properties of the substituent $E(CH_3)_3$ examined above was confirmed by non-empirical quantum-chemical calculations for the compounds $(CH_3)_{4-n}SnCl_n$ (n = 1, 2, 3), $[Sn(CH_3)_3]_2X$ and $[(CH_3)_2SnX]_3$ (X = S, Se).[136,137] The fragments $CH_3-\underset{|}{\overset{|}{Sn}}-$ exhibit in relation to chlorine atoms both resonance electron-accepting properties (the involvement of 5*d* orbitals of Sn in bonding) and electron-donating properties [σ,*n* mixing of the σ(Sn–C) orbitals and *n* orbitals of the lone pair of chlorine]. σ,*n* conjugation apparently predominates in the reonance interaction between the $Sn(CH_3)_3$ group and the sulphur (selenium) atom, which agrees, in particular, with the present author's experimental data.[133,134] The same type of conjugation is evidently responsible for the low values of the first ionisation potentials of compounds with the Si–C–S groups.[138,139]

Thus experimental data and non-empirical quantum-chemical calculations indicate, in conformity with the theoretical ideas described in Section II, a dual nature of the resonance interactions of substituents of the $E(CH_3)_3$ type with π and *n* systems. The electron-donating properties of these substituents are caused by their involvement in σ,π conjugation, σ,π* conjugation, and σ,*n* conjugation and possibly also in other versions of hyperconjugation, which have so far been scarcely investigated.

We shall now analyse the question to what extent experimental studies on the resonance electron-accepting properties of $E(CH_3)_3$ agree with the general approach to this problem (stages C and D in Section II of the review).

4. Resonance electron-accepting properties of the substituents $E(CH_3)_3$

We shall consider the simplest case, that of the compound $(CH_3)_3EY$, where only one group Y, having π electrons or a lone pair in the α-position relative to E, is linked to the E atom. In this situation, the overall electron-accepting effect of E in relation to Y diminishes with increase in the atomic number of the elements E

(i.e. from Si to Ge and Sn) and Y (in the sequences N > P, O > S > Se, and F > Cl > Br > I). The relative capacity of the substituents Y for conjugation with silicon or germanium atoms (i.e. the overall electron-donating effect of the conjugation of Y with E) is correlated with the resonance constants σ_R of the groups Y. These conclusions were reached from data obtained by NMR and IR spectroscopy.[6,42]

Here one should note that the energies of the initial orbitals E(E−C), $E(\pi)$, and $E(n)$, which are extremely significant for σ,π and σ,n conjugation [see Eqns. (1)−(3)] are not explicitly decisive for the resonance electron-accepting effect (designated as $d,\bar{\pi}$ or d,n conjugation in Section II).[134] The effects of the σ,n and d,n conjugation (as well as σ,π and d,π conjugation) can depend in different ways on the type of substituents X in X_3EY.

The influence of X on d,n conjugation for E = Si and Ge has been studied in fair detail.[42] The enhancement of electron-accepting properties increases the effective positive charge on E,[41,49,84,140] which induces, according to a widely held hypothesis,[41,42,51] the contraction of the diffuse unoccupied *nd* orbitals of E and hence improves the conditions for d,π or d,n conjugation in the molecule. Linear relations are known between experimental quantities characterising the charge on the E atom and the resonance electron-accepting effect of EX_3 (i.e. d,π or d,n conjugation under conditions where it clearly predominates over σ,π or σ,n conjugation): variation of the charge on E ensures the variation of the resonance electron-accepting properties of ER_3 within wide limits.[42]

On the other hand, the dependence of σ,π or σ,n conjugation on the nature of X in X_3EY is extremely complex. The enhancement of the electron-accepting properties of X (i.e. an increase in the charge on E) should increase the absolute energies E(E−C), $E(\pi)$, and $E(n)$. However, there are no grounds for the expectation that the form of the dependences of E(E−C), $E(\pi)$, and $E(n)$ on the charge on E is the same. Therefore, the relation between the charge on E and the values of ΔE [Eqns. (1)−(3)] as well as other quantities characterising the σ,π and σ,n conjugation is virtually unpredictable.[134]

The effects of σ,π and σ,n conjugation are determined by the interaction of the orbitals with the energies $E(\pi)$, $E(n)$, and E(E−C) leading to the formation of the HOMO. Therefore the methods based on the analysis of the orbital characteristics (photoelectron spectroscopy, UV spectroscopy of charge-transfer complexes[3,6]) are most effective for the study of hypoconjugation. The effects of d,π and d,n conjugation are maximum for E = Si and depend greatly on the charge on E; the π- or n-donor properties relative to $E(CH_3)_3$ (E = Si, Ge) are determined by the σ_R constants of Y.[6,42] Therefore the effective and sensitive methods for the study of d,π and d,n conjugation are based on the analysis of charge characteristics, for example, the intensities of the E−H (E = Si, Ge) bands in the IR spectra of Alk_2HEY (the effects of σ,π and σ,n conjugation are then comparatively small, i.e. the electron-donating component of the overall resonance effect of Alk_2HE relative to Y in Alk_2HEY is small). It must be emphasised that d,π and d,n conjugation undoubtedly affects the energy of HOMO and other orbitals (see, Section II and Fig. 1), but such dependence is complex, since the antibonding σ^* orbitals of E−C also participate in conjugation of this type together with *nd* and π (or n) orbitals [this was taken into account more than 20 years ago (see, for example, Pitt et al.[79])]. As regards the *nd* orbitals of the E atoms, they are stabilised under the influence of the electronegative substituents linked to E, i.e. their energy diminishes.[41,49,81,84] This last finding justifies the assumption that the *nd* orbitals are located between the π and π^* orbitals, i.e. their energy approaches that of the n orbitals; ultimately this should enhance d,π and d,n conjugation.

Thus all the foregoing considerations concerning the complexity of the resonance electron-accepting properties of the groups $E(CH_3)_3$ cast doubt on the legitimacy of the simplified view on these properties. Such a simplified approach can be encountered in many studies during the last decade (typical examples can be found in Refs. 65, 68−71, and 141 and in reviews[2,11,12,56]). In these studies, sometimes regarded as an alternative to the *nd* orbital hypothesis, the resonance electron-accepting properties of $E(CH_3)_3$ relative to Y are explained exclusively by the mixing of the antibonding σ^*(E−C) orbitals with π or n orbitals of Y. The only argument in support of this choice is the smallness of the *nd* orbital contributions according to the results of certain non-empirical quantum-chemical calculations.[60−63,65,72,141,142]

However, this argument is open to objection. Firstly, there have been non-empirical calculations[136,143−145] in which the involvement of the *nd* orbitals was found to be significant not only in silicon but also in tin derivatives. Secondly, in quantum-chemical studies[63,72,87,142] involving a rigorous approach to the problem of conjugation the necessity for further investigations for a correct assessment of the role of *nd* orbitals has been pointed out. The importance of these studies has been noted in a review.[46] Thirdly, even in non-empirical calculations for resonance interactions between systems and organic substituents not containing the atoms of Third Period elements, the results depend on the choice of the basis sets.[106] The current interest of this problem increases greatly on passing from organic[88] to organoelement[46,77,86,87] compounds. In non-empirical calculations for the latter, the authors of many investigations have noted an improvement of the agreement between the calculated and experimental data when *d* functions are included in the basis set.

For the reasons indicated, there are at present no well-founded grounds for the simplification of the idea, examined in Section II of the present review, that the resonance electron-accepting effects of the substituents $E(CH_3)_3$ relative to centres of the π or n type are complex. Therefore, in particular the overall resonance effect of the substituents $E(CH_3)_3$ on the HOMO and LUMO energies in benzene, ethylene, acetylene, thiophene, and furan derivatives[68−70] and on the HOMO energy in silyl ethers and siloxanes[141−146] as well as the effect of SiH_3 on the ionisation potentials of the lone pairs in $Y(SiH_3)_n$ (Y = N, O, S, and Se) [71] can be interpreted with greater justification not on the basis of hyperconjugation interactions with participation of the σ^*(E−C) and σ^*(Si−H) orbitals but as a result of the simultaneous operation of the electron-donating effect of the σ,π (or σ,π^*) as well as σ,n conjugation and the electron-accepting effect of the d,π (or d,π^*) as well as d,n conjugation. The large Si−O−C bond angles in compounds of the type $(CH_3)_3Si-O-Aryl$ and $(CH_3)_2ClSi-O-Aryl$ (where the oxygen atom has long been known[42] to participate in resonance interactions with both substituents) also cannot be accounted for within the framework of the concept of the electron-accepting properties of the Si−C and Si−Cl σ^* orbitals,[147] which casts doubt on the application of this concept by Reed et al.[65] to compounds with a related structure.

5. Electronic effects of the substituents $E(CH_3)_{3-n}X_n$

It was shown above that the substituents $E(CH_3)_3$ in the simple compounds $(CH_3)_3EY$ exhibit, together with the electron-donating inductive $+I$ effect in relation to π or n systems, also resonance electron-donating (σ,π or σ,n conjugation intensifies in the sequence Si < Ge < Sn < Pb) and electron-accepting (d,π and d,n conjugation weakens in the sequence Si > Ge > Sn) properties. We shall now consider the more complex systems $(CH_3)_{3-n}X_nEY$, where two or three groups X and Y having π electrons or lone pairs in the α-position relative to E, are linked to the latter.

The enhancement of the electron-accepting properties of X and/or the increase in the number of groups X is accompanied by a change in the sign and increase in magnitude of the I effect of $E(CH_3)_{3-n}X_n$ compared with $E(CH_3)_3$. Thus, for any element E, the groups EHal are typical $-I$ inductive σ-acceptors.[6,21]

The resonance interactions between $E(CH_3)_{3-n}X_n$ and Y are distinguished by a greater variety [compared with those in $(CH_3)_3EY$], since they depend not only on the nature of E and Y but also on the type and number of the groups X. Only the simplest versions of these interactions have been investigated hitherto. We shall now consider the main ideas formulated in this field.

1. Judging from the values of the constants σ_R, the overall resonance effect of the substituents $(CH_3)_{3-n}X_nE$ in benzene, ethylene, and acetylene derivatives intensifies with enhancement of the electron-accepting properties of the groups X and their number.[6] In the study of silane and germane derivatives $(CH_3)_{3-n}X_nEH$ by IR spectroscopy, where the situation at the indicator centre (E–H bonds) is determined predominantly by the charge characteristics (see Section III. 4), it was shown that the overall resonance interactions in the EX_n fragments are regulated by the effective charge on the silicon or germanium atom, which depends in its turn on the inductive and mesomeric effects of X.[42,148,149] In the analysis of the integral intensities of the E–H bands in the IR spectra, which was especially sensitive to the effect of conjugation, linear relations were established between the overall resonance effect in the EX_n fragments and the positive charge on the E atom (Si or Ge).[42,150]

2. The groups $E(CH_3)_{3-n}X_n$ for any X possess not only an electron-accepting component (which decreases in the sequence Si > Ge > Sn) but also an electron-donating component of the overall resonance effect. Unambiguous proof of the existence of the electron-donating component has been obtained both for the substituents $E(CH_3)_3$ (see Section III. 2) and for $E(CH_3)_{3-n}X_n$ in the analysis of the constants σ_p and σ_p^+ characterising the overall electronic effect (inductive and resonance) respectively in the absence and presence of a positive charge on the benzene ring to which these substituents are linked.[93]

The difference between the constants σ_p and σ_p^+ is caused by the enhancement of the electron-donating component (i.e. σ,π conjugation) of the overall resonance effect when a charge appears on the ring. Such enhancement is determined by the polarisability of the E–C and E–X bonds in $E(CH_3)_{3-n}X_n$. Thus the SiF_3 acceptor ($\sigma_p = +0.66$), which is strongest among silicon-containing acceptors, does not lose its electron-accepting properties appreciably in the presence of a positive charge on the ring in $C_6H_5SiF_3$ because of the low polarisability of the Si–F bonds. However, the electron-accepting properties of the substituent $GeCl_3$ ($\sigma_p = +0.79$) diminish sharply ($\sigma_p^+ = +0.33$) owing to the high polarisability of the Ge–Cl bonds.

Other features of the σ,π conjugation with participation of the groups $E(CH_3)_{3-n}X_n$, for example the enhancement of the effect, other conditions being equal, in the sequence Si < Ge < Sn, have been examined in detail.[6,93] Although the ratio of the resonance electron-donating and electron-accepting properties of these substituents, bound to the benzene ring, varies within wide limits as a function of the type and number of the groups X in $E(CH_3)_{3-n}X_n$ (the values of σ_p and σ_p^+ can differ not only in magnitude but also in sign), the electron-accepting resonance effect predominates in the groups $EHal_3$.[6,21,104] This predominance evidently persists also in those cases where the groups $EHal_3$ are linked to other reaction centres, for example to a double bond.[151] The strong resonance electron-accepting properties of the $SiCl_3$ group at the iron atom in $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiCl_3$ are caused, according to the authors,[152] by both the antibonding σ^*(Si–Cl) orbitals and the d orbitals of silicon.

The electronic effects of the substituents $E(CH_3)_{3-n}X_n$ with groups X of the same type were examined above. If the atoms X or X and Y, having lone pairs in the α-position relative to E, are of different types in $(CH_3)_{3-n}X_nEY$, then an additional conjugation channel arises in the molecule. In compounds with the O–E–Cl and N–E–Cl fragments, the occurrence of additional resonance interactions can be observed by NQR [3,153–155] and IR spectroscopic[3,51,156] methods.

Initially, such interactions were established in carbon compounds with F–C–Cl [157] and X–C–Cl (X has a lone pair in the α-position relative to C)[158] groups and were explained by σ,p conjugation.[157] A modern interpretation of this effect, close in its significance to that of Lucken,[157] in the X–A–Y (A = Be, Mg, B, Al, C, N, P, O, S) or X–O–Y systems is based on the idea of the n,σ^* interaction (negative hyperconjugation) of the lone pair of the atom X with electron-accepting σ^*(A–Y) [7,9,64,65] or σ^*(E–Y) orbitals.[7,64,65]

The significant role of n,σ^* conjugation is indicated by quantum-chemical[7,9,64,65] and experimental studies using indicator centres sensitive to charge[3] and especially orbital interactions.[7,9,64,77,159] In view of the appreciable influence of the n,σ^* interaction in silicon, phosphorus, and sulphur compounds and the less definite situation involving nd orbitals, the contributions of the latter to conjugation have been altogether denied in certain quantum-chemical studies[64,65,160] or are believed to be relatively insignificant. However, this view appears to be insufficiently supported by arguments, in view of the simplification of the complex pattern of electronic effects, for the following reasons.

Firstly, the effect of n,σ^* conjugation cannot serve as an alternative to the nd orbital hypothesis, since it occurs, for example, in carbon and nitrogen compounds,[7,9] while the contribution of the nd orbitals can be neglected *a priori*. Secondly, the ambiguity of the quantum-chemical conclusions concerning the involvement of nd orbitals has already been examined above (see Section III. 4). Nevertheless, we may note that non-empirical calculations for hypervalent compounds indicate an appreciable role of the nd orbitals of phosphorus, sulphur, and chlorine.[77] Thirdly, application of the standard procedure[20,22,31,158] adopted in the interpretation of experimental data[3,153,155,156,161] by the methods of correlation analysis to the separation of electronic effects indicates a significant difference between the resonance interactions in compounds containing X–E–Y fragments with groups X and Y of the same or different types. For X and Y of the same type, the above interactions include the inductive effect as well as d,n and σ,n conjugation. For X and Y of different types, the interpretation

of the experimental data becomes impossible without invoking the idea of the additional effect of n,σ^* conjugation.

IV. Conclusion

The analysis in this review of the available theoretical ideas in the literature concerning conjugation in organic compounds of the silicon-subgroup elements and their comparison with experiment permits a series of general conclusions.

None of the existing theoretical concepts (Pauling's *d*-orbital hypothesis, hyperconjugation as an alternative to this hypothesis, the involvement of the antibonding σ^* orbitals of the E–C or E–X bonds in conjugation), invoked to account for the nature of the resonance π-acceptor properties of the substituents $E(CH_3)_{3-n}X_nE$, where E = Si, Ge, or Sn, withstands criticism both from the standpoint of demonstrating the inadequacy of alternative systems of views and as regards the possibility of an exhaustive interpretation on their basis of the entire set of experimental data accumulated hitherto. The general theoretical concept in which the resonance electron-accepting properties of the groups $E(CH_3)_{3-n}X_n$ are treated from the standpoint of the joint involvement in conjugation of the *nd* orbitals of E and also of the antibonding orbitals $\sigma^*(E-C)$ and/or $\sigma^*(E-X)$ is consistent with experimental data most completely and with least contradiction. The ratio of these two contributions to the overall electron-accepting effect remains, however, obscure and reliable quantum-chemical approaches to its estimation are so far lacking. It has apparently been finally demonstrated merely that the transition of the E atoms to the sp^3d or sp^3d^2 hybridised state does not occur and the involvement of *nd* orbitals constitutes a special case.

Systematic comparative studies on the resonance electron-accepting properties of the groups $E(CH_3)_{3-n}X_n$ in the electronic ground and excited states have not so far been carried out.

Together with electron-accepting properties, the substituents $E(CH_3)_{3-n}X_n$ possess also resonance electron-donating properties in relation to π systems (σ,π conjugation) and groups containing an atom with lone pairs in the α-position relative to E (σ,n conjugation). Whereas the resonance electron-accepting effect is diminished as E is varied in the sequence Si > Ge > Sn, the σ,π- and σ,n-conjugation effects are actually enhanced with increase in the atomic number of E.

The resonance electron-donating and electron-accepting properties of the substituents $E(CH_3)_{3-n}X_n$ are responsible for the significant dependence of the relative contributions of these properties on the type of reaction centre. Therefore the variation of the nature of the latter (for example, the appearance of a positive charge) can lead not only to a change in the overall resonance effect of the substituents but also to a change in its sign. Such inversion of the donor–acceptor properties of the substituents $E(CH_3)_{3-n}X_n$ is of fundamental importance in the study of the reactivities of systems with these groups. It appears that accumulation and systematic treatment of facts and a deeper consideration of the characteristic features of the changes in the donor–acceptor properties of $E(CH_3)_{3-n}X_n$ compared with the behaviour of the substituents $(CH_3)_{3-n}X_nECH_2$, which do not have resonance electron-accepting properties, will make it possible in the future to avoid speculative constructions in the analysis of reactivity. Instead experimentally tested elements of the theory being created will be invoked.

It is essential to note also the fruitfulness of the orbital ideas, which are being used to an increasing extent in the organoelement chemistry of Group IVB elements. A complex organoelement molecule contains as a rule several indicator centres sensitive in different experiments, the application of physical research methods to charge and/or orbital interactions. The accumulation and analysis of such data together with non-empirical quantum-chemical calculations is important for the development of concepts concerning the charge and orbital control of reactions with participation of organoelement compounds and for the more active incorporation of the principle of hard and soft acids and bases in its modern interpretation. In its turn, progress on these lines will promote the improvement of our knowledge about conjugation effects in organic compounds of silicon-subgroup elements.

References

1. G Wilkinson, F D A Stone, E W Abel (Editors) *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, Vol. 1.
2. G Wilkinson, F D A Stone, E W Abel (Editors) *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, Vol. 2.
3. A N Egorochkin *Usp. Khim.*, 1984, **53**(5) 772 [English translation in *Russ. Chem. Rev.*, 1984(5)]
4. V F Traven', B I Stepanov *Usp. Khim.*, 1984, **53**(6) 897 [English translation in *Russ. Chem. Rev.*, 1984(6)]
5. Yu P Egorov *Stroenie i Spektroskopicheskie Svoistva Organicheskikh Soedinenii so Svyaz'yu E=N* (The Structure and Spectroscopic Properties of Organic Compounds with an E=N Bond), Naukova Dumka, Kiev, 1987, 251 pp
6. A N Egorochkin, G A Razuvaev *Usp. Khim.*, 1987, **56**(9) 1480 [English translation in *Russ. Chem. Rev.*, 1987(9)]
7. A E Reed, P v R Schleyer *Inorg. Chem.*, 1988, **27** 3969
8. V I Nefedov, V I Vovna *Elektronnya Struktura Organicheskikh i Elementoorganicheskikh Soedinenii* (The Electronic Structure of Organic and Organoelement Compounds), Nauka, Moscow, 1989, 199 pp
9. R P Arshinova *Metalloorg. Khim.*, 1990, **3**( ) 1127 [English translation in *Organomet. Chem. USSR*, 1990( )]
10. P P Shorygin, K Ya Burshtein *Usp. Khim.*, 1991, **60**(1) 3 [English translation in *Russ. Chem. Rev.*, 1991(1)]
11. S Patai, Z Rappoport (Editors) *The Chemistry of Organic Silicon Compounds*, Wiley, Chichester, 1989, Part 1
12. S Patai, Z Rappoport (Editors) *The Chemistry of Organic Silicon Compounds*, Wiley, Chichester, 1989, Part 2
13. G G Pitt *J. Organomet. Chem.*, 1973, **61** 49
14. R R Holmes *Chem. Rev.*, 1990, **90** 17
15. V A Pestunovich, Doctoral Thesis in Chemical Sciences, Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences, Irkutsk, 1985, 453 pp
16. S N Tandura, M G Voronkov, N V Alekseev *Top. Curr. Chem.*, 1985, **131** 99
17. I Birgele, A Kemme, E Kupce, et al. *Kremniiorganicheskie Proizvodnye Aminospirtov. Fiziko-khimicheskie Issledovaniya* (Organosilicon Derivatives of Aminoalcohols. Physicochemical Studies (Edited by E Lukevics), Zinatne, Riga, 1987, 230 pp

18. S N Tandura, S N Gurkova, A I Gusev, N V Alekseev *Stroennie Biologicheski Aktivnykh Soedinenii Germaniya s Rasshirennoi Koordinatsionnoi Sferoi* (The Structure of Biologically Active Germanium Compounds with an Expanded Coordination Sphere), Izd. NIITEKhIM, Moscow, 1983, 31 pp
19. R J P Gorriu *J. Organomet. Chem.*, 1990, **400** 81
20. O Exner *Correlation Analysis of Chemical Data*, Plenum Press, New York–London, 1988, 275 pp
21. C Hansch, A Leo, R W Taft *Chem. Rev.*, 1991, **91** 165
22. K Johnson *The Hammett Equation* (Translated into Russian), Mir, Moscow, 1977, 240 pp
23. P G Sennikov, A N Egorochkin *Usp. Khim.*, 1982, **51**(4) 561 [English translation in *Russ. Chem. Rev.*, 1982(4)]
24. A N Egorochkin, S E Skobeleva, V L Tsvetkova, et al. *Metalloorg. Khim.*, 1991, **4**( ) 362 [English translation in *Organomet. Chem. USSR*, 1991( )]
25. A N Egorochkin, S E Skobeleva, V L Tsvetkova *Metalloorg. Khim.*, 1991, **4**( ) 992 [English translation in *Organomet. Chem. USSR*, 1991( )]
26. A N Vereshchagin *Induktivnyi Effekt* (The Inductive Effect), Nauka, Moscow, 1988, 325 pp
27. S Marriott, W F Reynolds, R W Taft, R D Topsom *J. Org. Chem.*, 1984, **49** 959
28. R W Taft, R D Topsom *Prog. Phys. Org. Chem.*, 1987, **16** 1
29. C K Ingold *Structure and Mechanism in Organic Chemistry* (Translated into Russian), Mir, Moscow, 1973, Chapter 2
30. M J S Dewar, R Dogherty *Theory of the Perturbation of Molecular Orbitals in Organic Chemistry* (Translated into Rusian), Mir, Moscow, 1977, p. 228
31. V Palm *Osnovy Kolichestvennoi Teorii Organicheskikh Reaktsii* (Fundamentals of a Quantitative Theory of Organic Reactions), Khimiya, Leningrad, 1977, 359 pp
32. A Pross, L Radom, R W Taft *J. Org. Chem.*, 1980, **45** 818
33. A R Katritzky, R D Topsom *Chem. Rev.*, 1977, **77** 631
34. A N Egorochkin, M A Lopatin, A A Tumanov *Dokl. Akad. Nauk SSSR*, 1985, **280** 905
35. J A MacPhee, A Panaye, J-E Dubois *Tetrahedron*, 1978, **34** 3553
36. A N Egorochkin *Usp. Khim.*, 1985, **54**(8) 1335 [English translation in *Russ. Chem. Rev.*, 1985(8)]
37. C A Tolman *Chem. Rev.*, 1977, **77** 313
38. L N Zakharov, G A Domrachev, Yu T Struchkov *Zh. Strukt. Khim.*, 1983, **24** 75
39. L N Zakharov, A N Egorochkin, M A Lopatin, et al. *Metalloorg. Khim.*, 1988, **4**( ) 809 [English translation in *Organomet. Chem. USSR*, 1988( )]
40. V I Galkin, R D Sayakhov, R A Cherkasov *Metalloorg. Khim.*, 1990, **3**( ) 986 [English translation in *Organomet. Chem. USSR*, 1990( )]
41. H Kwart, K G King *d-Orbitals in the Chemistry of Silicon, Phosphorus and Sulphur*, Springer, Berlin, 1977, 196 pp
42. A N Egorochkin, S Ya Khorshev *Usp. Khim.*, 1980, **49**(9) 1687 [English translation in *Russ. Chem. Rev.*, 1980(9)]
43. W Kutzelnigg *Angew. Chem.*, 1984, **96** 262
44. D G Anderson, A J Blake, S Cradock, et al. *Angew. Chem.*, 1986, **98** 97
45. N Janes, E Oldfield *J. Am. Chem. Soc.*, 1986, **108** 5743
46. Y Apeloig *The Chemistry of Organic Silicon Compounds* (Edited by S Patai, Z Rappoport), Wiley, Chichester, 1989, Part 1, p. 57
47. L O Brockway, F T Wall *J. Am. Chem. Soc.*, 1934, **56** 2373
48. L Pauling *The Nature of the Chemical Bond*, Cornell Univ. Press, New York, 1960
49. E A V Ebsworth *Organometallic Compounds of the Group IV Elements. The Bond to Carbon* (Edited by A G MacDiarmid), M Dekker, New York, 1968, Vol. 1, p. 1
50. C J Attridge *Organomet. Chem. Rev. A*, 1970, **5** 323
51. A N Egorochkin, N S Vyazankin, S Ya Khorshev *Usp. Khim.*, 1972, **41**(5), 829 [English translation in *Russ. Chem. Rev.*, 1972(5)]
52. A P Sadimenko, Yu V Kolodyazhnyi, O A Osipov *Fizika Molekul*, 1978, **6** 77
53. A N Nesmeyanov *Uch. Zap. Mosk. Univ.*, 1950, **132** 5
54. G T Traylor, G J Bervin, J Jerkunica, M L Hall *Zh. Vses. Khim. Ova im. D I Mendeleeva*, 1972, **17** 392
55. H Sakurai *Pure Appl. Chem.*, 1987, **59** 1637
56. H Bock *Angew. Chem.*, 1989, **101** 1659
57. C G Pitt *J. Chem. Soc., Chem. Commun.*, 1971, 816
58. R Ponec, V Chvalovsky *Collect Czech. Chem. Commun.*, 1973, **38** 3845
59. R Ponec, V Chvalovsky *Collect Czech. Chem. Commun.*, 1974, **39** 1185
60. F Bernardi, M Guerra, G F Pedulli *Tetrahedron*, 1978, **34** 2141
61. A C Hopkinson, M H Lien *J. Org. Chem.*, 1981, **46** 998
62. M L Hendewerk, R Frey, D A Dixon *J. Phys. Chem.*, 1983, **87** 2026
63. E Magnusson *Tetrahedron*, 1985, **41** 2945
64. A E Reed, P v R Schleyer *J. Am. Chem. Soc.*, 1987, **109** 7362
65. A E Reed, C Schade, P v R Schleyer, et al. *J. Chem. Soc., Chem. Commun.*, 1988, 67
66. R West *J. Organomet. Chem.*, 1986, **300** 327
67. C L Wadsworth, R West *Organometallics*, 1985, **4** 1664
68. J C Giordan, J H Moore *J. Am. Chem. Soc.*, 1973, **105** 6541
69. J C Giordan *J. Am. Chem. Soc.*, 1983, **105** 6544
70. A Modelli, G Distefano, D Jones, G Seconi *J. Electron Spectr. Relat. Phenom.*, 1983, **31** 63
71. D B Beach, W L Jolly *Inorg. Chem.*, 1984, **23** 4774
72. P v R Schleyer, T Clark, A J Kos, et al. *J. Am. Chem. Soc.*, 1984, **106** 6467
73. A A Korkin *Metalloorg. Khim.*, 1990, **3**(5), 969 [English translation in *Organomet. Chem. USSR*, 1990(5)]
74. L V Ermolaev, R P Arshinova *Metalloorg. Khim.*, 1990, **3**(5) 1156 [English translation in *Organomet. Chem. USSR*, 1990(5)]
75. E N Tsvetkov, V S Gamayurova *Metalloorg. Khim.*, 1990, **3**(5) 1168 [English translation in *Organomet. Chem. USSR* 1990(5)]
76. E A Rykova, Zh E Grabovskaya, G M Chaban, et al. *Metalloorg. Khim.*, 1990, **3**(5) 1091 [English translation in *Organomet. Chem.*, 1990(5)]
77. A E Reed, P v R Schleyer *J. Am. Chem. Soc.*, 1990, **112** 1434
78. G Sini, G Ohanessian, P C Hiberty, et al. *J. Am. Chem. Soc.*, 1990, **112** 1407
79. C G Pitt, R N Carey, E C Toren *J. Am. Chem. Soc.*, 1972, **94** 3806
80. D P Santry, G A Segal *J. Chem. Phys.*, 1967, **47** 158
81. K A Levison, P G Perkins *Theor. Chim. Acta*, 1969, **14** 206
82. B C Webster *J. Chem. Soc. A*, 1968, 2909
83. R West *J. Organomet. Chem.*, 1965, **3** 314
84. D W J Cruickshank *J. Mol. Struct.*, 1985, **130** 177
85. M A Ratner, J R Sabin *J. Am. Chem. Soc.*, 1977, **99** 3954
86. W J Pietro, M M Francl, W J Hehre, et al. *J. Am. Chem. Soc.*, 1982, **104** 5039

87. B T Luke, J A Pople, M-B Krogh-Jesperson, et al. *J. Am. Chem. Soc.*, 1986, **108** 260
88. K Ya Burshtein, P P Shorygin *Kvantovokhimicheskie Raschety v Organocheskoi Khimii i Spektroskopii* (Quantum-Chemical Calculations in Orgnaic Chemistry and Spectroscopy), Nauka, Moscow, 1989, 103 pp
89. H Bock, B Solouki *The Chemistry of Organic Silicon Compounds* (Edited by S Patai, Z Rappoport), Wiley, Chichester, 1989, Part 1, p. 555
90. A R Bassindale, P G Taylor *The Chemistry of Organic Silicon Compounds* (Edited by S Patai, Z Rappoport), Wiley, Chichester, 1989, Part 2, p. 893
91. T N Mitchell, C Nettelbeck *Magn. Res. Chem.*, 1987, **25** 879
92. A Lycka, J Jirman, A Kolonicny, et al. *J. Organomet. Chem.*, 1987, **333** 305
93. A N Egorochkin, G A Razuvaev, M A Lopatin *J. Organomet. Chem.*, 1988, **344** 49
94. A N Egorochkin, M A Lopatin, S E Skobeleva, et al. *Metalloorg. Khim.*, 1988, **1**(2) 350 [English translation in *Organomet. Chem. USSR*, 1988(2)]
95. P P Shorygin, K Ya Burshtein, A N Isaev, V M Promyslov *Dokl. Akad. Nauk SSSR*, 1989, **304** 158
96. J B Lambert *Tetrahedron*, 1990, **46** 2677
97. A N Egorochkin, S E Skobeleva, V L Tsvetkova, et al. *Metalloorg. Khim.* (in press)
98. V F Traven', M Yu Eismont, V V Redchenko, B I Stepanov *Zh. Obshch. Khim.*, 1980, **50** 2007
99. V F Traven', V V Redchenko, M Yu Eismont, B I Stepanov *Zh. Obshch. Khim.*, 1981, **51** 1297
100. H Sakurai *J. Organomet. Chem.*, 1980, **200** 261
101. J Ohshita, H Ohsaki, M Ishikawa, et al. *Organometallics*, 1991, **10** 880
102. A Sekiguchi, T Yatabe, C Kabuto, et al. *J. Organomet. Chem.*, 1990, **390** C27
103. P K Bischof, M J S Dewar, D W Goodman, et al. *J. Organomet. Chem.*, 1974, **82** 89
104. T Veszpremi, J Nagy *J. Organomet. Chem.*, 1983, **255** 41
105. T Veszpremi, L Nyulaszi, J Nagy *J. Orgamomet. Chem.*, 1987, **331** 175
106. S Marriott, R D Topsom *J. Mol. Struct.*, 1984, **106** 277
107. E Liepins, I Birgele, E Lukevics, et al. *J. Organomet. Chem.*, 1990, **393** 11
108. J Allwohn, R Hunold, M Pilz, et al. *Z. Naturforsch. B, J. Chem. Sci.*, 1990, **45** 290
109. E Liepins, M N Petrova, E T Bogoradovsky, et al. *J. Organomet. Chem.*, 1991, **410** 287
110. K Ya Burshtein, P P Shorygin *Dokl. Akad. Nauk SSSR*, 1987, **296** 903
111. C Cauletti, C Furlani, F Grandinetti, et al. *J. Organomet. Chem.*, 1986, **315** 287
112. K Ya Burshtein, P P Shorygin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1330
113. W Ensslin, H Bock, G Becker *J. Am. Chem. Soc.*, 1974, **96** 2757
114. R Gleiter, W Schäfer, H Sakurai *J. Am. Chem. Soc.*, 1985, **107** 3046
115. B G Zykov, N P Erchak, V I Khvostenko, et al. *J. Organomet. Chem.*, 1983, **253** 301
116. V O Reikhsfel'd, S G Semenov, I P Yakovlev, et al. *Teor. Eksp. Khim.*, 1981, **17** 818
117. M N Paddon-Row, S S Wong, K D Jordan *J. Am. Chem. Soc.*, 1990, **112** 1710
118. E Zeek *Theor. Chim. Acta*, 1974, **35** 301
119. O Takahashi, K Morihashi, O Kikuchi *Bull. Chem. Soc. Jpn.*, 1991, **64** 1178
120. H Matsumoto, K Akaiwa, Y Nagai, et al. *Organometallics*, 1986, **5** 1526
121. K Siam, M Dakkouri, J D Ewbank, et al. *THEOCHEM*, 1990, **63** 291
122. C Cauletti, C Furlani, G Granozzi, et al. *Organometallics*, 1985, **4** 290
123. S Cradock, R H Findlay, M H Palmer *J. Chem. Soc., Dalton Trans.*, 1974, **1650**
124. A N Egorochkin *Advances in Organosilicon Chemistry* (Edited by M G Voronkov), Mir, Moscow, 1985, p. 39
125. V F Traven' *Tr. Mosk. Khim.-Tekhnol. Inst. im D I Mendeleeva*, 1978, **103** 96
126. V F Traven', M I German, M Yu Eisomont, et al. *Zh. Obshch. Khim.*, 1978, **48** 2232
127. V B Knyazhevskaya, V F Traven', B I Stepanov *Zh. Obshch. Khim.*, 1980, **50** 606
128. G Distefano, A Ricci, F P Colonna, et al. *J. Organomet. Chem.*, 1974, **78** 93
129. A N Egorochkin, S E Skobeleva, V L Tsvetkova *Metalloorg. Khim.*, 1988, **1**(1) 89 [English translation in *Organomet. Chem. USSR*, 1988(1)]
130. A Hosomi, T G Traylor *J. Am. Chem. Soc.*, 1975, **97** 3682
131. E Magnusson *J. Am. Chem. Soc.*, 1986, **108** 11
132. V N Baidin, I I Kritskaya, M M Timoshenko, et al. *Uspekhi Fotoniki* (Advances in Photonics), Izd. Leningrad. Gos. Univ., Leningrad, 1983, No. 8, p. 8
133. A N Egorochkin, S E Skobeleva, V L Tsvetkova *Metalloorg. Khim.*, 1990, **3**(3) 570 [English translation in *Organomet. Chem. USSR*, 1990(3)]
134. A N Egorochkin, S E Skobeleva, V L Tsvetkova *Metalloorg. Khim.*, 1990 **3**(3) 576 [English translation in *Organomet. Chem. USSR*, 1990(3)]
135. A N Egorochkin, S E Skobeleva, V L Tsvetkova *Metalloorg. Khim.*, 1990 **3**(3) 565 [English translation in *Organomet. Chem. USSR*, 1990(3)]
136. R Bertoncello, J R Daudey, G Granozzi, et al. *Organometallics*, 1986, **5** 1866
137. C Cauletti, F Graninetti, G Granozzi, et al. *Organometallics*, 1988, **7** 262
138. H Bock, J Meuret, U Stein *J. Organomet. Chem.*, 1990, **398** 65
139. M Yu Maroshina, N N Vlasova, M G Voronkov *J. Organomet. Chem.*, 1991, **406** 279
140. G N Dolenko *Stroenie Veshchestva i Svoistva Molekul* (The Structure of Matter and Molecular Properties) (Edited by V V Gorchakov), Izd. Dal'nevostoch. Univ., Vladivostok, 1987, p. 225
141. S Shambayati, J F Blake, S G Wierschke, et al. *J. Am. Chem. Soc.*, 1990, **112** 697
142. B Rempfer, H Oberhammer, N Auner *J. Am. Chem. Soc.*, 1986, **108** 3893
143. F F Roelandt, D F Van de Vondel, G P Van der Kelen *J. Mol. Struct.*, 1978, **50** 147
144. A C Hess, P F McMillan, M O'Keeffe *J. Phys. Chem.*, 1986, **90** 5661
145. A C Hess, P F McMillan, M O'Keeffe *J. Phys. Chem.*, 1987, **91** 1395

146. J A Tossell, J H Moore, K McMillan, et al. *J. Am. Chem. Soc.*, 1991, **113** 1031
147. M D Healey, A R Barron *J. Organomet. Chem.*, 1990, **381** 165
148. A N Egorochkin, S Ya Khorshev, J Statge, et al. *J. Organomet. Chem.*, 1975, **99** 239
149. A N Egorochkin *Metalloorganicheskie Soedineniya i Radikaly* (Organometallic Compounds and Radicals) (Edited by M I Kabachnik), Nauka, Moscow, 1985, p. 265
150. A N Egorochkin, E I Sevast'yanova, S Ya Khorshev *J. Organomet. Chem.*, 1978, **162** 25
151. E Liepins, I Birgele, E Lukevics *J. Organomet. Chem.*, 1990, **385** 185
152. D L Lichtenberger, A Rai-Chandhuri *J. Am. Chem. Soc.*, 1991, **113** 2923
153. I P Biryukov, M G Voronkov, E Lukevics, et al. *Teor. Eksp. Khim.*, 1970, **6** 566
154. V P Kazakov, Yu D Koreshkov, E V Bryukhova *Zh. Fiz. Khim.*, 1979, **53**(1) 99 [English translation in *Russ. J. Phys. Chem.*, 1979(1)]
155. V P Feshin, M G Voronkov, G Ya Zueva, et al. *Dokl. Akad. Nauk SSSR*, 1977, **232** 1370
156. S Ya Khorshev, A N Egorochkin, E I Sevast'yanova, et al. *Zh. Obshch. Khim.*, 1977, **47** 1795
157. E A C Lucken *J. Chem. Soc.*, 1959, 2954
158. G K Semin, T A Bubushkina, G G Yakobson *Primenenie Yadernogo Kvadrupol'nogo Rezonansa v Khimii* (Chemical Applications of Nuclear Quadrupole Resonance), Khimiya, Leningrad, 1972, 536 pp
159. Y Apeloig, A Stanger *J. Organomet. Chem.*, 1988, **346** 305
160. P Aped, Y Apeloig, A Ellencweig, et al. *J. Am. Chem. Soc.*, 1987, **109** 1486
161. A N Egorochkin, S Ya Khorshev, N S Ostasheva, et al. *J. Organomet. Chem.*, 1976, **105** 311

Translated from *Uspekhi Khimii* **61** 1114–1141 (1992) U.D.C. 543.42

Aggregation of dye molecules and its influence on the spectral luminescent properties of solutions

V I Yuzhakov
Faculty of Physics, Lomonosov Moscow State University

ABSTRACT. The principal results of studies carried out in recent years on the molecular aggregation of organic dyes and pigments in solutions are examined and surveyed in the present review. Attention is concentrated on the influence of association on the photoenergetics of the dye molecules. Theoretical studies on the spectral-luminescent spectroscopic characteristics of the molecular aggregates are briefly considered. Studies on the anisotropy of the absorption and on the emission from the associated species are described. Investigations of the concentration depolarisation and concentration quenching of the fluorescence of dye solutions are subjected to a critical analysis. The results of studies of the mixed association of dye molecules and of its influence on the lasing characteristics of the solutions are presented. The physicochemical conditions affecting the efficiency of the association process are examined.

The bibliography includes 251 references.

Contents

I. Introduction 613
II. Theoretical study 613
III. The photoenergetics and structure of the associated species 615
IV. Polymethine dyes 618
V. Mixed association 620
VI. Polarisation studies 621
VII. Concentration-induced depolarisation and the quenching of luminescence 622
VIII. Association and lasing properties of the solutions. Factors influencing the effectiveness of association 623

I. Introduction

The wide-scale employment of organic dyes in science and engineering has stimulated research into the photophysical and photochemical properties of their molecules. Since dyes are most often used in liquid and solid solutions, where their spectral luminescent characteristics are complicated by intermolecular interactions, studies on the associated molecular forms of such compounds have become important. One may point out several aspects responsible for the interest in molecular association. This is in the first place the necessity to create a non-contradictory theory of the liquid state and solutions. The study of the photoenergetics of dye solutions always requires the knowledge of the spectral-luminescent characteristics of their molecular aggregates in order to be able to isolate in a pure form the optical manifestations of various intermolecular interactions, which are frequently complex and varied. It is impossible to overestimate the importance of studies on molecular association for the investigation and modelling of biological processes at the molecular level since under these conditions the molecules, functioning as reaction centres, are usually associated.

The employment of dye solutions as the lasing media in lasers has given rise to interest in problems such as that of the influence of solvents and various additives on the development of molecular association, which has a negative effect on the lasing efficiency. The application of dye solutions in quantum electronics as passive modulators, optical filters, shutters, etc., when appreciable absorption in the absence of luminescence is required, has given rise to additional interest in their associated molecular forms. Under these conditions, the appreciably different spectral-luminescent properties of the associated dye molecules and their monomeric forms can serve as a factor expanding their application in this field. The idea of a shift from the set of elements used in electronics to the molecular level will greatly expand the research into the problem of the molecular dye aggregates which is thus related to a number of fundamental aspects. Since the association of dye molecules lead as a rule to the quenching of the luminescence, it is essential to know the physicochemical factors inducing association or reducing its effectiveness. On the other hand, luminescent associated species can be used in concentrators of light energy, which requires conditions for the intensification of the association process. It is virtually true that whatever aspect of the study or use of dyes is considered (the study of relaxations of different kinds, Langmuir-Blodgett films, micellar systems, etc.), the problem arises of molecular association and its luminescence-spectroscopic manifestations. This is in fact why the number of studies devoted to the association of dye molecules and their spectroscopy has been continuously increasing. The previous review devoted to this problem[1] no longer reflects the current state of research in this field. The development of the spectroscopic techniques and the use of quantum-chemical modelling methods have made it possible to obtain a series of new luminescence-spectroscopic effects, arising on dimerisation of organic dye and pigment molecules. This review is based on studies published during the last 15 years.

II. Theoretical study

The luminescence-spectroscopic properties of the molecules of organic compounds in aggregates are a result of their collective interaction and are caused by the change on association of the oscillator strengths for optical transitions and selection rules and by

the manifestation of vibronic interactions. They involve the splitting of spectral bands, the displacement of electronic spectra, and changes in the intensity and anisotropy of absorption and emission and in molecular vibration frequencies, and the appearance of new vibrational transitions.

As regards their theoretical aspect, many of these problems have still not been solved even in a general form and for this reason there has been no weakening of interest in the theoretical description of the optical spectra of molecular aggregates (absorption, luminescence, and circular dichroism spectra), attention being concentrated on the effects of vibronic interaction.[2] The following aspects of the theoretical study of the molecualr aggregates have yielded most results: (1) the classical theory of the polarisability of bound oscillators; (2) the study of the exciton–phonon interaction as a stoichastic process which depends on time and the potential; (3) numerical calculation of the positions of the lines and intensities on the basis of a simple microscopic model; (4) the application of the sums rule as the theorem of moments for a vibronic band.

However, the quantitative application of theoretical methods to real systems remains problematical and the optical characteristics of associated species are calculated only for ordered structures, for example, sandwich type structures.

The most significant results have been obtained using the theory of excitons. The shape of the absorption bands of molecular dimers has been predicted with the aid of the model of incoherent exciton scattering.[3] The Hamiltonian of the dimer is represented by the sum of the Hamiltonians of the monomers and of the intermolecular interaction operator, whose matrix elements are expressed in terms of the eigenfunctions of the monomers. The energy levels and the matrix elements of the dipole moments of the dimer have been calculated in this way. The absorption coefficient and the absorption contours are expressed in terms of these quantities for different molecular interaction energies. The form of the absorption spectrum of the dimer depends on the relation between the nuclear relaxation and the exchange energy between the monomers. As an example, the absorption spectrum of the 9-chloroanthracene dimer was calculated and was found to be close to the experimental spectrum.

Allowance for the exciton effects, the electron–phonon interaction, and the local disorder among phosphor molecules made it possible to calculate the form of these individual transitions in the vibronic spectra of the molecular aggregates.[4] Best agreement between calculation and experiment was then achieved for pseudocyanine on the assumption that the aggregates contain eleven molecules arranged helically.

The same workers proposed a method for calculating the electronic absorption spectra of aggregates permitting the separate description of the vibrational structure of the non-uniform broadening.[5] The applicability of the method was demonstrated for the *J*-aggregates of 1,1-diethyl-*N*,*N*′-isocyanine chloride in water. It was found that the aggregate consists of six monomers.

A new approach to the calculation of the optical properties of molecular aggregates is based on allowance for the non-uniform spectra broadening caused by the non-equivalence of the environments of phosphor molecules comprising the molecules of the medium.[6] One considers an assembly of chemically identical aggregates in an isotropic medium (liquid, glass, etc.) in which it is necessary to take into account the distribution of non-equivalent states and to average out the form of the spectral lines with respect to the distribution. The functional form of the Hamiltonian corresponding to each six system is uniform but the magnitude of the parameter can differ from system to system. In this model, the medium is characterised by vibrations (modes) which can be divided into strong and weak in terms of their interaction with the aggregates. Strong modes are regarded as the usual exciton–phonon interaction and weak modes are responsible for the statistical non-uniformity. The Hamiltonian is constructed as follows:

$$H = \sum_i \varepsilon_i A_i^+ A_i + \sum_n \omega_n B_n^+ B_n +$$
$$+ \sum_j \sum_i \sum_n g_{ij}^n \omega_n \left(B_n + B_n^+\right) A_i^+ A_j ,$$

where ε_i are the electronic energy levels of the aggregates, A and B are operators of the exciton–phonon formation and annihilation, and g_{ij}^n is the parameter of the exciton–phonon coupling for a separate mode on transition between levels i and j. The vibrational modes ω_n of the solvent and the molecule are grouped in the last two terms. Non-uniform local perturbations of any of the parameters (ε, ω, g) can differ for different species in the ensemble, but it is postulated that during the absorption of a photon the parameters are constant. Calculation showed that even in simple systems dimer spectra can be completely different from the monomer spectrum (depending on the vibronic and non-uniform contributions to the line width and the variation of any one parameter). The possibility of applying these theoretical results to real molecular systems, in which individual vibronic lines are not resolved, has been discussed in a study,[7] where analytical expressions were obtained for the form of the absorption and circular dichroism bands of the dimer.

The study of exciton–nuclear interactions in aggregates showed[8,9] that such interactions predominate in real dimers. The parameters used in this case were obtained by adjusting the theoretical spectra to agree with the experimental spectra of solutions of xanthene dyes (rhodamine B, pyronines B and Y).

The dimers of eosin Y have been investigated.[10] The visible absorption spectrum of its monomers refers to a single electronic transition, but includes several different vibration bands. The spectra of the dimers are therefore regarded as a result of their exciton interaction between vibronic levels. The difficulties in the interpretation of the experimental spectra proposed by Jones, et al.[11] are indicated and an approximation, constituting a further development of the exciton theory, is proposed for the analysis of the spectra of the dimers. It is suggested[10] that such spectra be considered on the basis of exciton interactions between vibronic states.

The electronic transitions between the split components of the electronically excited dimers have been analysed using perturbation theory.[12] It was shown that the one-photon transition between the ground state and one of the components of the excited state is prohibited for dimers in the case where the transition moments of the monomers constituting the associated species are parallel. However, the components forbidden in a one-photon transition can be manifested in a two-photon process. The theoretical treatment adopted in the above study[12] is equivalent to the strong bond limit.

The properties of the electronic states of metalloporphyrin dimers have been investigated by quantum-chemical methods.[13,14] Calculations have been carried out for the sandwich dimer, where the centres of the monomers are located on the axis perpendicular to the molecular plane.[13] The singlet and triplet states of the dimers of this compound have been obtained[14] for structures where the molecules are in one and in different parallel planes. Quantitative

agreement with experiment were not always obtained but the parameters of the structure attributed to the dimers agree with EPR data.

The dimers of a series of porphyrins[15] with different geometries[16] were investigated by this method. The energy changes and the orbital nature of the excited electronic states of the xanthene dyes during their dimerisation were established by direct quantum-chemical calculation,[17] dimers with a sandwich structure being considered.

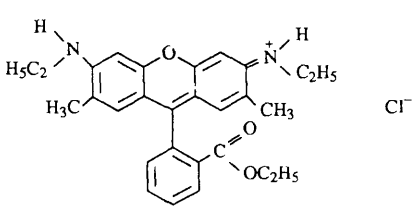
The results obtained when the theoretical parameters are determined from experimental data are of interest.[9,10,18] Not only the form of the electronic spectra of the dimers but also quantities such as the association constant, the quenching constant etc. are then obtained. Thus, using the method of least squares and the experimental spectra of Acridine Orange in the hydrochloride form, the dimerisation constant and the molar exctinciton coefficients of the dimers were obtained.[19] However, in their analysis the authors had to assume that the dye solutions consists only of monomers and dimers.

The approach to the description of the contours of the electronic bands of associated dye molecules, based on the hypothesis that the total absorption spectrum consists of "elementary" spectra (uniform relaxation components), has been proposed.[20] The initial postulate is that the line width and the probability of the transition between two electronic states are functions of the transition frequencies only. With the aid of the expression obtained for the description of the spectra of associated species and the experimental spectra, the parameters of the absorption spectra of the associated species were determined by minimising the corresponding function. No temperature dependence of the width of the Lorentzian component of the spectra of the associated species was observed for rhodamine 6G, in contrast to the monomers where such a dependence exists.

The optical properties of aggregates of chromophores have been studied theoretically using the incoherent dynamics model in the theory of Green's functions.[21]

III. The photoenergetics and structure of the associated species

Aggregates are molecular objects which occupy an important place in traditional spectroscopic research whose aim is the elucidation of spectral-luminescent changes occurring on association, the influence of this process on photophysical phenomena in solutions of dyes (the quenching of luminescence, the migration of energy), the influence on the lasing properties of solutions etc. The association of dye molecules alters significantly the probabilities of their vibronic transitions. The redistribution of the radiative and non-radiative transitions in associated rhodamine 6G species, occurring when their structure and composition are altered, has been investigated.[22,23]

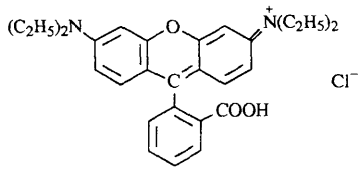


Rhodamine 6G

Earlier studies on aggregates of this compound have already been reviewed.[24] Different degrees of association of the dye were obtained in mixtures of polar and non-polar sovlents. The associated species are arbitrarily divided into "simple" and "complex" (the simple species arise when the content of the non-polar component is up to 90% of the volume of the mixture and the complex species arise when its content is higher). The luminescence with λ_{max} - 570 nm (20% of ethanol and 80% of CCl_4) was attributed to type *P* slow fluorescence due to the triplet–triplet annihilation of the simple associated species. For a higher CCl_4 content the intensity of the above glow falls and a new band arises with a maximum in the region of 620 nm, which is attributed to slow type *E* fluorescence due to the thermal activation of the associated triplet molecules to the excited singlet state with subsequent emission. For complex rhodamine 6G associated species, the $S_1 - T$ splitting is ~ 1500 cm^{-1}. The association of the molecules of this dye in binary mixtures takes place with participation of the anion[23] and the latter behaves as a heavy atom accelerating the intersystem crossing processes in the simple associated dye species.

The luminescence maximum at $\lambda = 670$ nm is attributed[22,23,25] to the phosphorescence of the rhodamine 6G associated species.

The absence of sensitised phosphorescence or slow fluorescence of stilbene has in fact been explained by the aggregation of rhodamine 6G following its adsorption from aqueous solution on the surface of a stilbene crystal.[26] This is associated with the fact that the *T* level of stilbene lies above the S_1 level of the rhodamine 6G aggregates. The aggregation of the molecules of rhodamines B and 3B, adsorbed on crystals (SnO_2, ZnO, etc.)[27–29] and on amorphous quartz,[30] is responsible for the anomalous spectroscopic-kinetic effects and the electron and hole injection in such systems.



Rhodamine B

Comparison of the optical properties of the associated species formed under different conditions can allow conclusions about their structure and the nature of the forces inducing association. The comparison for rhodamine 6G showed[31] that in dye solutions with $c \simeq 10^{-4}$ M and with a non-polar component content up to 90%, associated species are formed with a geometry such that they are incapable of luminescence. An increase in the content of the non-polar component (to 98–99%) increases the degree of association of the dye molecules and alters the geometry of the associated species (the angle between the planes of the molecules becomes less than 90°), whereupon the associated species fluoresce. More complex associated species, which do not fluoresce, are formed in virtually non-polar media. The fluorescence spectra of the rhodamine 6G associated species, formed in alcoholic solutions at –150 °C and in a binary mixture with a 99% content of the non-polar component, are identical.[31,32]

A more complete study of the optical properties of the luminescent associated species formed in cooled highly concentrated alcoholic solutions of dyes with different molecular structures (rhodamine 6G, Neutral Red, Crystal Violet, and Methylene Blue) showed that there is a definite qualitative agreement between the

luminescence-spectroscopic characteristics of the associated species of these dyes, despite the fact that the optical characteristics of the monomeric forms differ significantly.[32] Thus the fluorescence quantum yield of the associated species of the dyes investigated is low even at 77 K ($\sim 10^{-2}$), while the phosphorescence yield is lower still by 2–3 orders of magnitude. The electronic spectra of Neutral Red in ethanol at $c = 3 \times 10^{-2}$ M, where the dye molecules are almost all associated, are presented in Fig. 1, while Table 1 lists the wavelengths of the maxima in the spectra of the different types of luminescence, their quantum yields, and the phosphorescence decay times. The luminescence excitation spectra of the associated species have an appreciable maximum on the long-wavelength edge of the absorption band where the extinction coefficient is extremely low. Studies have shown[32] that complex associated species with non-uniformly broadened electronic spectra luminesce.

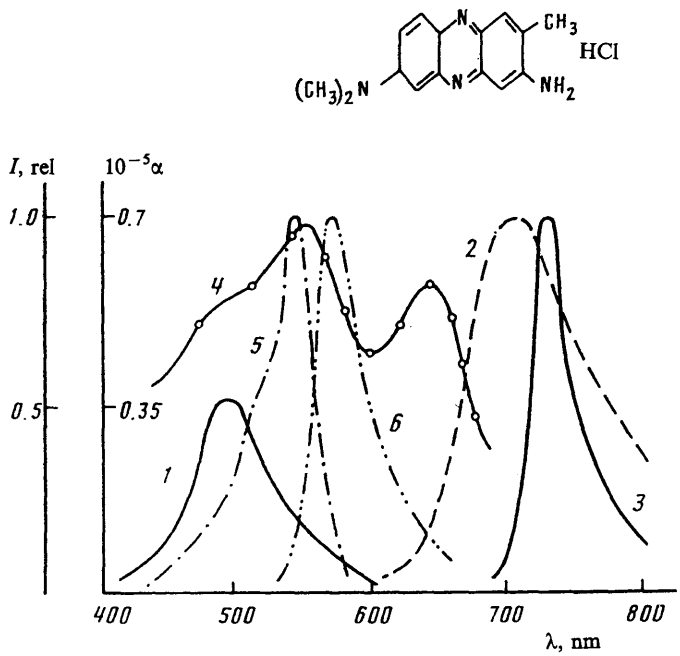


Figure 1. Electronic absorption (α) (curve *1*), fluorescence (curve *2*), phosphorescence (curve *3*), and excited fluorescence (*I*) (curve *4*) spectra of Neutral Red associated species in ethanol at 77 K; curves *5* and *6*—absorption and fluorescence spectra of the monomeric form at 77 K.[32]

It is essential to note that in binary mixtures of polar and non-polar solvents, the structure of the dye aggregates and the composition of their solvation shells vary non-linearly with the ratio of the solvent components.[33] This is related to the fact that the macroproperties of the binary solvent differ appreciably in the majority of instances from its microproperties, which exert a decisive influence on the spectral-luminescent characteristics of the phosphor molecules.[34] The polarisation characteristics of the luminescence and the axial moments of inertia of the rhodamine 6G assocated species give grounds for the assumption that in such mixtures their geometry is either of the "house of cards" or sandwich type.[33] The same geometry has been postulated for rhodamine B dimers in aqueous solutions. The separate aggregation of this dye in the neutral and cationic forms has been considered.[35] The energy of the exciton interaction (~ 560 cm^{-1}) and the angle between the dipole moments of the monomers ($\sim 70°$) of both forms are virtually identical, but the greater tendency towards the association of the neutral form is due to the electrostatic interaction between the carboxy- and xanthene groups of the monomers. The monomeric molecular forms of rhodamine B in water have also been investigated.[36]

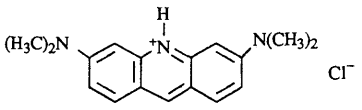
Table 1. The wavelengths of the maxima in the absorption (λ_a), fluorescence (λ_{fl}) and phosphorescence (λ_{ps}) spectra, the fluorescence (B_{fl}) and phosphorescence (B_{ps}) quantum yields, and the phosphorescence decay times (τ_{ps}) of associated dye species in ethanol and $T = 77$ K.[32]

Dye	λ_a, nm	λ_{fl}, nm	λ_{ps}, nm	B_{fl}	B_{ps}	τ_{ps}, ms
Rhodamine 6G	502 534	628	695	$3 \cdot 10^{-2}$	$2 \cdot 10^{-6}$	1200
Crystal Violet	584 592	732	745	$5 \cdot 10^{-3}$	$4 \cdot 10^{-4}$	345
Neutral Red	514	715	732	$8 \cdot 10^{-4}$	$1 \cdot 10^{-6}$	200
Methylene Blue	569	700	-	$3 \cdot 10^{-2}$	-	-

The maxima in the induced absorption spectra of the rhodamine 6G and B associated species in aqueous solutions are respectively at $\lambda \simeq 430$ and 510 nm, while the lifetimes of the excited states are $\tau \simeq 160$ and 120 ps.[37] Smirl, et al.[38] obtained $\tau = 100$ ps for rhodamine B.

The formation of associated species of different types has been established for ethanol solutions of Arcridine Orange at 77 K[39] and the total emission spectra undistorted by reabsorption were obtained for different concentrations of the solutions. The authors were able to isolate four fluorescence bands of different aggregates, characterised by different durations τ of the afterglow, with maxima at $\lambda = 535$ nm ($\tau = 12$ ns), which is attributed to the dimers, $\lambda = 572$ nm ($\tau = 24$ ns), $\lambda = 605$ nm ($\tau = 42$ ns), and $\lambda = 645$ nm ($\tau = 33$ and 25 ns); τ for the monomers was 6 ns. It was proved that the higher aggregates do not phosphoresce. The increase in the average lifetime of the excited states for more complex aggregates implies an increase in the forbiddeness for the lowest sublevel, i.e. the approach of the angle between the molecular planes of the dye in the associated species to 90°. We observed an increase in the yield and duration of the luminescence of the associated species of acridine compounds also in polymer matrices at room temperature.[40] It was found[41] that $\tau = 4.2$ ns for Acridine Orange monomers in alcoholic solutions and $\tau = 14.7$ ns for the aggregated forms.

The study with the aid of Stark modulation spectroscopy of the aggregation of rhodamine 6G,[42] acriflavin, and Acridine Orange[43] in polymer matrices also confirmed that the structure of the dimers is of the house of cards type, but in Acridine Orange the molecular planes are almost parallel.



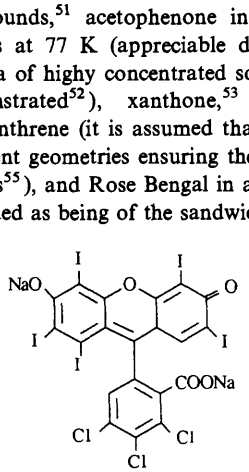
Acridine Orange

It was established that the dipole moments of the associated species of the compounds investigated change by less than a factor of 2 on electronic excitation as compared with monomers. Theoretical study within the framework of the simple exciton theory of the Stark effect in the aggregates confirmed this.[44]

Despite the fact that, in the first approximation of the theory, the triplet states of the aggregate should not differ from the monomer states in the case of large aggregates the T_1 states differ signifciantly. The phosphorescence band of Acridine Orange with λ_{max} = 680 nm has been atttributed[45] to the luminescence of large aggregates, while the phosphorescence band with λ_{max} = 615 nm, which virtually coincides with the phosphorscence spectrum of the monomers, was attributed to simple associated species. The long-wavelength phosphorescence quantum yield is ~0.05 and τ = 0.3 s (smaller by a factor of 15 than for the monomers).

The conclusions reached concerning the structure of the associated species of xanthene dyes, based on optical spectroscopy, have been confirmed also by NMR spectroscopy.[45,47] The molecular pattern in the associated species of azo-dyes in water and their micro-environment have been established by this method.[48,49]

The structures of the dimers in aqueous solutions of benzothiazole[50] (distance between the molecules 3.8 Å, angle between the molecules 18–25°, bond energy 5 kcal mol^{-1}), β-dicarbonyl compounds,[51] acetophenone in methylcyclohexane and isopentane glasses at 77 K (appreciable deformations in the phosphorescence spectra of highy concentrated solutions of this compound have been demonstrated[52]), xanthone,[53] thionine in H_2O and D_2O,[54] phenanthrene (it is assumed that the dimers of this compound have different geometries ensuring the stacking interaction of the chromophores[55]), and Rose Bengal in aqueous and methanol solutions[56] are regarded as being of the sandwich type.



Rose Bengal

It is believed[57] that the aggregation of Rose Bengal in aqueous solutions containing added KNO_3 develops in two stages: a neutral complex is formed initially between the dye anion and the K^+ ion, which is followed by the reaction between the neutral complex and a second dye anion. Multistage association with increase in concentration has also been proposed for vat dyes, which give rise to dimers and trimers in aqueous solutions.[58] The concentration variations of the absorption spectra of stilbene in a water–dioxane mixture have shown that association takes place directly between the molecules of this compound by virtue of van der Waals forces.[59] Certain aggregation parameters for dyes in solutions, obtained in the studies quoted above, are listed in Table 2.

Table 2. The dimerisation constants K, bond energies ΔH, the angles θ, and the distances R between the molecules in the associated species.[18,35,48,49,54,57,59]

Dye	Solvent	K, litre mol^{-1}	ΔH, kcal mol^{-1}	θ, deg	R, Å
Rhodamine 6G					
dimers	Ethanol	0.27	–	82	5.0
trimers		44.5	–		
Rhodamine B	Water	2100	10.0	64	6.4
	Ethanol	1.7	–	–	–
Rhodamine 3B	Water	790	5.8	67	6.7
Rhodamine 3G	"	945	6.9	48	6.8
Rhodamine S	"	710	7.5	40	3.5
Rhodamine 19	"	4400	–	–	–
Fluorescein	"	5.0	5.8	76	4.6
Rose Bengal	"	56700	–	82	–
Thionine	"	–	7.4	–	–
Methylene Blue	"	2400	6.7	–	–
Pseudoisocyanine	"	–	1.8	–	–
Azo-dye	"	510	3.5	–	–
Stilbene	Water + dioxane	–	4.8÷7.5	–	–

The photoenergetics of associated dye species and its relationship with structure can be understood by studying the aggregates of other compounds with a similar molecular structure, for example, porphyrins. The photophysics of the aggregates of these compounds has been thoroughly investigated.[60–70] From the standpoint of the problem considered in this review, the principal results of these studies reduce to the following.

Aggregation does not alter the probability of fluroescence per molecule, while the probability of intersystem crossing increases. There is a significant increase in the probability of internal conversion, while the probability of intersystem deactivation of the triplet state hardly changes on aggregation. The relative positions of the molecules in the associated species and the distances between them play an important role in altering the probability of non-radiative transitions. The electronic spectra of chemical dimers are determined by the exciton interaction of the dipole moments of the transitions of the monomers and by the intermolecular vibronic interaction. However, such interactions do not cause significant changes in the probability of non-radiative deactivation processes involving singlet and triplet excited states compared with the monomers and the main pathway to the deactivation of excitation in vibrationally linked dimers is interconversion to the T state. The overlap of the π-conjugated systems plays a significant role in the spectroscopic and energetic properties of the associated species. The

structure of the dimers was established and the oscillator model of the interacting chromophores was justified on the basis of spectroscopic-polarisation studies, data for the linear dichroism of oriented polymer films, and ^{1}H NMR data.

A series of covalently bonded Zn—H_2 porphyrin dimers have been investigated.[71] Two representatives of porphyrin dimers joined via the benzene ring have been studied by resonance Raman spectroscopy,[72] whilst in another study,[73] the photoelimination of the dip in the absorption spectra of aetioporphyrin in organic glasses showed that in the case of dimers the phase and energy relaxation of the excited electronic state are faster than for the monomers.

Both hypsochromic and bathochromic band shifts are observed in the electronic absorption spectra on formation of physical dimers of porphyrin compounds. The structure of the associated species is determined by the nature of the solvent and the substituents in the porphyrin ring.[74,75] The quantum yield of the luminescence of the dimers of certain porphyrins [for example, *meso*-tetrakis(*N*-methyl-4-pyridyl)porphin] is similar to the yield of the monomeric forms which aggregate at very low concentrations (10^{-7} M).[76] In contrast to the monomer, the aetioporphyrin I dimers exhibit optical activity and their fluroescence yield is 0.9 of the yield of the monomer.[70] Tetra(4-aminophenyl)porphin and its derivatives exhibit a high tendency to associate in solutions and in films.[77–79] The form of the associated species, having their own characteristic features of deactivation of the electronic excitation, depends greatly on the conditions in the association process and on the nature of the solvent. Thus in dimethylformamide the associated species of this compound exhibit, in addition to the fluorescence with a maximum at λ = 702 nm, a broad luminescence band with $\lambda_{max} \simeq 1000$ nm.[80] The pathways to the deactivation of the excitation of porphyrin associated species depend to a considerable extent on their structures and on the characteristic features of the interaction of the monomeric molecules in them. These questions have also been discussed in other communications.[81,82]

The structure of the associated species indicated by the appreciable influence of the properties of the solvent affects very greatly their spectra and energetics. However, hitherto there has been no unanimous view concerning the nature of the spectral changes in the association of dye molecules. In a number of studies,[83–91] this problem was solved taking into account the solvation of phosphor molecules. It was shown that the change in the absorption spectra on association of the same dye molecules can be various depending on the composition and structure of the sovlation shells. The concentration-induced changes in the absorption spectra of rhodamines, anthracene, erythrosine, trypaflavin, and other compounds have been investigated in various solvents and their mixtures at different temperatures of the solutions. The authors initial postulate was that, when the dye molecules are in the immediate vicinity of one another, the deformation of their electronic absorption spectra is caused by resonance interactions. For an intermolecular distance of ~10 Å, the molecules in the associated species are surrounded by individual solvation shells whose structures are not the same and are dynamic in character as a consequence of the thermal motion of the solvent molecules. On the other hand, a change in the immediate environment of the phosphor molecules infringes the resonance conditions and leads to an increased role of dispersion forces. Therefore, it is suggested in the above studies that the main cause of the hypsochromic effect on association is the dispersion interaction between the molecules in the aggregate when each monomeric molecule of the latter has its own solvation shell. Associated species having a common solvation shell give rise to a splitting in the absorption spectrum. The conditions have been examined for the occurrence and the spectroscopic manifestation of aggregation, wheruepon associated species of both types (contact and solvent separated) may be formed in the solution.[87]

It is noteworthy that the question of the solvation of the aggregates is extremely complex and has been solved only in a broad outline.

Studies of mixed solutions of rhodamine 6G, Bromothymol Blue, and benzopurpurine 4B,[88] showed that the nature of the distortions of the electronic absorption spectra on association of dye molecules of different kinds is similar to that for homogeneous associated species.

The study of this problem for ultraviolet absorpt on spectra[91] showed that the nature of the distortion of such spectra on association is the same.

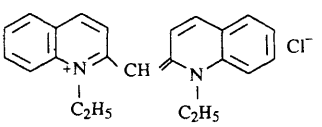
Thus the wide variety of concentration-induced changes in the absorption and luminescence spectra of dye solutions have been explained[83–91] from a single standpoint postulating the possibility of the formation of associated complexes differing in the nature of the solvation processes.

IV. Polymethine dyes

Until recently, the association of polymethine dyes was investigated in polar, mainly aqueous, solutions.[92–95] Attention was concentrated on *J*-aggregates (Scheibe aggregates).[96–100] The study of these compounds in weakly polar media is hindered by their sparing solubility and the problem is solved by introducing "aliphatic" groups into their molecules. Such cyanine dyes with long alkyl chains readily form Langmuir—Blodgett layers,[101–105] which have found extensive applications in various branches of science and engineering.[106]

J-Aggregation occurs not only in solutions but also in adsorption on the surfaces of microcrystals,[107,108] on oppositely charged polymer units,[109] and in adsorption of dyes from solution to give monolayers[110,111] or porous bilayers.[112,113] Cyanine dyes without long alkyl chains form *J*-aggregates at the air-water interface[110,114] if they are moderately soluble in water. In Langmuir—Blodgett films, the occurrence of aggregation has been established not only for cyanine dyes but also for other compounds, for example spiropyrans[115] and pyrene.[116]

The development of the spectroscopic technique has made it possible to obtain additional data about the development of the aggregation of cyanine dyes. A new model of aggregation and a critical discussion of earlier concepts concerning such aggregation have been described in a study[117] where aqueous solutions of pseudoisocyanine (PIC) were considered, while the *J*-band (the sharp peak at λ = 573 nm at room temperature and $c \simeq 10^{-3}$ M) was measured with a high spectral resolution (~5 cm^{-1}) on excitation by a dye-based laser.



Pseudoisocyanine

It has been established that the PIC monomers exist only at a very low concentration and at fairly high temperatures. As the temperature of the solution is reduced (the concentration is increased), dimers of the above dye are formed with a bond energy of ~ 1.8 kcal mol^{-1} and an angle between the monomeric transition moments of about 70°. Before the *J*-band appears in the spectrum, virtually all the molecules are in the dimeric state.[118] A further decrease in temperature leads to aggregation, the constant position of the *J*-band indicating a rapid growth of large aggregates with a narrow distribution of *n*-meric species, which are highly extended with their dipole moments parallel to the long axis. By studying the long-wavelength edge of the *J*-band for very low absorption coefficients, Kopainsky, et al.[117] established that the aggregates have an intrinsic absorption "tail" and that the *J*-band is to a large extent non-uniformly broadened.[119] Aggregation at very low concentrations ($\sim 10^{-6}$ M) has been demonstrated for solutions of furocoumarins.[120] The authors believe that only aggregated forms of furocoumarins exhibit an appreciable fluorescence, but these conclusions are rather tentative and require a more rigorous experimental justification.

It has been established by non-linear spectroscopic methods that the PIC *J*-aggregates have a fluorescence lifetime of 600–800 ps, but, for high intensities of the exciting light, it diminishes to 15 ps.[121] The emission time has been established for PIC bromide *J*-aggregates in ethylene glycol and water glasses with the aid of the photon echo method (~ 14 ps).[122] The luminescence lifetime of the 1,1-diethyl-2,2-cyanine bromide *J*-aggregates in water is 20 ps, while for the monomers it is 300 ps[123] and for microcrystals adsorbed on AgBr it amounts to 230 ps.[108]

At the same time, the question of the architecture of the *J*-aggregates and of its influence on the fluroescent properties remains open.[124] Aggregation numbers both ranging from 4 to 100 molecules[121] and amounting to 500 molecules[122] have been quoted for PIC. The effectiveness of the association of cyanine dyes can be increased by adding certain compounds to the solution.[125] The question of the structure of Scheibe aggregates can be of fundamental importance in the practical use of such systems. For example, when a thiacyanine dye is introduced into a monolayer of an oxacyanine dye organised into *J*-aggregates and present at a concentration greater by a factor of 10^4, an anomalously pronounced transfer of excitation energy from the "host" to the "guest" is observed,[126] its effectiveness depending greatly on the temperature of the system. The determination of the degree of association of naphthalocyanines in water, toluene, and acetone, showed that the associated species are either dimers or trimers.[127–130]

The influence of association on the spectral-luminescent properties of polymethine dyes with one chromophore as a function of their structure in mixtures of polar and non-polar solvents has been investigated.[131–134] The increase in the content of the non-polar solvent (hexane) to 90% induces a sharp fall in the intensity of the long-wavelength absorption band and an increase in the short-wavelength band. The latter is then narrower than the band in the spectrum of the solution in pure chloroform and undergoes a hypsochromic shift, whilst the long-wavelength band undergoes a bathochromic shift. These spectroscopic changes are accompanied by the quenching of fluorescence. The spectroscopic effects noted above depend on the characteristics of the molecular structure of the dyes and on the nature of the anion. On the basis of electronic and NMR spectra, it has been established that polymethine dyes whose molecules contain no bulky substituents form ion pairs with a sandwich structure. In weakly polar media, the structure of these associated species is more stable since the cations of their constituent molecules are rigidly fixed at both ends by anions as a consequence of the electrostatic attraction of unlike charges. Owing to the dissociation of the dyes, in polar solutions the counterion does not participate in association, which takes place as a result of dispersion interactions. The same cationic cyanines form different types of associated species in media of different polarity depending on the electronic and steric structures of the dye molecules.

The aggregation of cyanines with two chromophores was first examined by Herz,[96] but the chromophores of the test compounds were not rigidly linked, so that the spectroscopic changes were caused not only by aggregation but also by the change in the angle between the chromophores. Depending on the molecular structure of biscyanines with rigidly fixed chromophores, their association leads to the appearance of new short-wavelength or long-wavelength absorption and luminescence bands.[135,136] The effects in the absorption spectra occuring with increase in the content of the non-polar component depends on the nature of the anion. The results of these studies confirmed the marked dependence of the spectral-luminescent characteristics of the associated species on the nature of their solvation.[83–86] In contrast to cyanines with one chromophore, biscyanines exhibit a considerable tendency to associate.[137,138]

The form of the absorption bands of polymethines in a polymeric matrix is determined by the capacity of their ion pairs for association.[139] This process can be consistently regulated by introducing bulky substituents into the heterocyclic residues and the polymethine chain and also by altering the polarity of the polymeric medium.

The study of the molecular **aggregates of dyes in polymers** has become important, because such systems are used as scintillators,[140] radiation converters,[141] carriers for the recording of holograms,[142,143] laser media,[144,145] materials for the recording of information,[146] etc. The dye molecule association processes in polymeric media and its influence on the spectral-luminescent characteristics of these systems were analysed in a review.[147] Here we may note that dye molecules usually associate in polymers less effectively than in liquids, but the photophysical properties of the associated molecules can differ appreciably from the monomeric ones. For example, the associated species of Golden Yellow vat dye (dibenzopyrenequinone) in poly(vinyl alcohol) are more photostable than the monomers[148] and the sensitising effect in such a system depends on the ratio of the molecular and associated forms and on the operation of factors inducing the deaggregation of the dye. The fluorescence quantum yield of the dimers of a series of acridine dyes in polymers is higher than the yields of the monomeric molecules[149] but more complex associated species formed at $c > 2.5 \times 10^{-3}$ M have a low fluorescence yield.

In such systems, it is difficult to determine the degree of association of phosphor molecules. This has been done[150] for acridines and rhodamines in poly(vinyl alcohol) films, where the equilibrium constants of monomers and dimers were also determined. However, no account was taken in the above study of complex aggregates. The concentrations of the dimers and complex associated species of acridines were determined in our study[149] and their absorption spectra were identified ($\lambda_{max} = 470$ nm for the dimers and 435 nm for complex associated species), while in another study[40] their fluorescence spectra were identified and the decay times were estimated (8.0 and 2.0 ns respectively). The study of the kinetics of the polarisation of the fluorescence of these compounds showed that, in contrast to the monomeric forms, in poly(vinyl

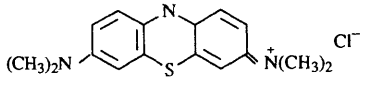
alcohol) the associated species of acridine compounds do not rotate after their photoexcitation.[151]

The association of dye molecules exerts a significant influence on the activity of the systems employed. Thus the polymeric lattices with incorporated dyes used in biotechnology and medicine undergo a change in their properties[152] and the diffraction efficiency of gelatine grids activated by Methylene Blue is impaired at high dye concentrations.[153]

V. Mixed association

Mixed association is the aggregation of the molecules of different dyes. In the literature, this is referred to as heterogeneous association. The study of mixed association processes has become important in connection with the fact that mixtures of different dyes are used as working media in dye lasers,[155] in radiation converters,[141] and in other systems based on the phenomenon of sensitised luminescence.[156] The study of heterogeneous association is complicated because it occurs against the background of homogeneous association which as a rule takes place more efficiently.

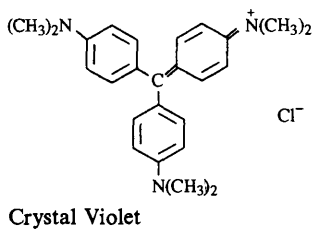
Heterogeneous association is manifested in the study of the electronic excitation energy migration processes in mixed solutions of dyes. In the study of the concentration dependences of the yield of the luminescence and of its polarisation,[157] it was noted that the main role in the quenching of the luminescence of rhodamine 6G is played by associated species comprising this dye and benzopurpurine 4B. It has been shown by absorption spectroscopy[83,88] that, on formation of mixed associated species of these compounds, there is an appreciable diminution of the absorbing capacity of the solutions. The procedure has been proposed[157,158] for the determination of the degree of heterogeneous association based on the measurement of the luminescence characteristics of the dye solutions. Thus the degree of heterogeneous association for an aqueous solution of rhodamine 6G ($c = 2 \times 10^{-6}$ M) and Methylene Blue ($c = 1 \times 10^{-4}$ M) at room temperature was found to be 0.33.



Methyl Blue

The bond energies in such associated species (4.6 kcal mol^{-1}) are smaller by a factor of ~2 than the bond energy in homogeneous rhodamine 6G associated species in water.[159]

The heterogeneous association of the same compounds as well as Crystal Violet, Methylene Red, Brilliant Yellow, and Methylene Orange in water has been studied[160] and the absorption spectra of such aggregates have been identified. The splitting of the absorption band characteristic of homogeneous associated species is absent from such spectra.

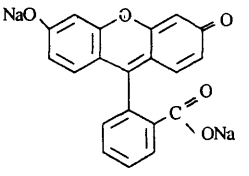


Crystal Violet

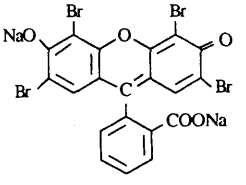
This can be understood bearing in mind that the splitting of the electronic levels on association is induced by resonance interactions which are impossible for molecules of the individual compounds. It was concluded[160] that heterogeneous associated species are formed as a result of dispersion interaction forces. The stability of such aggregates may depend on the addition of electrolytes to the solution.[161] Mixed associated species comprising rhodamine 6G and oxazine 17 are formed also in polar organic solvents.[162] The solvents apparently exert their main influence on the heterogeneous association of dye molecules through their microproperties, i.e the properties of solvent molecules in the solvation shells and the composition of the latter. This conclusion was reached[163] in a study of the spectroscopic characteristics of mixtures of rhodamine dyes with Methylene Blue in various solvents (water, glycerol, ethanol, formamide), the effectiveness of mixed asociation depends on the parameter which reflects the ability of the solvent to form hydrogen bonds. The major role of the nature of the solvent in mixed association of dyes has been pointed out also by Dzhumadinov, et al.[164] However, like homogeneous association, heterogeneous association is most effective in binary mixtures of polar and non-polar solvents. In such media, it was possible to record not only fluorescence but also slow fluorescence and phosphorescence for mixed associated species of rhodamines with Methylene Blue.[165,166] Since the singlet level is appreciably lowered and the energy gap between the S_1 and T_1 levels diminishes in such association, this leads to the quenching of the fluorescence and the excitation of slow fluorescence. It has been established with the aid of IR spectrosocpy that mixed associated species of these compounds are formed via hydrogen bonding.

The heterogeneous association of rhodamines and Methylene Blue has been studied in solutions of polyelectrolytes[167,168] and in aqueous solutions of surfactants[169,170] but an unambiguous interpretation of its spectral-luminescent manifestations in such systems is difficult. The mixed association of Methylene Blue and organic anions (naphthalene-1-disulphonate, etc.) in water has been detected with the aid of absorption and luminescence spectra, which undergo a bathochromic shift under these conditions.[171] The thermodynamic quantities and equilibrium constants were determined for such complexes and it was concluded that they arise in the reaction between the Methylene Blue cation and the aromatic ring of the organic anion. At high concentrations of the polyanion (naphthalene-2,7-disulphonate) such complex formation predominates over the dimerisation of the dye.

The formation of mixed sandwich dimers in aqueous solutions of a number of basic dyes has been established.[172,173] Such aggregation in the presence of natural or synthetic polymers occurs at lower concentrations.[174] The temperature dependences of the absorption and fluorescence spectra of mixtures of Na-fluorescein Na-eosine, trypaflavin, and Acridine Orange showed that the mixed associated species are formed by those dyes whose molecules are capable of being linked by a hydrogen bond.[175]



Na-Fluorescein



Na-Eosine

Mixed aggregation has been observed also for cyanine dyes in Langmuir–Blodgett monolayers.[176] For a certain combination of Na-octadecyl-substituted cyanines in films formed from the solution, mixed *J*-aggregates are produced, whose single absorption and luminescence bands occupy, in spectroscopic terms, an intermediate position between the spectra of *J*-aggregates of the individual components of the dyes. It was established that the appearance of such aggregates requires a very particular compatibility of the molecules, since even slight structural changes in them disrupt the mixed association. Thus the dyes 1′methyl-3-octadecylthia-2′-cyanine and 1-methyl-3-octadecylselena-2′cyanine form mixed aggregates with 1′-methyl-1-octadecyl-2,2′-cyanine but not with 1′-methyl-3-octadecyloxa-2′-cyanine. The luminescence spectra of such mixed *J*-aggregates undergo a slight Stokes shift, while the homogeneous *J*-aggregates exhibit resonance fluorescence.

The formation of mixed associated species has been demonstrated for many dyes, but the available data on their photoenergetics are in the main qualitative. These systems require much attention by investigators using modern methods. Thus it has been established by differential spectrosocpy that the absorption spectrum of mixed associated species of rhodamine 6G and Crystal Violet in poly(vinyl alcohol) matrices contains four maxima,[177] which agrees fully with the general pattern in the electronic absorption spectra of dye dimers.[178]

VI. Polarisation studies

According to the exciton theory, the oscillators of the sandwich dimers, referring to different absorption bands, should be mutually perpendicular and hence should be polarised in different directions. This is also indicated by the theory of the circular dichroism of aggregates.[179] However, there are virtually no theoretical data on the characteristics of the polarisation of the luminescence of the aggregates and the experimental data are not numerous and are contradictory. This is associated with the fact that the degree of polarisation of the emission by the dye associate species has different causes (both the structure of the emitter and the depolarising factors).[180]

An attempt has been made to devise a theory of the polarised luminescence of dimers with the aid of the non-linear Schrödinger equation.[181] The donor–acceptor pair of identical molecules, whose transition dipole moments are either located in a single plane or are mutually perpendicular, was adopted as the dimer model. The average degree of polarisation of the fluorescence of the dimers was calculated as a function of the parameter characterising the non-linearity of the interaction of the molecules, which was varied from 0.7 to 0.776. However, the applicability of the results for practical purposes is extremely problematical.

The depolarisation of the fluorescence of molecular aggregates as a result of energy transfer between the molecules within the framework of the model of a randomly arranged pair of electronically linked molecules[182] has been investigated in a study[183] where the theory was compared with experiment for chlorophyll and phaeophytin. As the author himself notes, analysis of the equations obtained is difficult. Nevertheless, using experimental results together with the equations, it is possible to obtain a number of parameters characterising the energy transfer in the associated species.

At the same time, the polarisation methods for the investigation of aggregation make it possible to extract valuable information, which is frequency difficult to obtain by other methods. Thus by investigating the polarisation fluorescence and circular dichroism of covalently linked ethylene–bisporphyrin dimers in viscous solvents in a magnetic field, it was established that electronic-vibrational exchange with participation of both totally symmetric and non-totally symmetric vibrations is intensified in such dimers. Such exchange smoothes out the polarisation spectra of the dimers, while the changes in the circular dichroism spectra in the region of the Soret band are due to exciton effects.[63]

It has been shown with the aid of absorpton-polarisation measurements that the absorption spectra of the rhodamine 6G associated species in poly(methyl methacrylate) matrices have four absorption bands with maxima at λ = 491, 512, 547, and 561 nm, the bands of the short-wavelength doublet having identical amplitudes and being polarised at right angles to one another.[184,185] Since the dimer contour of the short-wavelength doublet is retained at different dye concentrations, the authors concluded that the rhodamine associated species consists of many molecules in the form of a polymer chain with a dimeric unit cell in which the exciton and vibronic interactions determine the nature of the splitting in the absorption spectrum. The energy of the exciton interaction between the molecules and the associated species has been estimated as 430 cm^{-1}. A similar absorption spectrum of the associated species has been observed also for rhodamine B in aqueous solutions at low temperatures.[186]

Measurements of the polarisation characteristics of the fluorescence and dichroism makes it possible to determine the structure of the associated species. This method has been demonstrated on alcoholic solutions of rhodamine 6G.[187] It has thus been shown that the hydrogen-bonded dimers of pyrromethenone amides have a nearly coplanar structure.[188] Polarisation measurements and the use of the Levshin–Perren formula[180] made it possible to determine the composition of the associated species of asphaltenes.[189] The effect of the association of the molecules of rhodamine dyes, eosine, and erythrosine in aqueous glycerol solutions on the polarisation of the fluorescence has been investigated.[190–193] The increase in the degree of polarisation of the long-wavelength luminescence of the solution with increase in the concentration of the dyes was explained by the formation of their luminescent associated species but no evidence was adduced to show that the associated species in the test solutions are capable of luminescing. The increase in the degree of polarisation of the fluorescence can apparently be explained in this case by the non-uniform broadening of the electronic spectra and by directional energy transfer (the Weber effect).[194] Furthermore, calculation showed that the degree of polarisation of the luminescence of the dimers is smaller than that of the monomers.[195] It has been established[196] that the degree of polarisation of the fluorescence of different forms of *p*-(dialkylamino)benzylidenemalononitrile in poly-(vinyl acetate) matrices diminishes in the sequence monomer (0.5) > dimer (0.2) > complex associated species (0.03). However, it has been found for a series of dyes in frozen ethanol solutions that the degree of polarisation of the luminescence of the associated species can be both smaller and greater than the degree of polarisation of the luminescence of their monomeric forms.[32]

VII. Concentration-induced depolarisation and the quenching of luminescence

When dyes are used in different systems, the problem of the quenching of the luminescence is of primary importance. Numerous studies have established that the concentration-induced quenching in solutions of organic dyes is associated with molecular association,[1] whilst the concentration-induced depolarisation of the fluorescence is associated with electronic excitation energy transfer.[180,197] Until recently, it was assumed that the associated dye molecules do not fluoresce under the usual conditions.[1] However, modern experimental techniques make it possible to record the luminescence of associated species for which the luminescence quantum yield is very low.[198–200] The luminescence of associated species of rhodamine dyes in alcoholic[201] and aqueous[202] solutions at room temperature was observed. The luminescence spectrum of the associated dye molecules is appreciably displaced towards longer wavelengths relative to the spectra of the monomers.

The question of the contribution to the concentration-induced quenching of luminescence by the migration of the electronic excitation energy between the monomers remains controversial. It has been shown for rhodamine dyes in various solvents and for different degrees of association, taking into account the diffusion of molecules, that non-radiative energy transfer between identical monomeric molecules does not lead to the quenching of luminescence.[203,204] Energy is transferred without losses from acriflavin to rhodamine B.[205] The energy transfer between the molecules of different dyes can lead to non-radiative deactivation in the molecules of an acceptor dye and the effectiveness of such losses depends on the spectral luminescent characteristics of the test dyes.[206] The migration of excitation between the monomeric molecules under the conditions of spectral non-uniformity of the systems can induce the quenching of fluorescence.[207–212]

The problem of the concentration-induced depolarisation of fluorescence has been solved for solid solutions by assuming that the probability of transfer is isotropic.[213] The influence of fluctuations in the concentration of the luminescing molecules on the anisotropy of the emission has been examined in a study[214] where an expression was obtained for the anisotropy as a function of the concentration of the molecules, which was identical with the formula derived by Bodunov.[213] These problems were examined in detail by Gaisenok and Sarzhevskii.[180]

The expression for the concentration induced depolarisation of the fluorescence of non-viscous solutions, examined on the basis of Boyarskii's theory[1,215] and the Levshin–Perren formula,[180] has been obtained[216] (in terms of the anisotropy of the emission r):

$$r/r_0 = d_m/d_d,$$

where r_0 is the anisotropy of the "frozen" highly dilute solution in the absence of acceptor associated species and d_m the depolarising factor due to the transfer of excitation both between the monomers and from monomers to the associated species:

$$d_m = (1-\alpha\left[1+\frac{1}{2}\frac{(\alpha f)^2}{1-\frac{3}{4}(\alpha f)^2}\right],$$

$$f\sqrt{\pi}\gamma\exp(\gamma^2)\left[-\frac{2}{\sqrt{\pi}}\int_0^{\gamma}\exp(-t^2)dt\right],$$

$$\alpha = \alpha_0\left[\frac{\gamma_m}{\gamma_m+\gamma_a}\right],\ \gamma = \gamma_m+\gamma_a = \frac{\sqrt{\pi}}{2}\left(\frac{c_m}{c_{0m}}+\frac{c_a}{c_{0a}}\right),$$

where c_m, c_{0m}, c_a, and c_{0a} are the concentrations and critical concentrations of the monomers and associated species, α_0 is the probability that the excitation energy is not degraded during migration between the monomers, and d_d is the rotational depolarising factor:

$$d_d = 1-\frac{3}{2}<\sin^2\theta>$$

(θ is the angle between the directions of the moments of the transition when the molecule is excited and deactivated).

The averaging procedure was carried out[217] and reabsorption and secondary emission, which exert a significant influence on r at high concentrations, were taken into account in another study.[218]

The above expressions were confirmed experimentally for aqueous glycerol solutions of rhodamine 6G.[219] At high concentrations of dyes, the theoretical relations indicated an increase in anisotropy, which was in fact observed experimentally for both Stokes and anti-Stokes excitation.

On the assumption of a multistep non-radiative energy transfer from the monomers to the associated species, an expression was obtained for the relative decay time τ of the fluorescence of phosphors:[220,221]

$$\frac{\tau}{\tau_0} = \frac{1+\gamma^2-(1.5+\gamma^2)f(\gamma)+\alpha_0\alpha f(\gamma)\left[f(\gamma)+\gamma^2-0.5\right]-\alpha_0\alpha\gamma^2}{[1-f(\gamma)]\,[1-\alpha_0\alpha f(\gamma)]}.$$

It was tested experimentally for rhodamine dyes in solutions where the dye molecules exhibit different tendencies to associate.[222–224]

A critical analysis of the above formulae was carried out by Bodunov and co-workers.[225] Using the graphical method proposed by Loring, et al.,[226] theoretical expressions were obtained for the anisotropy r and the yield B of the luminescence, with the aid of which it is possible to analyse the experimental data:

$$\frac{r}{r_0} = 1+\frac{\pi}{2\sqrt{2}}q^{0.5}\gamma_m+0.1887q\gamma_m^2+(0.3832-\delta)q\gamma_m\gamma_a,$$

$$\frac{B}{B_0} = q\frac{r_0}{r},$$

$$q = \left\{-\frac{\pi}{4}\gamma_a-\frac{\pi}{4\sqrt{2}}\gamma_m+\left[1+\left(\frac{\pi}{4}\gamma_a+\frac{\pi}{4\sqrt{2}}\gamma_m\right)^2-\right.\right.$$

$$\left.\left.-0.5258\gamma_m^2-(0.13716-\delta+\beta)\gamma_m\gamma_a\right]^{0.5}\right\}[1\text{-}0.371\gamma_a^2-$$

$$-0.1887\gamma_m^2-(0.13716-\delta+\beta)\gamma_m\gamma_a],$$

$$\gamma_{m(a)} = \frac{c_{m(a)}}{c_{0m(a)}}.$$

δ and β have been tabulated.[226]

The above formulae agree with the exact theoretical results obtained previously[180] in the corresponding limiting cases.

For an experimental test of the above formulae, it is essential to know the degree of association (the fraction of the associated dye molecules) and the order of the association (the number of molecules in the associated species) of the solutions. These characteristics permit the determination of the concentration of the monomers and associated species in dye solutions. A number of methods for their

determination have been described.[1] The dimerisation constant has been calculated from the quenching of the fluorscence of rhodamine and acridine compounds in poly(vinyl alcohol) matrices[150,227] and a method for the determination of the degree of association has been proposed.[228]

At the same time, the formulae quoted above can be used to determine the degree of association (the concentration of associated molecules). For this purpose, it is essential to obtain experimentally the concentration variations of r/r_0, B/B_0, and τ/τ_0. The numerical solution of the resulting equations makes it possible to determine the degrees of association for different concentrations of the solutions. The concentration dependence of the degree of association of rhodamine 6G molecules in poly(vinyl alcohol) matrices was obtained by this method[229] and is illustrated in Fig. 2 (curve *4*). The same figure presents the experimental concentration dependences of the anisotropy of the emission (curves *1*), the quantum yield (curve *2*), and the lifetime of the fluorescence (curve *3*). Curve *1* in Fig. 2 shows that, at high concentrations of rhodamine 6G, an increase in the relative anisotropy of the emission r_{rel} is observed.

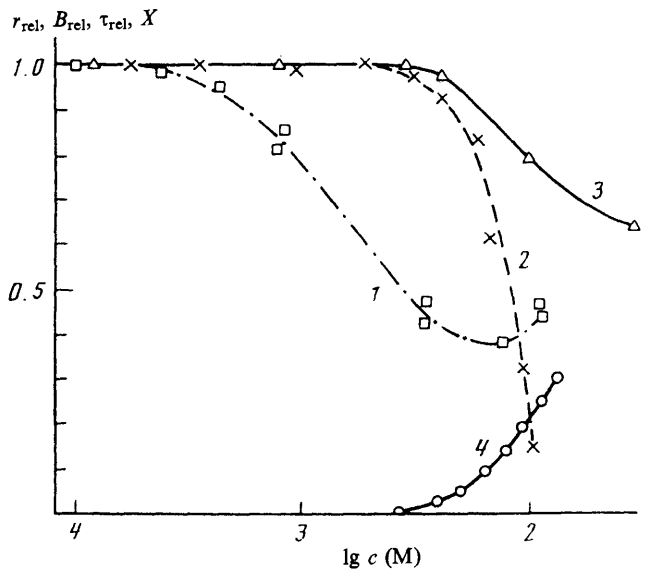


Figure 2. Concentration variation of the relative anisotropy of the emission (curve *1*), relative quantum yield (curve *2*), and relative decay time (curve *3*) of the fluorescence of rhodamine 6G in poly(vinyl alcohol) films; curve *4*—fraction of associated rhodamine 6G molecules (X).[229]

Comprehensive analysis of the association processes and of the concentration-induced quenching of fluorescence in different media linked to them has been performed for dyes widely used in science and engineering. The structural aspects of the fluoroescein aggregates in water have been examined in a study[18] where the association constants were determined by absorption spectroscopy and the absorption spectra of the dimers and trimers of this dye were identified. The calculated exciton parameters for the dimers satisfy two different geometrical models ("sandwich" and "jointed"). The trimers appear at $c \simeq 10^{-1}$ M. The authors suggest that the exciton theory predicts an increase in the trimerisation constant. The quenching of the fluorescence in water occurs up to limiting concentrations ($\sim 3 \times 10^{-1}$ M) and is due both to the migration of excitation between monomeric molecules and to energy transfer to aggregates, quenching by trimers being more effective.[230]

The aggregation of coloured neutral and cationic forms of rhodamine B in aqueous solutions has been studied.[35,231] The greater effectiveness of the association of the neutral form is caused by the electrostatic attraction between the carboxyl and xanthene groups of the monomers. The thermodynamic characteristics of the dimerisation of both forms are similar.

The quenching of the luminescence of rhodamine 6G in ethanol and water takes place starting from concentrations of $\sim 5 \times 10^{-3}$ M and 2×10^{-4} M respectively.[232,236] The quenching is attributed to the formation of dimers and trimers and to the transfer to them of excitation energy from their monomers via the Forster mechanism. However, the authors believe that in the case of ethanol solutions energy is transferred also via an exchange mechanism and that molecular diffusion plays a major role. Quenching by trimers is more effective as a consequence of their greater size compared with dimers, while migration of excitation via monomers does not lead to quenching.[18,237] For aqueous solutions of rhodamine 6G, the collision mechanism does not play a role. The association and quenching processes involving rhodamine 19 have been examined by Arbeloa, et al.,[238] while the mechanisms of the concentration-induced quenching of the luminescence of sulphorhodamine,[101] encapsulated in phospholipid vesicles, has been examined by Plant,[239] who investigated the influence of concentration on the fluorescence lifetime, which becomes shorter for higher concentrations owing to energy transfer to complexes and the collisions between dye molecules.

It is noteworthy that, in the study of the lumienscence of dye solutions, the above investigators[230–238] did not take into account the role of the inactive absorption by associated species in this process. The considerations which they have put forward concerning the formation of dye trimers and the quenching effect of the migration of excitation energy between monomers are not very convincing.

VIII. Association and lasting properties of the solutions. Factors influencing the effectiveness of association

The association of the molecules of laser dyes leads to an appreciable impairment of the lasing properties of their solutions. Polar organic solvents are usually employed for laser dyes. They prevent the development of the self-association of their molecules. However, as noted above, associated species are formed at high concentrations also in such media. Numerous studies have been devoted to the influence of association on the lasing characteristics of dye solutions.[162,240–243] It was established that an increase in dye concentrations in a series of lasing systems entails a fall in the laser energy and shifts of the laser emission spectrum. The spectral shifts are particularly notable in the case of two-component solutions.[162] At the same time lasing by rhodamine 6G associated species has been noted in aqueous solutions[202] in which the associated species do not luminesce under the conditions of stationary excitation. The wavelength of the laser radiation is 640 nm and, although the lasing

efficiency is not high it is nevertheless almost the same as the efficiency of the monomers in aqueous solutions of rhodamine 6G.

The effectiveness of the association process in dye solutions depends on many factors and it is not always a simple problem to determine whether it occurs or not. Association is determined by the molecular structure of the dyes and the nature of the solvents. It increases for molecules containing groups capable of forming hydrogen bonds and also for weakly polar solvents where the dye molecules are not surrounded by a solvation shell which prevents their mutual approach.

The association fof dyes is also prevented by the addition of detergents to the solutions.[41,244,245] In the case of aqueous solutions, the addition of electrolytes diminishes the degree of association of dye molecules,[246] while in the case of alcoholic solutions salts (electrolytes) do not affect the association process[247] but induce an additional orientational broadening of the spectrum. For rhodamine 6G in mixtures of polar and non-polar solvents, the addition of salts to the solution disrupts the complex associated species into monomers, which shows that the association of the molecules of this compound in weakly polar media involves the formation of ion pairs.[137,248] A decrease in the degree of association of dyes is observed after the addition of cyclodextrins and water-soluble polymers to the solution.[249] Data indicating an increase in the association of rhodamine dyes at high (up to kbar) pressures have been published.[250,251]

- - - o0o - - -

Investigators working in the field of quantum electronics, spectroscopy, photochemistry, molecular biology, etc. have devoted much attention at the present time to the molecular aggregation of dyes and its physicochemical manifestations. This is related both to the wide-scale application of dyes and to the good prospects for the use of individual organic molecules and their aggregates as information processing elements, high speed memory devices, etc. The study of the photonics of the molecular aggregates of dyes will make it possible in the future to regulate the radiative and non-radiative relaxation of the excited states of organic molecules at the structural level.

Definite views based on a series of theories, which agree to some extent with experimental data, have arisen in the literature as regards the spectral luminescent manifestation of aggregation. The influence of aggregation on the probabilities of various transitions in molecular systems has been established for many compounds. The view that, together with dimers, complex associated species with characteristic optical properties are formed under certain conditions has been generally accepted. The problems of the influence of the solvent microenvironment on the structure of the aggregates and on their spectral luminescent characteristics have been solved in broad outline. Vigorous studies have been initiated on associated molecules in polymeric media. The problem of the concentration-induced depolarisation and quenching of the luminescence of dye solutions can be regarded as solved in broad outline taking into account molecular aggregation. Extensive data are available on the development of the association process in solutions of a large series of dyes and of the influence of various factors on it.

However, despite the availability of numerous experimental data, there is so far no unanimous view on the nature of the changes in the spectroscopic characteristics of molecules during their association. The elucidation of this process would make it possible to solve the converse problem—the determination of the nature and energetics of intermolecular interactions in the aggregation of dye molecules. The cause of the loss of capacity for luminescence by aggregates and the structure and photochemical properties of complex dye species (including those of dimers) need to be elucidated. For this purpose, it is essential to determine the orbital structure of the excited electronic states of the associated molecules. One should note that, despite the elucidation of the general characteristics of the optical manifestations of aggregation, the individual properties of compounds frequently play a decisive role in such manifestations. It is therefore so far impossible to carry out a sufficiently complete analysis of the results of studies on aggregation in terms of classes of dyes, since many problems (the influence of the medium, of the structural characteristics of dye molecules, of the nature of the counterion, etc.) have been investigated sporadically. The relations between the structure of aggregates and their spectral-luminescent characteristics have been established mainly only for dimers and ordered *J*-aggregates, while for complex associated species this problem still has to be solved. The establishment of these relations will make it possible to use organic dyes more effectively and studies on the aggregation of their molecules and of its influence on the spectral-luminescent properties of their solutions therefore still remain of current interest.

References

1. V I Yuzhakov *Usp. Khim.*, 1979, **48**(11) 2007–2033 [English translation in *Russ. Chem Rev.*, 1979(11)]
2. M D Frank-Kamanestskii, A V Lukashin *Usp. Fiz. Nauk*, 1979, **116**(3) 193–229
3. Alessandro, Del Re Giuseppe *Chem. Phys.*, 1978, **28**(1–2) 155–165
4. E W Knapp, P O Scherer, S F Fischer *Chem. Phys. Lett.*, 1984, **111**(4–5) 481–486
5. P O Scherer, S F Fischer *Time Resolved Vibr. Spectrosc. Proc. II. Int. Conf. Emil-Warbug Symp. Bayreuth-Bischofsgrun, June 3–7*, Berlin, etc., 1985, pp 297–300
6. R Friesner, R Silbey *Chem. Phys. Lett.*, 1981, **84**(2) 365–369
7. R Friesner, R Silbey *J. Chem. Phys.*, 1981, **75**(12) 5630–5639
8. L P Gianneschi, A Cant, T Kuruscsev *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**(11) 2095–2104
9. L P Gianneschi, A Cant, T Kuruscsev *J. Chem. Soc., Faraday Trans. 2*, 1977, **73**(5) 664–668
10. D Fornasiero, T Kuruscsev *J. Chem. Soc., Faraday Trans. 2*, 1986, **80**(1) 15–19
11. G R Jones, D A Duddell, Murray, et al. *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**(10) 1181–1199
12. B Scharf, Y B Band *Chem. Phys. Lett.*, 1983, **98**(2) 125–128
13. V A Kuz'mitskii, O V Kravchuk, K N Solov'ev *Zh. Prikl. Spektrosk.*, 1980, **33**(2) 326–337
14. V A Kuz'mitskii *Zh. Prikl. Spektrosk.*, 1983, **38**(2) 267–273
15. V A Kuz'mitskii, K N Solov'ev *Zh. Prikl. Spektrosk.*, 1985, 43(6) 959–967
16. V A Kuz'mitskii *Zh. Prikl. Spektrosk.*, 1983, **38**(3) 424–428
17. E B Kruglova, Yu F Pedash, V O Kruglov *Zh. Prikl. Spektrosk.*, 1990, **52**(1) 159–163
18. L I Arbeloa *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**(10) 1725–1733
19. C A Brignoli, H De Voe *J. Phys. Chem.*, 1978, **82**(24) 2570–2575

20. V I Yuzhakov, V M Boitsov *Vestn. Mosk. Univ., Ser. 3: Fizika, Astronomiya*, 1986, **27**(4) 58–61
21. M Kamiya *Chem. Phys.*, 1989, **138**(1) 11–23
22. V V Bryukhanov, G A Ketsle, L V Levshin *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1978, **42**(2) 393–398
23. V V Bryukhanov, G A Ketsle, L V Levshin *Zh. Prikl. Spektrosk.*, 1978, **28**(2) 262–267
24. A K Chibisov, T D Slavnova *J. Photochemistry*, 1978, **8**(3) 285–297
25. V V Bryukhanov, G A Ketsle, L V Levshin *Zh. Prikl. Spektrosk.*, 1978, **28**(4) 741–747
26. A G Vitukhnovskii, N D Zhevandrov *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1978, **42**(2) 323–327
27. K Itch, Y Chiyokawa, M Nakao, K Honda *J. Am. Chem. Soc.*, 1984, **106**(6) 1620–1627
28. E R Roberts, H G Drickamer *J. Phys. Chem.*, 1985, **89**(14) 3092–2095
29. K Kemnitz, N Tamai, I Yamazaki, et al. *J. Phys. Chem.*, 1986, **90**(21) 5094–5101
30. P A Anfinrud, D E Hart, J F Hedstrom, W S Struve *J. Phys. Chem.*, 1986, **90**(14) 3116–3123
31. V I Yuzhakov, N V Abrosimova *Zh. Fiz. Khim.*, 1981, **55**(3) 630–634 [English translation in *Russ. J. Phys. Chem.*, 1981(3)]
32. V I Yuzhakov, L V Levshin, V A Shekunov *Zh. Fiz. Khim.*, 1989, **63**(2) 415–419 [English translation in *Russ. J. Phys. Chem.*, 1989(2)]
33. L V Levshin, A M Saletskii, V I Yuzhakov *Zh. Strukt. Khim.*, 1985, **26**(6) 95–99
34. B Z Gorbunov, V S Kozlov, Yu I Naberukhin *Zh. Strukt. Khim.*, 1975, **16**(5) 808–815
35. L I Arbeloa, R P Ojeda *Chem. Phys. Lett.*, 1982, **87**(6) 556–560
36. L I Arbeloa, R P Ojeda *Chem. Phys. Lett.*, 1981, **79**(22) 347–350
37. A V Aristov, V S Shevandin *Opt. Spektrosk.*, 1985, **58**(3) 555–558
38. A L Smirl, J R Clark, E W Van Stryland *J. Chem. Phys.*, 1982, **77**(2) 631–640
39. V A Rapoport, A Z Khrustalev, M D Yakovlev *Opt. Spektrosk.*, 1979, **47**(3) 496–501
40. A V Grachev, A N Ponomarev, V I Yuzhakov *Khim. Fiz.*, 1991, **10**(4) 459–464
41. J Knof, F-J Theiss, J Weber *Z. Naturforsch, A*, 1978, **33**(1) 98–103
42. N V Dubinin, L M Blinov, S V Yablonskii *Opt. Spektrosk.*, 1978, **44**(4) 807–809
43. L V Mel'tser-Shafran, V L Rapoport *Vestn. Leningr. Univ.*, 1982, (10) 82–87
44. N V Dubinin *Opt. Spektrosk.*, 1977, **43**(1) 91–94
45. M D Yakovlev, V A Rapoport *Opt. Spektrosk.*, 1983, **55**(6) 1073–1075
46. A N Veselkov, L N Dymant, E L Kulikov *Khim. Fiz.*, 1984, **3**(8) 1101–1108
47. A N Veselkov, L N Dymant, S F Dreval' *Teor. Eksp. Khim.*, 1987, **23**(3) 373–376
48. K Hamada, H Kubota, A Ishimura, T Iijima *Ber. Bunsenges. Phys. Chem.*, 1985, **89**(8) 859–863
49. K Hamada, S Take, T Iijima, S Amiya *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**(10) 3141–3148
50. S Stoyanov, T Deligeorgiev, D Simov *J. Molecular Structure*, 1984, **115** 363–366
51. P Nikolov, F Fratev, I Petkov, P Markov *Chem. Phys. Lett.*, 1981, **83**(1) 170–173
52. T Wismontski-Knittel, T Kilp *Chem. Phys. Lett.*, 1983, **96**(3) 352–356
53. T Hoshi, J Okubo, Y Sakaguechi, et al. *Ber. Bunsenges Phys. Chem.*, 1989, **93**(6) 800–805
54. S L Fornili, G Sgroi, L Palumbo, V Izzo *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**(1) 255–258
55. N Tamal, H Masuhara, N Mataga *J. Phys. Chem.*, 1983, 87(22) 4461–4467
56. D Xu, D C Neckers *J. Photochem. Photobiol. A: Chemistry*, 1987, **40**(2–3) 361–370
57. O Valdes-Aguilera, D C Neckers *J. Phys. Chem.*, 1988, **92**(15) 4286–4289
58. K V Lunyaka *Zh. Prikl. Spektrosk.*, 1988, **49**(3) 435–440
59. S Astanov, L M Afanasidi, L Ya Malkes *Zh. Prikl. Spektrosk.*, 1980, **32**(6) 1042–1046
60. G P Gurinovich, A P Losev, E I Sagun *Zh. Prikl. Spektrosk.*, 1977, **26**(6) 1028–1034
61. G P Gurinovich, E I Zen'kevich, A P Losev, E I Sagun *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1983, **47**(7) 1410–1413
62. G P Gurinovich, E I Zen'kevich, A P Losev, et al. *Zh. Prikl. Spektrosk.*, 1984, **41**(3) 446–455
63. E I Zen'kevich, A M Shul'ga, G P Gurinovich, et al. *Zh. Prikl. Spektrosk.*, 1985, **42**(2) 207–213
64. E I Zen'kevich, A V Chernook, A M Shul'ga, et al. *Khim. Fiz.*, 1991, **10**(9) 1183–1191
65. E I Zen'kevich, M V Sarzhevskaya *Biofizika*, 1979, **24**(4) 771
66. E I Zen'kevich, M V Sarzhevskaya, T V Vitovtseva, G A Kochubeev *Mol. Biol.*, 1981, **15**(1) 145–153
67. E I Sagun, G P Gurinovich, A P Losev, E I Zen'kevich *Izv. Akad. Nauk Eston. SSR, Fizika, Matematika*, 1982, **32**(2) 170–173
68. G P Gurinovich, E I Zen'kevich, E I Sagun, A M Shul'ga *Opt. Spektrosk.*, 1984, **56**(6) 1037–1043
69. E I Zen'kevich, A V Chernook, A M Shul'ga, et al. *Khim. Fiz.*, 1989, **8**(7) 891–901
70. S S Dvornikov, K M Solov'ev, M P Tsvirko *Zh. Prikl. Spektrosk.*, 1983, **38**(5) 798–803
71. R L Brookfield, H Ellul, A Harriman, G Porter *J. Chem. Soc., Faraday Trans. 2*, 1986, **82**(12) 219–233
72. S P Greiner, J Winzenburg, B Von Maltzan, et al. *Chem. Phys. Lett.*, 1989, **115**(1) 93–98
73. J Pahapill *Izv. Akad. Nauk Eston. SSR, Fizika, Matematika*, 1986, **35**(4) 416–423
74. L P Brivina, S F Ginzburg, G V Ponomarev *Zh. Prikl. Spektrosk.*, 1978, **29**(4) 691–695
75. K Kano, T Nakajima, M Takei, S Hashimoto *Bull. Chem. Soc. Jpn.*, 1987, **60**(4) 691–695
76. R L Brookfield, H Ellul, A Harriman *J. Photochem.*, 1985, 31(1) 97–103
77. A V Udal'tsov, V S Pshezhetskii *Khim. Fiz.*, 1988, **7**(2) 199–203
78. V S Pshezhetskii, A V Udal'tsov *Vysokomol. Soedin., Ser. A*, 1988, **30**(1) 1470–1475
79. A V Udal'tsov, V S Pshezhetskii *Khim. Fiz.*, 1988, **7**(12) 1656–1660
80. A V Udal'tsov, K V Neverov, V S Pshezhetskii, A A Krasnovskii *Khim. Fiz.*, 1990, **9**(4) 2416–2423
81. R N Clark, D R Hobard, W R Leenstra *J. Am. Chem. Soc.*, 1979, **101**(9) 2416–2423

82. M J Pellin, M R Wasielewski, K J Kaufman *J. Am. Chem. Soc.*, 1980, **102**(6) 1868–1873
83. M G Reva, B D Ryzhikov, N R Senatorova *Vestn. Mok. Univ., Ser. 3: Fizika, Astronomiya*, 1980, **21**(3) 63–67
84. M G Reva, L V Levshin, B D Ryzhikov *Zh. Prikl. Spektrosk.*, 1980, **33**(4) 668–674
85. L V Levshin, M G Reva, B D Ryzhikov *Zh. Prikl. Spektrosk.*, 1981, **34**(4) 656–662
86. L V Levshin, M G Reva, B D Ryehikov *Vestn. Mosk. Univ., Ser. 3: Fizika, Astronomiya*, 1981, **22**(4) 75–77
87. L V Levshin, M G Reva, B D Ryehikov *Vestn. Mosk. Univ., Ser. 3: Fizika, Astornomiya*, 1981, **22**(4) 71–74
88. M G Reva, L V Levshin, B D Ryzhikov *Zh. Prikl. Spektrosk.*, 1980, **33**(5) 899–903
89. M G Reva, L V Levshin, B D Ryzhikov *Opt. Spektrosk.*, 1981, **50**(3) 561–568
90. B D Ryzhikov, L Yu Gorbunova, T P Karavicheva *Zh. Prikl. Spektrosk.*, 1984, **41**(6) 1039–1041
91. O N Glagoleva, M G Reva, B D Ryzhikov *Zh. Prikl. Spektrosk.*, 1982, **36**(5) 776–780
92. I I Levkoev *Organicheskie Veshchestva v Fotograficheskikh Protsessakh* (Organic Substances in Photographic Processes), Nauka, Moscow, 1982, 368 pp
93. B I Shapiro *Zh. Nauchn. Prikl. Fotogr. Kinematogr.*, 1981, **26**(3) 208–220
94. B I Shapiro *Zh. Nauchn. Prikl. Fotogr. Kinematogr.*, 1989, **34**(4) 254–266
95. L D Derkacheva *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1956, **20**(4) 410–418
96. A H Herz *Photogr. Sci. Eng.*, 1974, **18**(3) 323–335
97. H Stiel, K Teuchner, W Begker, et al. *Molecular Structure*, 1984, **114** 351–354
98. V I Vlaskin, R Nizamov, U Zakhidov *Zh. Prikl. Spektrosk.*, 1989, **50**(6) 295–299
99. V L Bogdanov, E N Viktorova, S V Kulya, A S Spiro *Pis'ma v Zh. Eksp. Teor. Fiz.*, 1991, **53**(2) 100–103
100. R R Zakirov, M A Kozhushner, R F Khairutdinov *Khim. Fiz.*, 1991, **10**(3) 361–368
101. L M Blinov *Usp. Khim.*, 1983, **52**(8) 1263–1300 [English translation in *Russ. Chem. Rev.*, 1983(8)]
102. C Duschi, M Losche, A Miller, et al. *Thin Solid Films*, 1985, **133**(1) 65–72
103. T Kawaguchi, K Iwata *Thin Solid Films*, 1988, **165**(1) 323–336
104. T L Penner *J. Chem. Phys.*, 1988, **85**(11–12) 1081–1084
105. V Mizzahi, G Stegeman, W Knoll *Chem. Phys. Lett.*, 1989, **156**(4) 392–396
106. V S Gevod, O S Ksenzhek, I L Reshetnyak *Biol. Membrany*, 1988, **56**(12) 1237–1269
107. M Tanaka, N Nakazawa, I Tanaka *Chem. Phys.*, 1985, **97**(3) 457–463
108. K Takahashi, K Obi, I Tanaka *Chem. Phys. Lett.*, 1989, **154**(3) 223–227
109. D M Sturmer *The Chemistry of Heterocyclic Compounds*, Wiley, New York, 1977, Vol. 30, p. 441
110. H Hada, R Hanawa, A Hanagachi, Y Yonezawa *J. Phys. Chem.*, 1985, **89**(4) 560–562
111. M Era, S Hayashi, T Tsutsui, et al. *Chem. Phys. Lett.*, 1986, **130**(1–2) 53–58
112. N Nakashima, A Tsuge, T Kunitake *J. Chem. Soc., Chem. Commun.*, 1985, (1) 41–*42*
113. T Kunitake *New J. Chem.*, 1987, **11**(2) 141–147
114. Y Yonezawa, D Mobius, H Kuhn *Ber. Bunsenges. Phys. Chem.*, 1986, **90**(12) 1183–1188
115. E Ando, J Miyazaki, K Uorimoto, et al. *Thin Solid Films*, 1985, **133**(1) 21–28
116. T Yamazaki, N Tamai, I Yamazaki *Chem. Phys. Lett.*, 1986, **124**(4) 326–330
117. B Kopainsky, J K Hallermeier, W Kaiser *Chem. Phys. Lett.*, 1982, **87**(1) 7–10
118. B Kopainsky, J K Hallermeier, W Kaiser *Chem. Phys. Lett.*, 1981, **83**(3) 498–502
119. B Kopainsky, W Kaiser *Chem. Phys. Lett.*, 1982, **88**(4) 357–361
120. E R Lysenko, V L Sukhorukov, Z Wunderlich, et al. *Zh. Fiz. Khim.*, 1989, **63**(10) 2768–2773
121. H Stiel, S Daehne, K Teuchner *J. Luminescence*, 1988, **39**(6) 351–357
122. S De Boer, K J Vink, D A Wiersma *Chem. Phys. Lett.*, 1987, **137**(2) 99–106
123. Z X Yu, P Y Lu, R R Alfana *Chem. Phys.*, 1983, **79**(2) 289–296
124. S Vaidyanathan, L K Patterson, D Mobius, H-R Gruniger *J. Phys. Chem.*, 1985, **89**(3) 491–497
125. K Kasatani, M Ohashi, H Sato *Carbohydrate Research*, 1989, **192**(2) 197–214
126. D Mobius, H Kuhn *J. Apl. Phys.*, 1988, **64**(10) 5138–5141
127. V V Sapunov, A P Tsvirko, K N Solov'ev *Zh. Prikl. Spektrosk.*, 1985, **42**(2) 219–222
128. V V Sapunov, A P Tsvirko, K N Solov'ev *Khim. Fiz.*, 1986, **5**(7) 948–954
129. V V Sapunov *Khim. Fiz.*, 1989, **8**(6) 747–751
130. V V Sapunov *Zh. Prikl. Spektrosk.*, 1990, **53**(5) 819–825
131. A A Ishchenko, N P Vasilenko, A G Maidannik, L V Balina *Dokl. Akad. Nauk Ukr. SSR, Ser. B*, 1988, (2) 46–49
132. A A Ishchenko, N P Vasilenko, A G Maidannik, L V Balina *Zh. Org. Khim.*, 1989, **25** 1086–1099
133. N Nizamov, T Sh Khidirova, U Zakhidov, et al. *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1990, **54**(3) 502–506
134. A A Ishchenko, F G Kramarenko, A G Maydannic, et al. *J. Int. Rec. Mater.*, 1991, **19**(3) 219–231
135. A A Ishchenko, I L Mushkalo, N A Derevyanko, et al. *Zh. Prikl. Spektrosk.*, 1989, **50**(2) 237–243
136. A A Ishchenko, I L Mushkalo, N A Derevyanko, et al. *J. Int. Rec. Mater.*, 1989, **17**(1) 39–51
137. N Nizamov, U Zakhidov, L K Atakhodzhaev, et al. *Zh. Prikl. Spektrosk.*, 1982, **36**(3) 422–430
138. A A Ishchenko, I L Mushkalo, N A Derevyanko, et al. *Zh. Prikl. Spektrosk.*, 1989, **50**(5) 772–779
139. A A Ishchenko, A F Dokunina, Z A Smirnova, A I Tolmachev *Dokl. Akad. Nauk SSSR*, 1985, **284**(6) 1407–1411
140. N N Barashkov, O A Gunder *Fluorestsiruyushchie Polimery* (Fluorescent Polymers), Khimiya, Moscow, 1987, 233 pp
141. A V Grachev, A A Ishchenko, E I Kareva, et al. *Zh. Prikl. Spektrosk.*, 1990, **52**(4) 644–649
142. USSR P. 1 529 975; *Byull. Izobret.*, 1989, (46)
143. C Carre, D Longnot *J. Chem. Phys.*, 1988, **89**(1) 485–493
144. V I Bezrodnyi, M V Bondar, O V Przhonskaya, E A Tikhonova *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1990, **54**(8) 1476–1483
145. V V Rodchenkova, S A Tsogoeva, T M Murav'eva, et al. *Optika i Spektrosk.*, 1986 **60**(1) 57–60
146. N G Rambidi, V M Zamalin *Poverkhnost.*, 1986, **8**(1) 5–30

147. A V Grachev, A N Ponomarev, V I Yuzhakov *Zh. Prikl. Spektrosk.*, 1991, **54**(3) 418–432
148. P V Mil'khiker, R N Nurmukhametov *Dokl. Akad. Nauk SSSR*, 1985, **281**(3) 640–644
149. A V Grachev, A N Ponomarev, V I Yuzhakov *Khim. Fiz.*, 1990, **9**(6) 780–784
150. J Marx, K Schiller *J. Prakt. Chem.*, 1979, **321**(1) 102–106
151. A V Grachev, A N Ponomarev, V I Yuzhakov *Vrashchatel'naya Relaksatsiya Molekul Krasitelei pri Ikh Agregatsii v Polimernykh Sredakh* (Rotational Relaxation of Dye Molecules during Their Aggregation in Polymeric Media), Preprint No. 6/1991. Faculty of Physics, Lomonosov Moscow State University, 1991, 5 pp
152. S N Shcherbo, Yu V Lukin, V I Yuzhakov, V N Zubov *Zh. Fiz. Khim.*, 1990, **64**(6) 1672–1675
153. N Capolla, C Carre, D J Lougnot, R A Lessard *Applied Optics*, 1989, **28**(19) 4050–4052
154. A I Akimov, L V Levshin, A M Saletskii, V I Yuzhakov *Kvantovaya Elektronika*, 1981, **8**(11) 2339–2344
155. B M Uzhinov, V I Yuzhakov, T A Dolenko *Kvantovaya Elektronika*, 1992, **19**(1) 7–17
156. T M Jovin, G Marriott, R M Clegg, D J Arndt-Jovin *Ber. Bunsenges. Phys. Chem.*, 1989, **93**(3) 387–391
157. S V Zhuravlev, L V Levshin, A M Saletskii, V I Yuzhakov *Optika i Spektrosk.*, 1984, **56**(6) 1044–1048
158. L V Levshin, A M Saletskii, I Yuzhakov *Zh. Fiz. Khim.*, 1984, **58**(3) 592–595
159. C Bojarski, G Obermiller *Acta Phys. Chem., A*, 1975, **250**(3) 389–411
160. B D Ryzhikov, A M Saletskii *Vestn. Mosk. Univ., Ser. 3: Fizika, Astronomiya*, 1991, **32**(4) 71–76
161. S V Zhuravlev, A Zuaui, L V Levshin, A M Saletskii *Teor. Eksp. Khim.*, 1990, (5) 600–605
162. V I Yuzhakov, A M Saletskii, B M Uzhinov *Zh. Fiz. Khim.*, 1985, **59**(7) 1664–1667
163. L V Levshin, A M Saletskii *Teor. Eksp. Khim.*, 1990, **26**(6) 669–675
164. R Kh Dzhumadinov, A N Nizamov, K U Umarov, N N Nizamov *Zh. Prikl. Spektrosk.*, 1988, **48**(1) 156
165. A K Bisenbaev, A Zuaui, L V Levshin, A M Saletskii *Khim. Fiz.*, 1989, **8**(12) 1721–1723
166. L V Levshin, A M Saletskii *Vestn. Mosk. Univ., Ser. 3: Fizika, Astronomiya*, 1990, **31**(4) 56–60
167. A K Bisenbaev, A Zuaui, L V Levshin, A M Saletskii *Zh. Prikl. Spektrosk.*, 1990, **52**(3) 424–429
168. M Shirai, Y Hanatani, M Tanaka *J. Macromol. Sci. Chem., A*, 1985, **22** 279–292
169. L V Levshin, A M Saletskii *Zh. Prikl. Spektrosk.*, 1991, **54**(5) 773–777
170. L V Levshin, A M Saletskii *Optika i Spektrosk.*, 1991, **70**(3) 439–453
171. S Hamm *Bull. Chem. Soc. Jpn.*, 1985, **58**(7) 2099–2106
172. M G Neumann, F Gessner, V A Oliveira *J. Chem. Soc., Faraday Trans.*, 1990, **86**(21) 3551–3555
173. S Ghosh, S P Monlik, A R Das *Can. J. Chem.*, 1981, **59**(16) 2449–2456
174. R Turner, M K Cowman *Arch. Biochem. Biophys.*, 1985, **237**(3) 253–259
175. I N Kozlov, V T Koyava, V I Popechits, et al. *Zh. Prikl. Spektrosk.*, 1979, **30**(2) 271–276
176. T L Penner, D Mobius *Thin Solid Films*, 1985, **132**(1–4) 185–192
177. A Zuaui, L V Levshin, A M Saletskii *Optika i Spektrosk.*, 1989, **66** 301–304
178. V I Yuzhakov *Zh. Prikl. Spektrosk.*, 1979, **31**(6) 1103–1105
179. E W Tulstrup, J Michl *J. Phys. Chem.*, 1980, **84**(1) 82–93
180. V A Gaisenok, A M Sarzhevskii *Anizotropiya Pogloshcheniya i Lyuminestsentsii Mnogoatomnykh Molekul* (Anisotropy of the Absorption and Luminescence of Polyatomic Molecules), Minsk, 1986, 318 pp.
181. V M Kenkre, G P Tsironis *Chem. Phys.*, 1988, **128**(1) 219–226
182. T S Rahman *Theory of Depolarization of Fluorescence in Molecular Aggregates*, Univ. Pochester Press, New York, 1977, 190 pp
183. Yu I Posudin *Ukr. Fiz. Zh.*, 1982, **2**(5) 655–659
184. A S Prishchepov, N Nizamov *Optika i Spektrosk.*, 1985, **59**(6) 1361–1363
185. A S Prishchepov, V D Zaripov, S I Astanov *Optika i Spektrosk.*, 1989, **66**(6) 1311–1315
186. R W Chambres, T Kajiwara, D R Kearns *J. Phys. Chem.*, 1974, **74**(4) 380–388
187. V I Yuzhakov, A M Saletskii *Zh. Prikl. Spektrosk.*, 1985, **42**(5) 762–766
188. D A Lightner, M Reisinger, W M D Wijekoon *J. Org. Chem.*, 1987, **52**(24) 5391–5395
189. R Z Syunyaev, L V Levshin, B D Ryzhikov *Zh. Prikl. Spektrosk.*, 1985, **42**(4) 579–582
190. J P Dudeja, S Chopra *Indian. J. Pure Appl. Phys.*, 1977, **15**(10) 736–738
191. M L Pandya, M K Machwe *Acta Phys. Acad. Sci. Hung.*, 1977, **42**(3) 179–184
192. M L Pandya, M K Machwe *Acta Phys. Polon., A*, 1979, **56**(2) 283–287
193. M L Mandya, M K Machwe *Proc. Indian Nat. Sci. Acad., A*, 1980, **46**(2) 158–166
194. V I Tomin, A N Rubinov *Zh. Prikl. Spektrosk.*, 1981, **35**(2) 237–251
195. D N De Vries Reilingh, R P H Rettschnick, G J Hoytink *J. Chem. Phys.*, 1971, **54**(6) 2722–2727
196. K Y Law, R O Loutfy *Macromolecules*, 1981, **14**(3) 587–591
197. L V Levshin A M Saletskii *Lyuminestsentsiya i Ee Izmereniya* (Luminescence and Its Measurement), Izd. Moskov. Gos. Univ., Moscow, 1989, 278 pp
198. A Penzkofer, Y Lu *Chem. Phys.*, 1986, **103**(2–3) 399–405
199. A Penzkofer, W Leupacher *J. Luminescence*, 1987, **37**(2) 61–72
200. A Penzkofer, W Leupacher, M Bernd, et al. *Chem. Phys.*, 1987, **115**(1) 143–150
201. V I Yuzhakov, V Z Pashchenko *Kvantovaya Elektronika*, 1980, **7**(3) 613–615
202. A I Akimov, L V Levshin, A M Saletskii *Vestn. Mosk. Univ., Ser. 3: Fizika, Astronomiya*, 1993, **34**(1)
203. L V Levshin, A M Saletskii, V I Yuzhakov *Zh. Prikl. Spektrosk.*, 1980, **32**(1) 41–48
204. S V Zhuravlev, L V Levshin, A M Saletskii, V I Yuzhakov *Optika i Spektrosk.*, 1982, **53**(2) 245–251
205. T C Pant, B C Bhatt, D D Pant *J. Luminescence*, 1982, **27**(4) 425–439
206. A M Saletskii, L V Levshin, V I Yuzhakov *Zh. Prikl. Spektrosk.*, 1980, **33**(1) 100–106
207. N R Senatorova, L V Levshin, B D Ryzhikov *Zh. Prikl. Spektrosk.*, 1979, **30**(4) 658–661

208. N A Nemkovich, A N Rubinov, V I Tomin *Pis'ma v Zh. Teor. Fiz.*, 1980, **6** 270–273
209. I M Gulis, A I Komyak *Zh. Prikl. Spektrosk.*, 1980, **32**(5) 897–902
210. L V Levshin, A M Saletskii, V I Yuzhakov *Optika i Spektrosk.*, 1983, **54**(3) 807–813
211. L V Levshin, A M Saletskii, V I Yuzhakov *Kvantovaya Elektronika*, 1983, **10**(7) 1413–1419
212. V I Yuzhakov *Kvantovaya Elektronika*, 1986, **13**(6) 1118–1131
213. E N Bodunov *Zh. Prikl. Spektrosk.*, 1977, **26**(6) 1123–1125
214. C Bojarski *J. Luminescence*, 1979, **10**(4) 373–378
215. C Bojarski *J. Luminescence*, 1972, **5**(6) 413–429
216. J Dudkiewicz *Acta Univ. Szeged. Acta Phys. Chem. (Hungary)*, 1981, **27**(1–4) 17–24
217. J Dudkiewicz *J. Luminescence*, 1982, **26**(3) 273–280
218. J Dudkiewicz *Acta Phys. Polon., A*, 1980, **58**(2) 227–236
219. J Dudkiewicz *Acta Phys. Polon., A*, 1984, **65**(4) 325–326
220. C Bojarski, E Grabowska *Acta. Phys. Hung.*, 1979, **46**(2) 113–123
221. R Twardowski, C Bojarski *Z. Naturforsch, A*, 1980, **35**(3) 345–349
222. E Grabowska, J Turzuk, C Bojarski *Acta Phys. Polon., A*, 1980, **57**(5) 753–764
223. C Bojarski, F Grabowski *Acta Phys. Polon., A*, 1981, **260**(3) 397–406
224. C Bojarski, G Zurkowska, J Turzuk *Z. Naturforsch, A*, 1982, **37**(1) 74–77
225. E N Bodunov, V A Malyshev, T A Shakhverdov *Optika i Spektrosk.*, 1986, **60**(1) 86–92
226. R F Loring, H C Andersen, M D Fayer *J. Chem. Phys.*, 1982, **76**(4) 2015–2027
227. J Marx, K Scholler *Wiss. Z. Techn. Hochsch. Leuna-Mersebg*, 1978, **20**(1) 40–44
228. V V Sapunov, M P Tsvirko, K N Solov'ev *Zh. Prikl. Spektrosk.*, 1985, **42**(2) 219–222
229. V I Yuzhakov, A V Grachev, V N Ponomarev *Optika i Spektrosk.*, 1990, **68**(1) 69–74
230. L I Arbeloa *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**(10) 1735–1742
231. F L Arbeloa, P R Ojeda, L I Arbeloa *J. Luminescence*, 1989, **44**(1) 105–112
232. F L Arbeloa, P R Ojeda, L I Arbeloa *J. Photochem. Photobiol. A: Chemistry*, 1988, **45**(3) 313–323
233. L I Arbeloa, M J Estevez, F L Arbeloa *J. Luminescence*, 1991, **48–49**(1) 405–409
234. F L Arbeloa, P R Ojeda, L I Arbeloa *J. Chem. Soc., Faraday Trans. 2*, 1988, **84**(12) 1903–1912
235. F L Arbeloa, I L Gonzales, P R Ojeda, L I Arbeloa *J. Chem. Soc., Faraday Trans. 2*, 1982, **78**(7) 982–994
236. P R Ojeda, A I A Kalime, O J Ramon, L I Arbeloa *J. Chem. Soc., Faraday Trans. 2*, 1988, **84**(1) 1–8
237. L I Arbeloa *J. Photochem.*, 1982, **18**(2) 161–168
238. F L Arbeloa, A Urrecha, L I Arbeloa *J. Chem. Phys.*, 1989, **130**(1–3) 371–378
239. A L Plant *Photochem. Photobiol.*, 1986, **44**(4) 453–459
240. A M Saletskii, V I Yuzhakov *Kvantovaya Elektronika*, 1985, 12(2) 294–305
241. J Knof, F-J Theiss, J Weber *Z. Naturforsch, A*, 1978, **33**(1) 98–103
242. A M Saletskii, V I Yuzhakov, V I Primak *Vestn. Mosk. Univ, Ser. 3: Fizika, Astronomiya*, 1983, **24**(6) 78–81
243. V M Krasnoshchekov, A B Nikolaev, A V Aristov, et al. *Optika i Spektrosk.*, 1983, **54**(1) 118–122
244. R C Kapoor, M K Jain, V N Mishra *J. Luminescence*, 1981, **22**(4) 429–439
245. H Katumitu, S Iwao, C T Kwak Jan, G Zhisheng *Colloids and Surfaces*, 1990, **50** 309–320
246. S I Golubev, L V Levshin, M G Reva, B D Ryzhikov *Vestn. Mosk. Univ., Ser. 3: Fizika, Astronomiya*, 1981, **22**(6) 60–64
247. V I Yuzhakov, A V Naumov *Zh. Fiz. Khim.*, 1986, **60**(10) 2518–2521
248. A M Saletskii, V A Shekunov, V I Yuzhakov *Teor. Eksp. Khim.*, 1987, **23**(3) 368–372
249. M M Asimov, V P Chuev, S N Kovalenko, et al. *Optika i Spektrosk.*, 1991, **70**(3) 644–646
250. E R Roberts, H G Drickamer *J. Phys. Chem.*, 1985, **89**(14) 3092–3095
251. H G Drickamer *Annu. Rev. Phys. Chem.*, 1982, **33** 25–47

Translated from *Uspekhi Khimii* **61** 1142–1179 (1992) U.D.C. 541.64

Silylation in polymer chemistry

R D Katsarava, Ya S Vygodskii
Institute of Molecular Biology and Biophysics, Academy of Sciences of Georgia
Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences

ABSTRACT. The review is devoted to the formation and other reactions of macromolecules using silylated monomers and reagents. The methods of synthesis, reactivities, and other properties of silylated monomers of different classes are examined. Polycondensation and polyaddition processes, on the one hand, and polymerisation processes leading to the formation of macromolecules, on the other, are analysed. Reactions in the chains of polymers involving silylated monomers and reagents are also described.

The bibliography includes 165 references.

Contents

I. Introduction 629
II. Synthesis of silylated monomers and their properties 629
III. Synthesis of polymers 632
IV. Reactions in polymer chains 646
V. Conclusion 647

I. Introduction

The replacement of an active hydrogen atom in a wide variety of organic compounds by tris(hydrocarbyl)silyl (usually trimethylsilyl) groups makes it possible to solve effectively many synthetic problems. Silylation proved useful in peptide synthesis for the acylation of the amino-groups of α-aminoacids (the formation of an amide linkage), for the protection of carboxy- and hydroxy-groups, and also for the preparation of a wide variety of agents—acyl group donors, silylated reagents used to remove an N-protecting group, and condensing agents.[1–7] The use of silylating agents for the synthesis of esters[8] and nitriles,[9] the oxidation of alcohols in the silylated form to carbonyl compounds,[10] the synthesis of acid chlorides under neutral conditions,[11] the preparation of acyl isocyanates and isocyanates using phosgene and in a phosgene-free scheme employing CO_2,[12] and the synthesis of a wide variety of heterocycles[13] and tetra-substituted polymethylenediamines and cyclic triamines.[14] Cyclic disilazanes are used to protect amino-groups,[15] the disilyl protecting group being readily removed in an acid or alkaline medium.

Volatile liquid silylated derivatives of solid substances are convenient in analysis, for example, for the gas-chromatographic separation of a mixture of aminoacids.[16–18]

The use of silylated monomers and reagents gives rise to new possibilities also in macromolecular chemistry. Certain characteristic features of processes leading to the formation of both known and new polymers with a high molecular weight have been examined.[1,19–25] In the present review, we attempted to survey critically the available data and we supplemented them by new ones, including those concerning both polycondensation and polymerisation reactions as well as reactions in polymer chains.

II. Synthesis of silylated monomers and their properties

Synthesis of silylated Monomers

The silylation of organic compounds containing a wide variety of functional groups has been described in detail in a number of reviews.[1,2,5] Chlorotris(hydrocarbyl)silanes, usually chlorotrimethylsilane (CTMS), are common and effective silylating agents. Silylation using these compounds proceeds under mild conditions in organic solvents and with high yields. However, hydrogen chloride, capable of catalysing side reactions, is evolved in these processes, which necessitates the employment of an acceptor—a tertiary amine (B_N):

$$R-XH + Me_3SiCl \xrightarrow[-B_N\cdot HCl]{B_N} R-X-SiMe_3,$$

where X = NH†, O, etc. and B_N is a tertiary amine.

Chlorotrimethylsilane is used successfully for the preparation of silylated diamines,[26–28] diols (usually bisphenols and aromatic hydroxyacids,[29–39] bisthiophenols,[40] and bis-*o*-aminophenols.[41,42]

Dialkyl(trialkylsilyl)amines (usually Me_3SiNMe_2 and Me_3SiNEt_2) are convenient silylating agents. Silylation with their aid can be carried out without an organic solvent with evolution of the readily removable volatile dialkylamines:

$$RXH + Me_3SiNR'_2 \longrightarrow RXSiMe_3 + HNR'_2,$$

where R′ = Me or Et.

The silazanes indicated are used to silylate diamines.[43] They are especially conveneient in the treatment of aliphatic diamines in a salt form;[4] the role of the acid acceptor in such processes is assumed by the evolved dialkylamine:

$$R-NH_2\cdot HCl + Me_3SiNR'_2 \longrightarrow RNHSiMe_3 + HNR'_2\cdot HCl\downarrow.$$

Diethyl(trimethylsilyl)amine proved to be effective also in the silylation of bisaminophenols.[45–47]

Hexamethyldisilazane, evolving gaseous ammonia during the reaction, is a readily available silylating agent. However, it is not a very active donor of the trimethylsilyl group and for this reason it is

† In the case of primary aromatic amines, only one hydrogen atom is substituted by the trimethylsilyl group under the conditions indicated (see below).

particularly useful in the silylation of compounds containing an acid proton, for example, phenol and carboxylic acids:[48,49]

$$HOArOH + Me_3SiNHSiMe_3 \longrightarrow Me_3SiOArOSiMe_3 + NH_3\uparrow$$

or

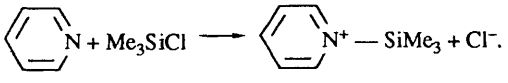
$$HOOCRCOOH + Me_3SiNHSiMe_3 \longrightarrow Me_3SiOCORCOOSiMe_3 + NH_3\uparrow.$$

O-Trimethylsilyl *N*-trimethylsilylcarbamate, in the reaction of which with alcohols gaseous side products are evolved, is an effective silylating agent of hydroxylated monomers:[50,51]

$$2ROH + Me_3SiNHCOOSiMe_3 \longrightarrow 2ROSiMe_3 + CO_2\uparrow + NH_3\uparrow.$$

N,O-Bis(trimethylsilyl)amides of carboxylic and carbonic acids [especially *N,O*-bis(trimethylsilyl)trifluoroacetamide], which are powerful donors of the trimethylsilyl group, are also promising.[2]

We may note that in many instances the silylation of monomers, particularly aromatic diamines, is carried out in solutions in inert organic solvents using a wide variety of catalysts [for example, $(NH_4)_2SO_4$,[2,43] acids, etc.[2]]. Pyridine, forming with chlorosilane a quaternary silylammonium complex (a silyl group donor), also exhibits a catalytic acitivty:[2]



Imidazole and heterocycles of similar structure are also effective agents for the transfer of the silyl group.[2]

It is essential to bear in mind that the silylation of aliphatic diamines proceeds so readily that exhaustive silylation of primary amino-groups is possible. This can lead in its turn both to the deactivation of the amino-groups and to the breakdown of stoichiometry in polycondensation (because disilylated amino-groups may be present in an indefinite amount) and to the formation of cross-linked polymers (see below).

The introduction of a second silyl group into aromatic amines (in contrast to aliphatic amines) constitutes a fairly difficult problem, which can be solved, for example,[52] using the corresponding lithium derivatives:

$$Ar-NH-SiMe_3 \xrightarrow[-C_4H_{10}]{C_4H_9Li} Ar-\underset{\displaystyle Li}{\underset{|}{N}}-SiMe_3 \xrightarrow[-LiCl]{Me_3SiCl} Ar-N(SiMe_3)_2.$$

Ethylmagnesium bromide can also be used for this purpose:[47]

$$Ar-NH_2 \xrightarrow[-2C_2H_6]{2C_2H_5MgBr} Ar-N(MgBr)_2 \xrightarrow[-MgBr_2,\ MgCl_2]{2Me_3SiCl} Ar-N(SiMe_3)_2.$$

Sodium iodide is used as the catalyst in the synthesis of silylated enolic forms of carbonyl compounds (silyl ethers of phenols—polymerisation monomers):[53]

$$CH_3-CO-R + Me_3SiCl + NaI \xrightarrow{CH_3CN} CH_2=\underset{\displaystyle O-SiMe_3}{\underset{|}{CR}}.$$

Properties of silylated monomers

The majority of silylated bisnucleophiles are liquid or comparatively low-melting substances which can be readily purified by vacuum distillation or (more rarely) recrystallisation. Silylation improves the solubility of the monomers, which significantly facilitates the choice of the solvent and polycondensation at high solution concentrations.

The silylated monomers, especially diamines, are resistant to the action of light and atmospheric oxygen.

In the condensed phase, the silylated monomers are fairly resistant also to atmospheric moisture, which may be due to their hydrophobic nature. However, in solutions in a polar organic solvent they readily split off the silyl group in the presence of traces of water (or impurities containing an active hydrogen atom). This leads to the "self-drying" and "self-purification" of the reaction system, which is important in some cases, for example in polycondensation in the vapour phase with silylated monomers of especially active biselectrophiles (acid dichlorides, bischloroformates, dianhydrides, etc.), which are capable of entering into side reactions with hydrogen-containing impurities. This is apparently one of the advantages of the silylated monomers in polycondensation ("silylated polycondensation"). On the other hand, in polymerisation silylation makes it possible to carry out processes which are difficult to achieve using the initial hydrogen-containing precursors.

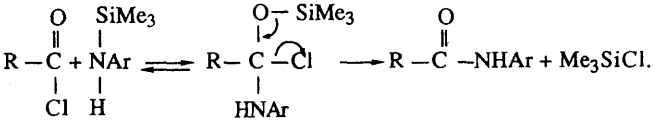
The introduction of a trimethylsilyl group into amino-groups of both aromatic and aliphatic amines lowers their electron-donating activity, which is attributed to the $(d-p)_\pi$ interaction via the Si–N bond.[54–56] An increase in the number of trimethylsilyl groups at the nitrogen atom lowers the basicity of amines still further.‡[57]

The decrease in the electron-donating activity of the silylating amino-groups together with the steric factors due to the replacement of the hydrogen atom by the bulky dimethylsilyl group lead to a decrease in the nucleophilic reactivity of aliphatic amines.[58]

On the other hand, an increase in reactivity has been noted for heterocycles, aromatic amines, and acid amides (the so called silyl activation of the nitrogen atom), at any rate in relation to acid chlorides,[1,13,59–62] which, however, requires more rigorous proof with the aid of kinetic measurements.§

The increase in the reactivity of aryl-*N*-dislylamines is attributed to a two-stage addition-elimination mechanism:[61]

Scheme 1

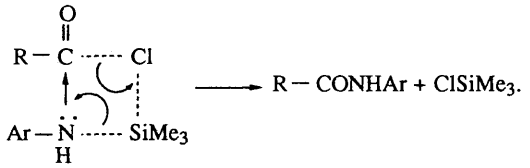


‡We may note that, in the determination of the basicity of silylamines by the titration method, special care must be excercised, because the silyl group can be transferred to the acid under the influence of protic acids, which has been indicated in particular by the results of NMR studies.[43]

§This is valid at least for monosilylated arylamines. One of the authors has established that the introduction of a second trimethylsilyl group actually entails a decrease in the activity of the amine to such an extent that it no longer reacts at an appreciable rate with benzoyl chloride on heating to 100 °C.

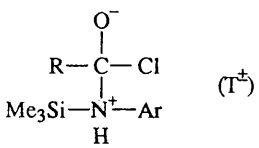
This uneconomical two-stage mechanism of the reaction occurring in the elimination stage with formation of a four-membered transition complex, is unlikely.¶ From our point of view, a single-stage concerted mechanism, similar to that proposed by Birkofer et al.,[60] is more likely. It involves the formation of a Cl–Si bond in the first stage [taking into account the increase in the reactivity of the functional groups in which the heteroatom–silicon bond is sufficiently loosened—$ArNH-SiMe_3$ and $ArS-SiMe_3$ (see below)] and further propagation of the reaction via the following transition state:

Scheme 2



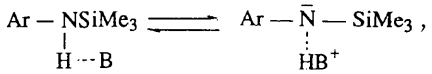
This mechanism of the reaction with acid chlorides may be supported indirectly by, for example, the lower, compared with free bases, reactivity of silylated alkylamines in relation to activated ethers.[58] In this case, the reaction apparently proceeds via the "traditional" pathway with formation of a tetrahedral zwitter-ionic intermediate or via a "reactant-like" transition state.[63,64] Under these conditions, silylation leads to a steady decrease in the nucleophilic reactivity of the amines

The formation of the silylated tetrahedral zwitter-ionic intermediate on interaction of arylsilylamines with acid chlorides, i. e.

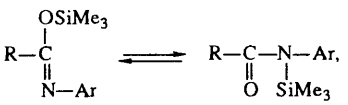


(the formation of $T^{\pm}$ is postulated in the interaction of arylamines with acylating agents[63]), which can subsequently rearrange to the neutral *O*-silylated tetrahedral intermediate see Scheme 1), is also unlikely because of steric factors.

The increase in the reactivity of the silylated primary arylamine can also be associated with the increase in the mobility of the NH proton[1] due to the effect of the electron-accepting silyl group and hence the increase in the nucleophilicity of the nitrogen atom in the presence of a proton acceptor:



¶ Bearing in mind the high oxygen affinity of silicon, in the operation of such a reaction mechanism one would expect the elimination of HCl (especially in a proton-accepting medium[1]) and the formation of a silylated amide:



which according to certain data either does not occur[62] or occurs extremely rarely.[64]

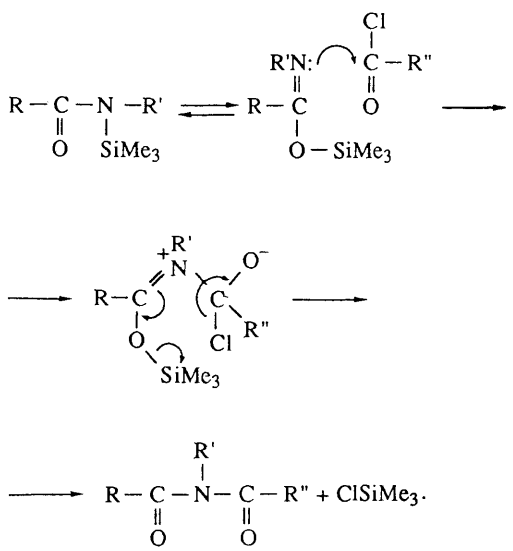
where B is the proton acceptor (solvent molecules, the amine itself, etc.).

In order to make finally sure about the "silyl activation" of aromatic amines and to give preference to one of the mechanisms examined, it is useful to compare the kinetics of the interaction of arylamines and their silylated analogues with acid chlorides and other electrophiles not containing a halogen (acid anhydrides, activated ethers, isocyanates, etc. in various media—proton-accepting and proton-inert).

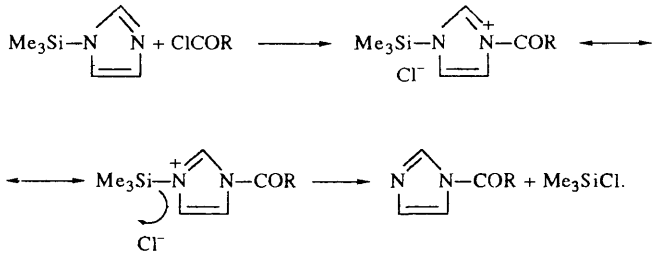
The "silyl activation" of the amide (urea) linkage has been convincingly demonstrated in a number of studies.[1,59,62] In this case there is no need for direct kinetic investigations, because the usual amides are hardly acylated by acid chlorides in the absence of tertiary amines, while silylated amides readily give rise to the corresponding acyclic imides.

The nature of the "silyl activation" of amides is in all probability somewhat different and is associated with the involvement in the reaction of the tautomeric *O*-silylated form of the amide:†

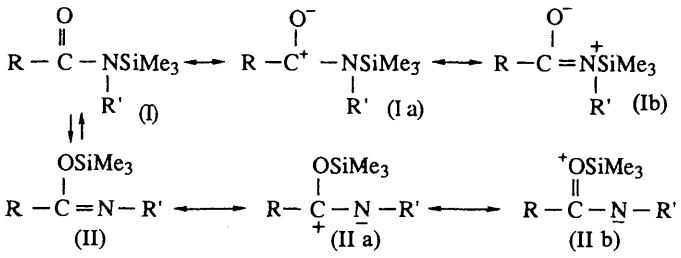
Scheme 3



† The tautomeric mechanism operates, for example, in the alkylation of heterocycles in the silylated imidol [hydroxyimide?] form.[1] It may be that a complex mechanism also underlies the "silyl activation" of the imidazole nitrogen atom and heterocycles of similar structure:[60]



It is known that silylated amides can exist in two tautomeric forms[2] (p. 63):



When R′ = alkyl, the *N*-silylated form (I) is thermodynamically preferable owing to the amide resonance [varieties (Ia) and (Ib)]. On the other hand, if R′ is capable of stabilising the negative charge on the nitrogen atom [for example in the case where R = CH_2=CH, Ph, etc.; varieties (IIa) and (IIb)], then the contribution of the *O*-silylated form (II) increases appreciably. We believe that the latter is kinetically more significant in amide acylation reactions.

The silylation of hydroxy-groups has different effects on their reactivity depending on the nature of the adjoining group. Whereas silylated alcohols readily interact with acid chlorides under mild conditions,[1,29,30] the corresponding phenols react only above 100–140 °C.[30] On the other hand, the reactivity of S-containing analogues—silylated thiophenols—approaches that of silylated amines.[40] This fact may indicate the importance of the effect of the degree of loosening of the heteroatom–silicon bond on the reactivity of the silylated nucleophile. Thus, when the nucleophilicity of the functional groups is reduced, it is possible to introduce electrophilic substituents into the molecule. For example, it is possible to obtain stable aliphatic diamines containing alkyl ester groups or hydroxyl-containing compounds with acid chloride groups, to carry out reactions with a high selectivity, etc. (see below), and, if necessary, to carry out the selective desilylation of the alcoholic and phenolic hydroxy-groups.[65]

III. Synthesis of polymers

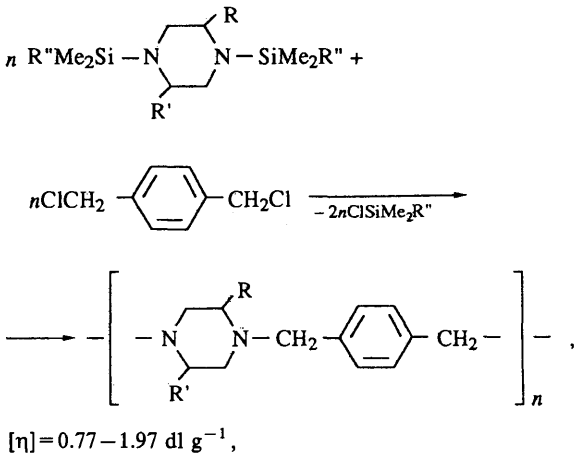
The polycondensation processes involving monomers with N–Si and O(S)–Si bonds are analysed separately below. Next to be considered are polycondensation processes *in situ* in the presence of silicon compounds, including silicon-containing condensing agents as well as polymerisation processes with participation of silylated initiators and monomers. Finally, examples of the modification of macrochains by their silylation are presented.

(a) Polycondensation

The new polycondensation methods of synthesis of polymers are based mainly on nucleophilic substitution reactions (or reactions of the type of nucleophilic substitution) with participation of silylated bisnucleophiles.

Syntheses Based on Monoers with a N–Si Bond

Polyamines. One of the first heterochain polymers synthesised using silylated monomers were polyamines obtained by Klebe[26] by the reaction of *N,N′*-disilylated piperidines with *p*-xylylene dichloride in bulk at 100 °C:

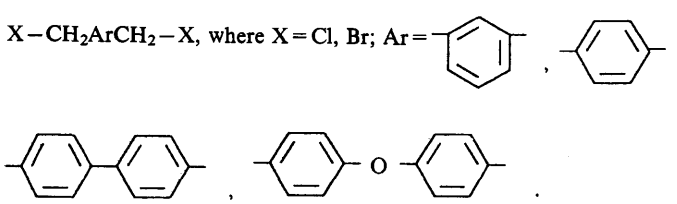


$[\eta] = 0.77 - 1.97$ dl g^{-1},

where R = R′ = H or Me or R = H and R′ = Me; R″ = Me or Ph.

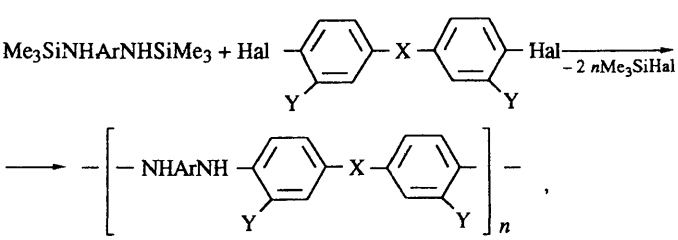
The polyamine with the highest molecular weight (M_n = 40 000—determined by osmometry), soluble in organic solvents, was obtained with R = H, R′ = Me, and R″ = Ph. It was shown that the reaction is accelerated (by a factor of 5–10) in the presence of ammonium salts and (to a lesser extent) tetramethylene sulphone (sulpholan).

Klebe[26] used in this process silylated *N,N′*-dimethylethylenediamine and alkylene halides:



Quaternisation of the polyamines synthesised with methyl iodide afforded polyelectrolytes soluble in polar solvents and water, while quaternisation with diiodopropane yielded cross-linked membranes insoluble in water.

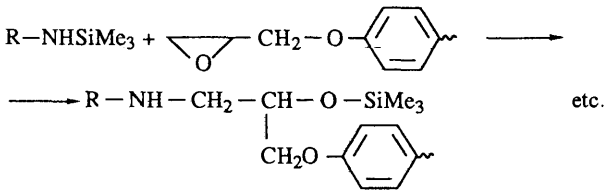
An aromatic nucleophilic substitution reaction with similar essential features has been used[66,67] to synthesise aromatic polyamines ($\eta_{init} \leqslant 0.93$ dl g^{-1}):



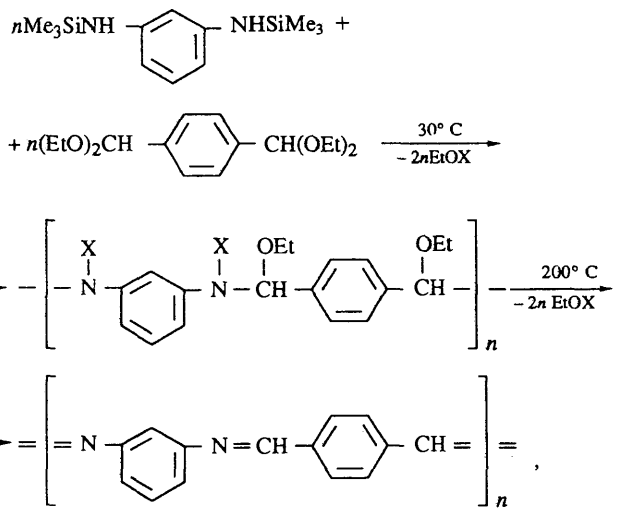
where X = NO_2 or CO, Hal = Cl or F, and Y = H or NO_2. The reaction was carried out in dimethyl sulphoxide (DMSO) at 150 °C.

The authors established that only fluorides are reactive and that the process is catalysed by CsF. Aromatic chlorides (Hal = Cl) are passive in the reactions but are appreciably activated after the introduction of a nitro-group in the *ortho*-position (Y = NO_2).

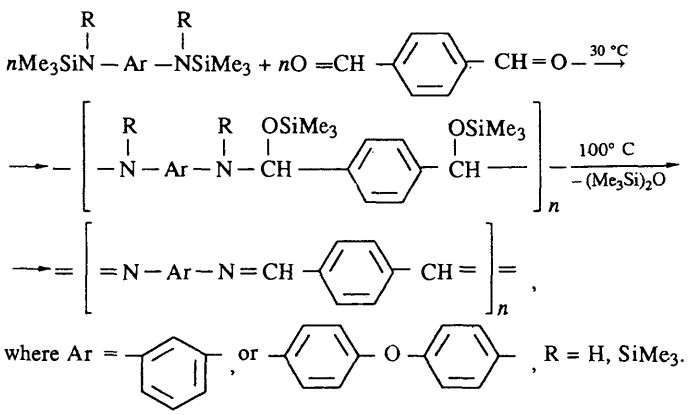
Silylamines can also be alkylated with the aid of oxiranes.[68] This process has been used to harden epoxide resins:[69,70]



Polyazomethines. Using silylated diamines as the initial monomers, high-molecular-weight polyazomethines were obtained, which made it possible to overcome difficulties associated with the insolubility and infusibility of their forms unsubstituted in the aromatic ring.[71,72] Either diacetals[71] or directly the dialdehydes[72,73] were used as the biselectrophiles:



where X = H or $SiMe_3$;

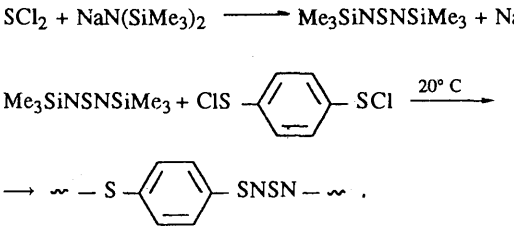


where Ar = , or , R = H, $SiMe_3$.

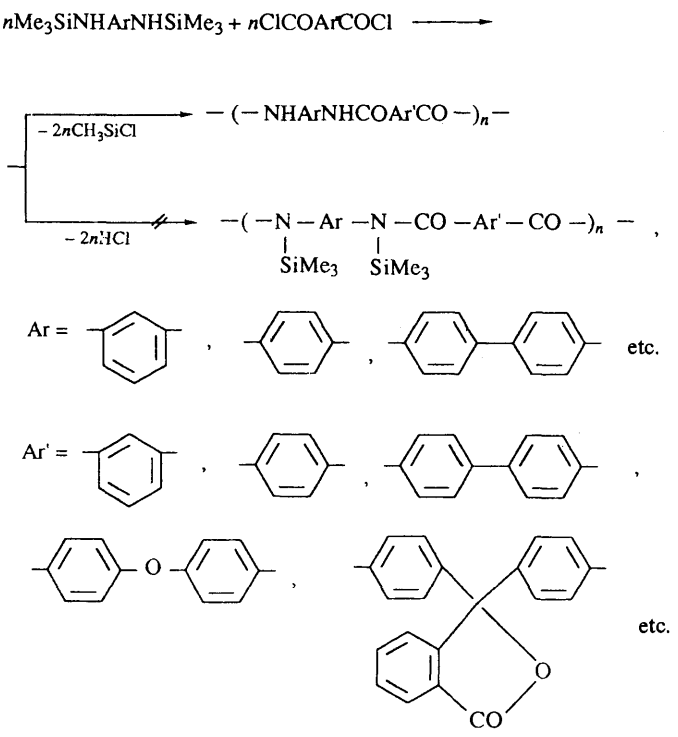
and R = H or $SiMe_3$.

The soluble film- and fibre-forming polymers formed in the first stage are converted into insoluble polyazomethines as a result of thermal β-elimination. It is of interest that in the second version fully silylated diamines were used together with *N,N'*-bistrimethylsilylated primary diamines in the reaction with the dialdehyde. As mentioned above, such fully silylated diamines should be appreciably less reactive. However, the lack of information about the molecular weights of the polyazomethines synthesised makes it impossible to decide that a particular silylated form of the diamine is preferable.

Polythiazyls. A polyconjugated electrically conducting poly-*p*-phenylenethiazyl was synthesised by a reaction similar to that for the formation of polyamines (see above).[74] Using Na-silylamide, a monomer was formed initially and was then used in polycondensation with *p*-phenylenebissulphenyl chloride in an inert solvent:



Polyamides. Since the beginning of the 1970's, silylated diamines began to be used also for the synthesis of polyamides.[75] High-molecular-weight arylamides were obtained by the polycondensation of silylated aromatic diamines with acid dichlorides in amide solvents under mild conditions:[75,76]



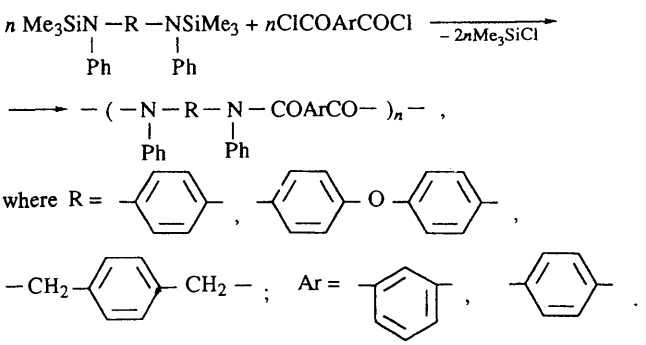
It was shown that the reaction proceeds virtually with elimination of Me_3SiCl and the formation of a "normal" polyamide. The absence of silicon from the polyamides and their solubility in organic solvents (i.e. the absence of intermolecular cross-links—see below) indicate that the alternative pathway involving the elimination of HCl and the formation of a silylated polyarylamide hardly operates.‡

Bearing in mind the increased solubility of the silylated monomers in the solvent used, it is possible to carry out the polycondensation in more concentrated solutions.[75] An advantage of this polyamide formation scheme is that it leads to the formation of polyamides with higher molecular weights ($\eta_{log} \leqslant 7.4$ dl g^{-1}) than in the case where free diamines are used ($\eta_{log} \leqslant 3.0$ dl g^{-1}).[76]

It is believed[76] that this is associated with the higher reactivity of the silylated diamine and hence with the higher rate of polycondensation, characterised by the time variation of the viscosity of the polyamides. However, these data are insufficient to draw unambiguous inferences about the rate of the process and it is essential to carry out direct kinetic studies, particularly since analysis of the numerous results of the investigation of the low-temperature polyamide formation does not provide grounds for such a conclusion. The formation of polyarylamides with higher molecular weights may be due to the following factors: (1) the greater purity and resistance to oxidation of the silylated aromatic diamines; (2) the absence of salt formation (protonation of the amino-group by HCl); (3) "self-purification" of the reaction system (see above). In the absence (more precisely on sharp reduction) of the contribution of side reactions, the rate of increase in the viscosity of the polyamides rises.[78]

The possibility of carrying out the process in inert solvents ($CHCl_3$, CH_3CN, $PhNO_2$), which do not exhibit a proton-accepting activity (this is essential in the formation of polyamides using free aromatic diamines), should be included among the advantages of the "silyl polyamide formation".

The "silyl polyamide formation" reaction has also been used to obtain high-molecular-weight ($\eta_{log} \leqslant 2.21$ dl g^{-1}) *N*-phenylated polyamides[27,79] from relatively unreactive bisphenylenediamines:[80]



‡It is known that chlorosilane is split off in an inert medium, while in the presence of a proton acceptor (triethylamine) the elimination of HCl and the formation of a silylated amide is actually observed.[1] In weak bases (forming, however, strong hydrogen bonds[77]), this pathway is nevertheless probably possible (see below). Apparently the silylated arylamides formed do not interact with terminal acid chloride groups and are readily desilylated by traces of moisture or HCl, which is not bound to the amide solvent quite so strongly as to triethylamine.

The reaction was carried out in sulpholan at elevated temperature (80–200 °C depending on R).

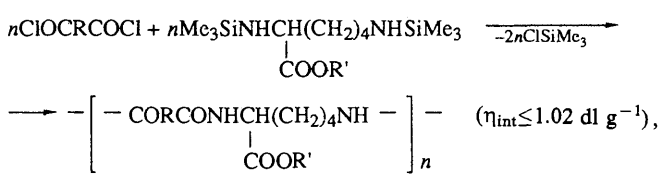
We may note that the ability of the system to undergo "self-purification" and the use of an acid solvent are especially important in the synthesis of *N*-phenylated arylamides, because the reaction proceeds under fairly severe conditions and *N,N*-diaryl-substituted polyamides, which belong to the category of "activated amides",[81] can interact destructively with a wide variety of impurities, especially basic ones.

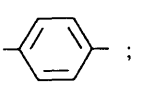
Silylation has been successfully used for the synthesis of polyamides from other relatively unreactive monomers—the weakly electrophilic perfluroisophthaloyl chloride[82] and the sterically hindered perfluoro-*m*-phenylenediamine.[83] This clearly indicates the silyl activation of aromatic amino-groups, although we repeat that direct kinetic measurements are essential for final conclusions.

The formation of high-molecular-weight polyamides with participation of weakly basic highly sterically hindered silylated secondary aromatic diamines, where direct lateral attack[84] on the carbonyl carbon atom with formation of a tetrahedral intermediate (Scheme 1) is unlikely, may serve as evidence in support of an alternative mechanism (see Scheme 2).

In order to obtain fine arylamide film coatings, the relatively high volatility of silylated aromatic diamines in their reaction with acid dichlorides involving deposition from the gas phase has been used successfully.[85] The advantage of the silylated diamines over the free bases consists in this case also in the ease of removal of the neutral, volatile chlorotrimethylsilane.

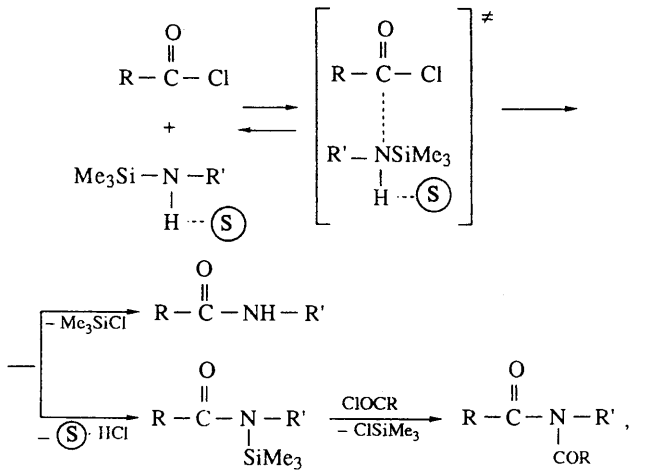
High-molecular-weight polyamides with functional group substituents have been obtained by the reaction of acid dichlorides with alkyl esters of N^{α},N^{ε}-bis(trimethylsilyl)lysine in an organic solvent:[44]



where R = $(CH_2)_4$ or  ; and R′ = Me or Et.

It is essential to note that this reaction is accompanied by the formation of a cross-linked polymer (particularly vigorous in the case of an aliphatic acid dichloride), which may be due to the partial formation of a trimethylsilylated amide in a solvent capable of forming strong hydrogen bonds [dimethylacetamide (DMA),

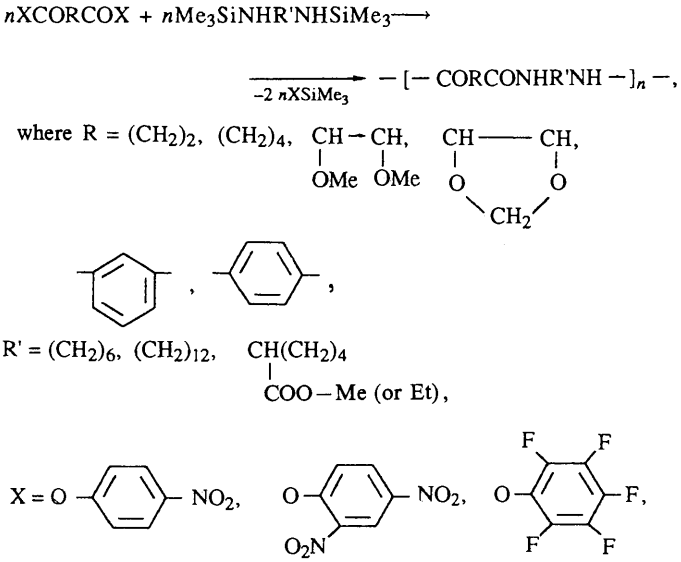
hexamethylphosphoramide (HMPA)] (see above) and its subsequent interaction with the acid chloride group:



where (S) = solvent molecule.

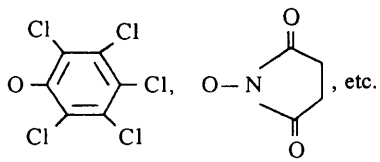
The proposed mechanism of the formation of intermolecular bonds is supported by the synthesis of a cross-linked polyamide also in the case of an aromatic acid dichloride, which, in contrast to aliphatic acid dichlorides[86] with a "normal" amide linkage, does not react under the conditions investigated. The reaction using an aromatic acid dichloride at a reduced temperature (−10 − 0 °C) leads to the formation of a soluble polyamide.

Yet another piece of evidence is the synthesis of soluble polyamides from an aliphatic acid dichloride and an alkyl ester of N^{α},N^{ε}-bis(trimethylsilyl)lysine in solvents with a weak proton-accepting capacity (acetonitrile, dichloroethane). Apart from acid dichlorides, a wide variety of activated dicarboxylic acid diesters react vigorously with trimethylsilyated aliphatic diamines. Such interaction under mild conditions in a wide variety of organic solvents, including inert ones, leads to the formation of high-molecular-weight (of the order of 40 000 − 60 000) polyamides:[44,87–90]



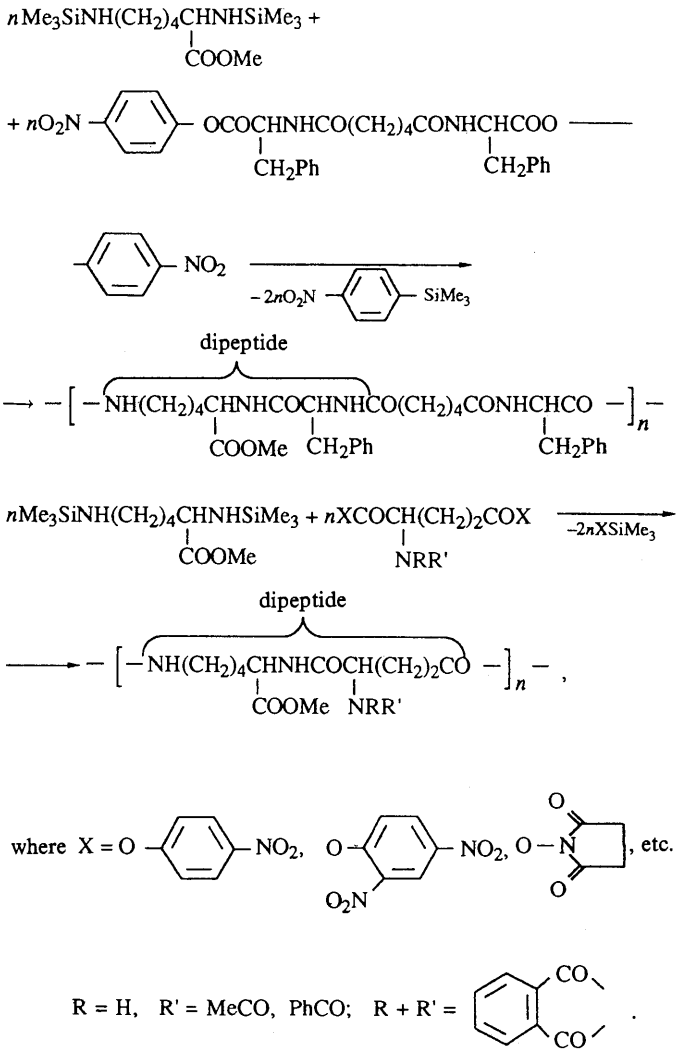
where R = $(CH_2)_2$, $(CH_2)_4$,

R' = $(CH_2)_6$, $(CH_2)_{12}$,



In this case, the role of the desilylating agent at different stages of the reaction can be fulfilled by the evolved acid hydroxylated compound HX[58,91] — a vigorous acceptor of the trimethylsilyl group,[2] which leads to the synthesis of the "normal" polyamide. This factor appreciably facilitates the synthesis of linear polyamides based on silylated aliphatic diamines.

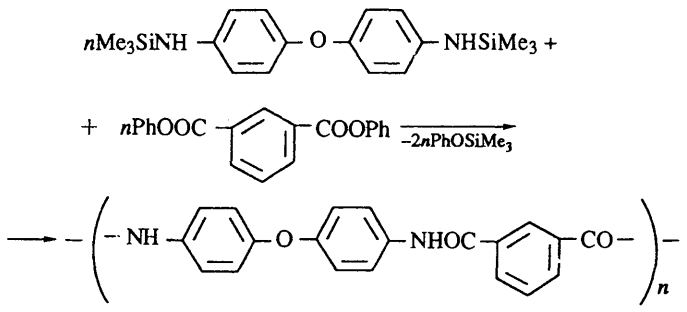
"Activated silylated" polycondensation has been used successfully to obtain polyamides with functional-group substituents from lysine[44] and can be useful for the introduction into the macrochain of fragments carrying additional functional groups, for example dipeptide units capable of undergoing enzymic cleavage:[92,93]



where X = O

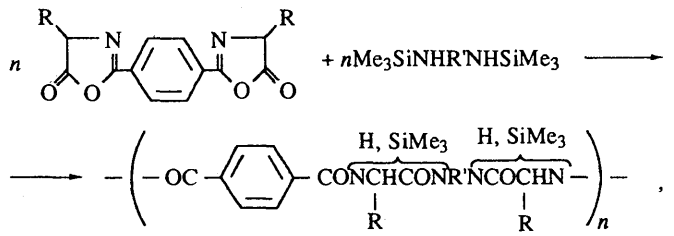
R = H, R' = MeCO, PhCO; R + R' =

We may note that under more severe conditions (100 °C) the non-activated diphenyl isophthalate enters into the reaction with the silylated diamine (even a comparatively unreactive aromatic diamine):[94]



(η_{log} = 0.43 dl g^{-1} in DMA).

High-molecular-weight ($\eta_{init} \leqslant 0.68$ dl g^{-1}) film-forming polyamides have also been synthesised by the reaction of silylated diamines with bisazlactones in DMA (in a number of instances in the presence of 5% of LiCl) at 70–100 °C:[95]



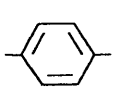
where R = Me, $(CH_2)_2Me$, $CH(Me)_2$, $(CH_2)_3Me$, $CH_2CH(Me)_2$, CH(Me)Et, $(CH_2)_2SMe$, CH_2Ph;

R' = $(CH_2)_6$, $CH(CH_2)_4$ (COOMe (or Et)).

This polyadditive scheme, leading to silylated polymers (cf. the synthesis of polyurethanes described below) has been used to obtain dipeptide-containing polyamides from L-lysine. Such polymers are promising as biodegradable temporary implants capable of undergoing bioerosion.[96]

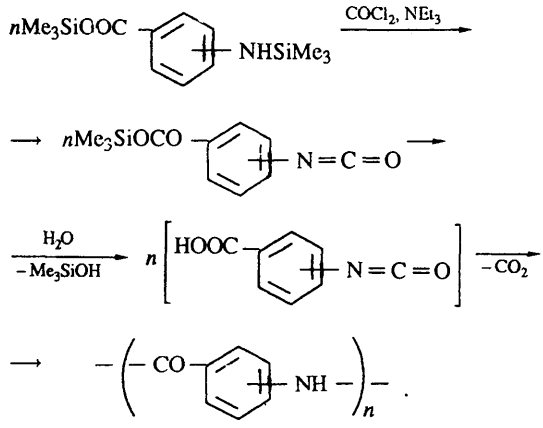
A novel method of synthesis of polyamides (with yields up to 94%) has been proposed by Kozyukov et al.[97] It consists in the high-temeprature AB-polycondensation in solution in *N,O*-disilylated aminoacids (glycine, *p*-aminobenzoic acid):

$$n\text{Me}_3\text{SiNHRCOOSiMe}_3 \xrightarrow[\text{DMF}]{150\ ^\circ\text{C}} -(-\text{NHRCO}-)_{\bar{n}} + n(\text{Me}_3\text{Si})_2\text{O},$$

where R = CH_2,  .

The process takes place in a polar medium and is catalysed by Lewis acids. This factor is apparently in fact responsible for the possibility of obtaining and purifying by vacuum distillation at fairly high temperatures disilylated aminoacids without appreciable self-condensation.

An alternative method, proposed by the same authors, involves the preliminary treatment of the *N,O*-disilylated monomer with phosgene:[98]



An essentially similar process has been used also in AA–BB-polycondensation to obtain a high-molecular-weight polyamide-6,6 without the intermediate formation of a salt AX;[99] under these conditions, one of the monomers can be used in the non-silylated form:

$$n\text{YHN}(CH_2)_6\text{NHY} + n\text{Y'OCO}(CH_2)_4\text{COOY'} \xrightarrow{220\text{–}250\ ^\circ\text{C, in bulk}}$$

$$\longrightarrow -(-\text{NH}(CH_2)_6-\text{NHCO}-(CH_2)_4-\text{CO}-)_n-,$$

where (a) Y = H and Y' = $SiMe_3$, (b) Y = $SiMe_3$ and Y' = H, and (c) Y = Y' = $SiMe_3$.

Polyurethanes. The processes leading to the formation of polyurethanes using silylated diamines are in many respects similar to those involved in "silylated polyamide formation".

Film-forming ($\eta_{int} \leqslant 0.48$ dl g^{-1}) linear polyurethanes have been obtained by the polycondensation of a silylated diamine with bischloroformates in dimethylacetamide (DMA) under mild conditions (0–20 °C):[100]

$$n\text{Me}_3\text{SiNH}(CH_2)_6\text{NHSiMe}_3 + n\text{ClCOOAlkOCOCl} \xrightarrow{-2\ \text{Me}_3\text{SiCl}}$$

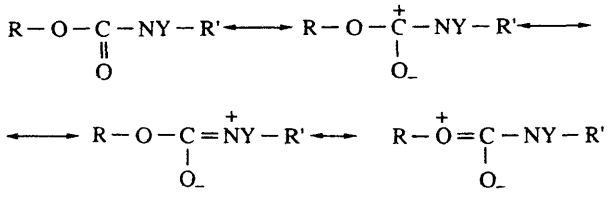
$$\longrightarrow -(-\text{NH}(CH_2)_6\text{NHCOOAlkOCO}-)_n -$$

Alk = $(CH_2)_3$, $(CH_2)_2CH(Me)$, etc.

The reaction of silylated diamines and bischloroformates, which occurs effectively in solution under mild conditions, leads to interesting possibilities in the synthesis of one of the most important classes of heterochain polymers. Since the neutral chlorotrimethylsilane and not HCl is evolved under these conditions, there is no need to use an acid acceptor (a tertiary amine), which interacts vigorously with chloroformates, such reaction involving the termination of the growing polymer chain. A side reaction of this kind is known[101] to limit significantly the application of the chloroformate method in the synthesis of polyurethanes in solution.

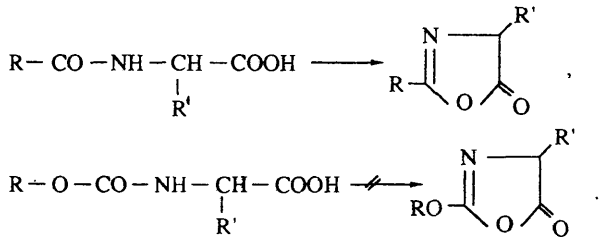
It is essential to note that in the interaction of silylated diamines with bischloroformates, in contrast to their reaction with aliphatic acid dichlorides, the formation of a cross-linked polymer was not observed even in a proton-accepting medium. This finding can

support the tautomeric mechanism of the acylation of a silylated amide examined above (see Scheme 3). Urethanes (and apparently also their silylated forms) showed a smaller tendency to undergo tautomeric transformations—they do not enter into reactions with participation of the tautomeric form of the NH–CO linkage. This may be associated with the greater loss of "resonance energy" because the carbonyl group in urethanes is conjugated with both nitrogen atoms and with the oxygen atom:

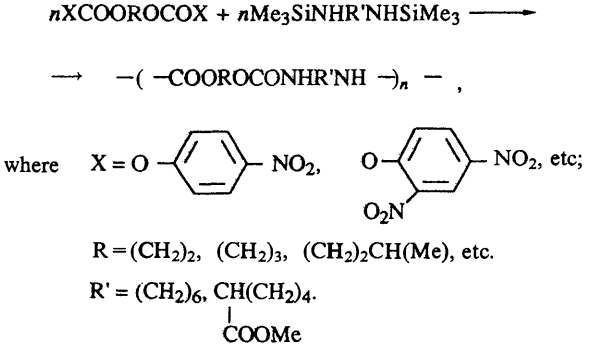


(Y = H, $SiMe_3$).

For example, in contrast to *N*-acyl-α-aminoacids, *N*-alkoxycarbonyl-α-aminoacids do not cyclise to the corresponding azlactones:[102]



High-molecular-weight polyurethanes ($\eta_{init} \leqslant 0.7$ dl g^{-1}) are formed readily on polycondensation of silylated diamines with activated diol biscarbonates—promising monomers for the synthesis of linear polyurethanes under polycondensation conditions in solution:[103]

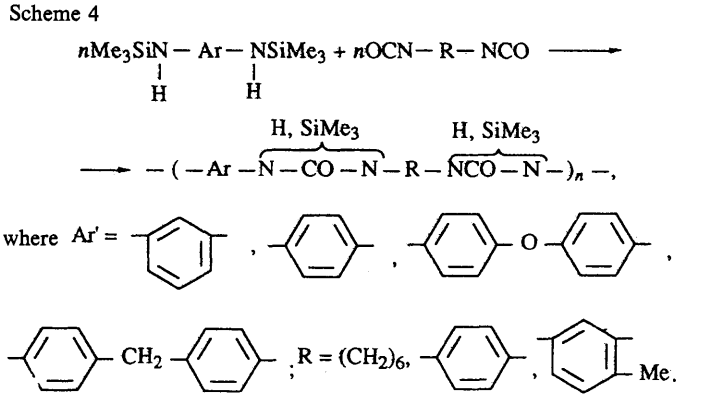


The polyurethane formation reactions using silylated diamines are convenient for the synthesis of polyurethanes with functional-group substituents, for example those based on L-lysine.[104]

Polyureas. One of the first representatives of heterochain polymers, synthesised using silylated diamines, were polyureas together with polyamines.

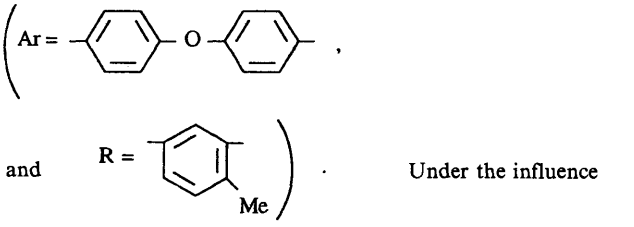
Klebe[105] achieved the synthesis of polyureas by the reaction of diisocyanates with silylated aromatic amines in tetrahydrofuran (THF), benzene, toluene, or their mixture:

Scheme 4



It is remarkable that the silylated secondary amine, containing no NH proton, reacts vigorously with the diisocyanate via a polyadditive mechanism with evolution of heat. In contrast to silylated primary diamines, a polyurea with a fixed N–Si bond is formed under these conditions.

Polyureas in which 50% of the NH protons have been substituted by the silyl groups exhibit an increased solubility in organic solvents. The fully silylated piperazine-based polymer is soluble in benzene and toluene, which may be associated, apart from the absence of intermolecular hydrogen bonds, with the presence of the bulky phenyl substituents in the silyl group. The silylated polyureas are also characterised by lower melting points, which (in contrast to non-silylated analogues) are lower than the decomposition temperatures. This greatly facilitates the formation of articles from them. Strong films have been obtained via Scheme 4 from silylated polyurea ($\overline{M}_W$ 120 000, light scattering)



Under the influence of atmospheric moisture, slow desilylation takes place in such films, which is significantly reflected in their properties (Table 1). Polyureas are rapidly desilylated when methanol is added to the final solution.

The reaction of diisocyanates with silylated diamines in DMA has been used successfully to obtain polyureas with functional-group substituents from natural carboxylic diaminoacids:[106]

$$n\mathrm{OCNRNCO} + n\mathrm{Me_3SiNHR'NHSiMe_3} \longrightarrow$$

$$\longrightarrow -(-\mathrm{COHNRNHCONHR'NH}-)_n-,$$

where R,R' = $\mathrm{CH(CH_2)_3}$ (COOEt), $\mathrm{CH(CH_2)_4}$ (COOEt), $\mathrm{CHCH_2}$ (COOEt), $\mathrm{SS-CH_2CH}$ (COOEt).

The difference from the scheme proposed by Klebe[105] consists in the fact that a diamine desilylated ina preliminary step participated in the reaction. The diamine was desilylated by introducing an equimolar amount of methanol.

Table 1. Properties of films of silylated urea and of its hydrolysed analogue.

Properties	Initial polyurea	Film after 30% surface hydrolysis
Tensile strength, kg cm^{-2}	560	450
Elongation at rupture, %	30	150

*The film was maintained for several weeks at room temperature in air. The hexamethyldisiloxane formed on hydrolysis and remaining in this film played the role of a plasticiser.

One of the authors of this review established that the reactions between aliphatic monomers proceed vigorously with evolution of heat also without preliminary desilylation. Thus the reaction of hexamethylene diisocyanate with *N,N'*-bis(trimethylsilyl)hexamethylenediamine in DMA results in the formation of a viscous solution of a 50% silylated polyrea:

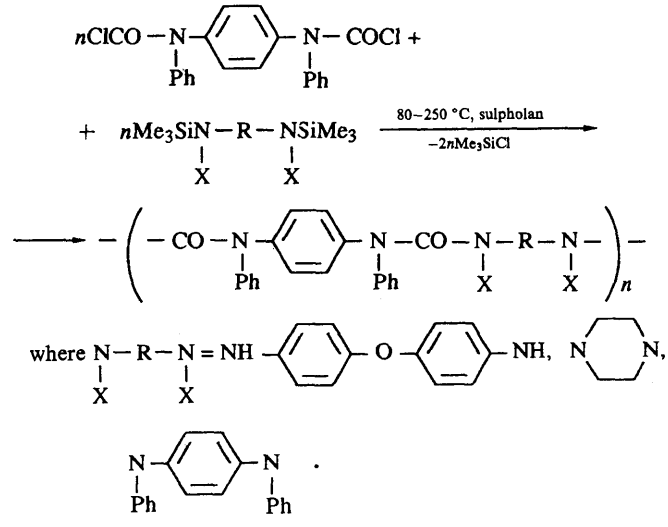
$$(n/2)\mathrm{OCN(CH_2)_6NCO} + (n/2)\mathrm{Me_3SiNH(CH_2)_6NHSiMe_3} \longrightarrow$$

$$\longrightarrow -\left[-(\mathrm{CH_2})_6-\overbrace{\mathrm{N-CO-N}}^{\mathrm{H,\ Me_3Si}}-\right]_n- \xrightarrow{\mathrm{MeOH}}$$

$$\longrightarrow -\left[-(\mathrm{CH_2})_6\mathrm{NHCONH}-\right]_n- .$$

After the addition of methanol to the reaction solution, a polyrea in the H-form is rapidly precipitated. It contains in all probability intermolecular cross-links, because it is insoluble in trifluoroacetic and sulphuric acids [a polyurea having a similar structure, obtained in a different way (see below), does not dissolve in DMA but is soluble in the acids indicated]. We may note that a tendency towards the rapid exchange of the trimethylsilyl group leads to interesting possibilities for the use of silylated polyreas as polymeric reagents—effective donors of the silyl group and especially convenient for the separation of the reaction products.

Polyureas have been synthesised by the reaction of *N*-phenylbiscarbamoyl chloride [*N,N'*-bis(chloroformyl)-*p*-dianilinobenzene] with silylated diamines, including secondary diamines:[28]



The viscosity of polyureas ($\eta_{\log} \leqslant 0.35$ dl g^{-1}), obtained in accordance with this scheme, is higher than that of the analogous specimens obtained by the reaction of *p*-dianilinobenzene with the corresponding diisocyanate ($\eta_{\log} \leqslant 0.18$ dl g^{-1});[107] best results were achieved using a piperazine derivative as the amine component.

High-molecular-weight polyureas are formed in the reaction of silylated diamines with phosgene:[108]

$$n\mathrm{COCl_2} + n\mathrm{Me_3SiNH-R-NHSiMe_3} \xrightarrow[-2n\mathrm{Me_3SiCl}]{}$$

$$\longrightarrow -(-\mathrm{CONH-R-NH}-)_n- .$$

Diphosgene and triphosgene, which are experimentally more convenient, are also used in this reaction instead of phosgene. The employment of other sources of the CO group—crystalline activated carbonates—likewise proved fruitful:[108]

$$n\mathrm{XCOX} + n\mathrm{Me_3SiNH-R-NHSiMe_3} \xrightarrow[-2n\mathrm{XSiMe_3}]{}$$

$$\longrightarrow -(-\mathrm{CONHRNH}-)_n-,$$

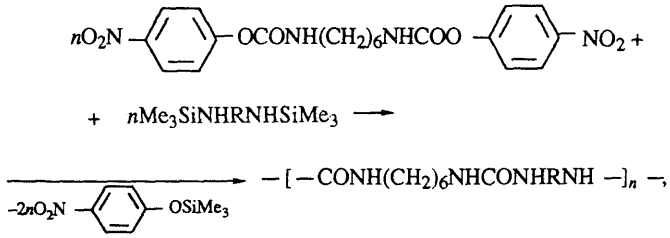
where X = O, NO_2; O, O_2N, NO_2; R = $(\mathrm{CH_2})_6$, $\mathrm{CH(CH_2)_4}$ (COOEt) etc.

The interaction of activated carbonates and silylated diamines takes place at room temperature in DMA. However, in many instances the temperature is raised to 90–100 °C and LiCl is added in order to homogenise the solution and complete the reaction

(under heterogeneous conditions, the polyurea chain propagation stops). Polyureas with $\eta_{int} \leqslant 0.95$ dl g^{-1}, soluble in organic solvents and possessing film- and fibre-forming properties, have been synthesised under such conditions.

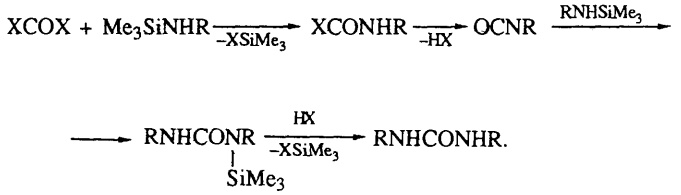
This scheme is particularly convenient in the synthesis of L-lysine-based polyureas with functional-group substituents.[104,108] A polymer with a microstructure in which symmetrical "head-to-head" and "tail-to-tail" triads predominate (with a microheterogeneity coefficient[109] $K_m = 0.6$) are formed in accordance with this scheme, while a polyurea with a normal statistical distribution of triads (with a slight predominance of the "head-to-tail" triads having $K_m = 1.1$) formed[110] in accordance with the isocyanate scheme presented above.[106]

The polycondensation of silylated diamines by reaction with an activated carbamate also leads to the synthesis of high-molecular-weight polyureas;[111]

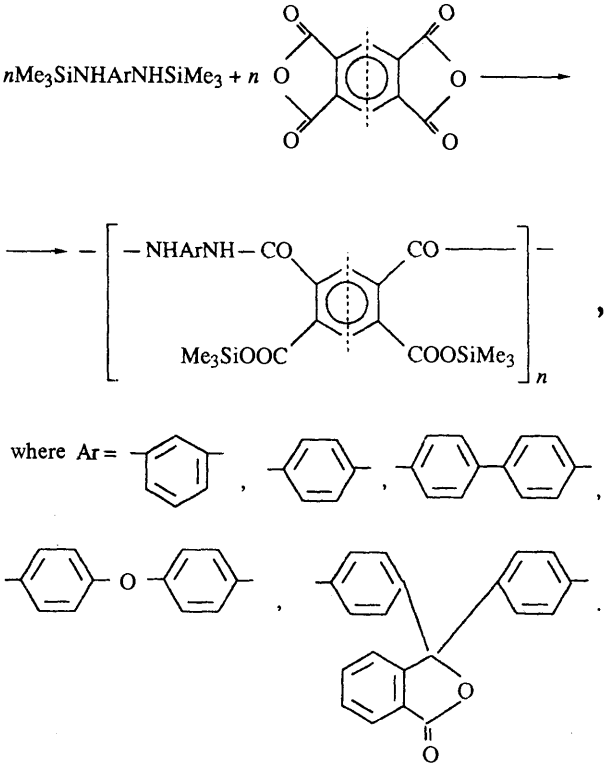


This scheme is also effective in the synthesis of L-lysine-based polyureas with functional-group substituents.

In contrast to polyamide and polyurethane formation processes, the synthesis of polyureas using phosgene and its derivatives proceeds via the intermediate formation of an isocyanate;[108]

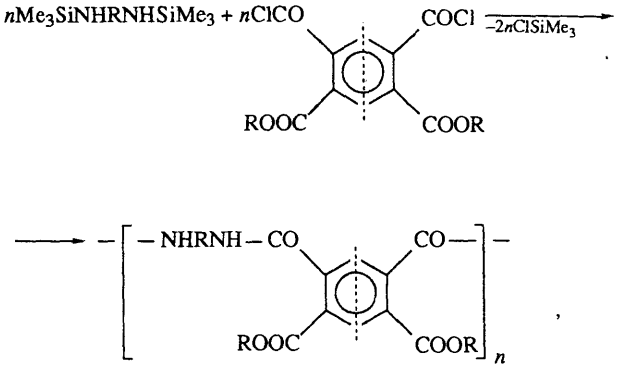


Polycycloimides. *The two-stage method.* The possibility of synthesising polymides via silylated diamines was first examined by Klebe.[1,112] In the polycondensation of cyclic anhydrides with trimethylsilylated aromatic diamines, trimethylsilyl esters of polyamidoacids (Si-PAA) are formed under mild conditions. The Si-PAA differ from the free PAA by their stability in inorganic solvents. For example, the viscosity of Si–PAA does not change during 120 days at room temperature in DMA,[113] which may also be a consequence of the "self-purification" of the system (see above):[1,94,112–117]



An interesting feature of these processes is that the $COOSiMe_3$ group "departs" in the reaction and a Si-PAA is formed.

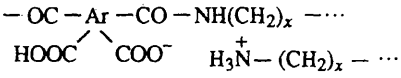
Precursors of the polyimides can be synthesised via an alternative scheme involving a reaction similar to that described above (see "Polyimides") between silylated diamines and tetracarboxylic acid diester dichlorides:



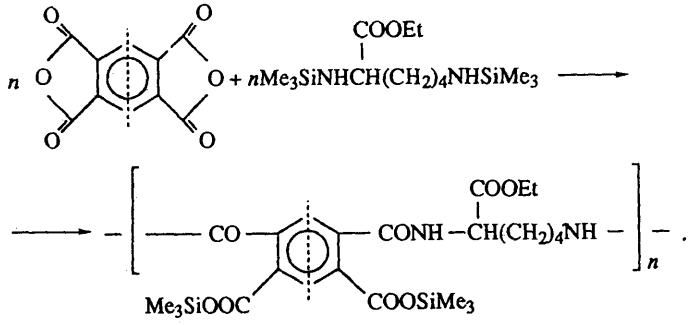
where R = Me, Et, etc.

An advantage of the formation of polyamides from silylated aliphatic diamines using cyclic acid dianhydrides is the formation of high-molecular-weight Si-PAA ($\eta_{log} \leqslant 1.0$ dl g^{-1}). When the corresponding free polymethylenediamines are employed, low-molecular-weight PAA are also obtained ($\eta_{log} \leqslant 0.2$ dl g^{-1}), which

is due to the strong inhibition of the process as a result of the formation of stable salts by highly basic aliphatic amines with the carboxyl side groups of the PAA, the salts precipitating:§ [118]



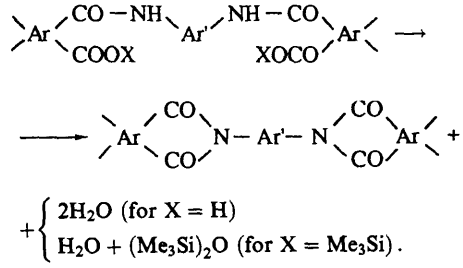
The interaction of silylated diamines with dianhydrides has been used for the synthesis of L-lysine-based polyamides with functional-group substituents:[115,116]



We may note that silylated forms of PAA are stable in the reaction solutions. During isolation by precipitation using an excess of a precipitant, they are readily desilylated (apparently by traces of moisture). Si-PAA can be maintained in an intact form only when the solvent (DMSO) is removed by lyophilising the solutions.

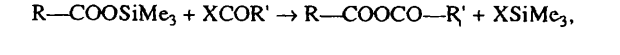
The thermal cyclisation of Si-PAA proceeds extremely effectively (according to certain data, it is faster than the cyclisation of free PAA) with formation of the target polyimides having a high molecular weight and basic properties identical with those of the polyimides obtained by the traditional method.[117]

It is significant that hexamethyldisiloxane and an amount of water smaller by a factor of 2 than in the conversion of PAA into the imide form are produced in the thermal cyclisation of Si-PAA:



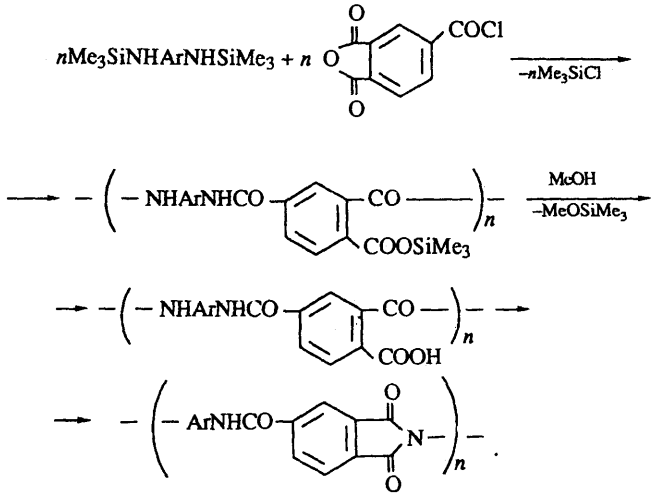
Water is formed in the case of Si-PAA on condensation of two molecules of trimethylsilanol, in all probability in the gas phase, which protects the PAA from hydrolysis (degradation).

Si-PAA also undergo readily chemical cyclisation in the presence of a pyridine–acetic anhydride (or acetyl chloride) mixture with intermediate formation of a mixed anhydride. This process can apparently be achieved in the absence of the organic base, because it is known that the silyl esters of carboxylic acids form anhydrides fairly readily on treatment with the acyl group donors indicated above:[1]

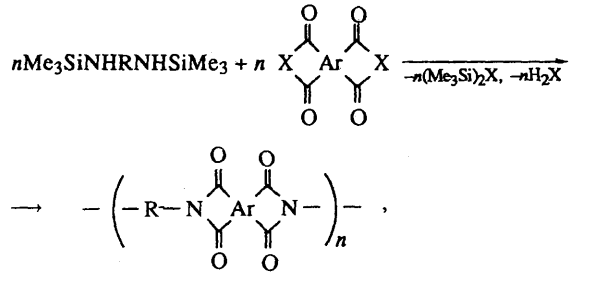


where X = Cl or MeCOO.

The advantages of the "silylated polyamide formation reaction" using cyclic dihydrides were taken into account in the synthesis of copolyimides (aliphatic and aromatic diamines were used as the comonomers), the microstructure of the chains of which was regulated (by means of degradative and exchange processes) in the stages involving the formation of Si-PAA and their cyclisation.[114] We may note that high-molecular-weight copolyimides were obtained both from the Si-alkylenediamine/Si-arylenediamine pair despite the possible exchange of the silyl group in the latter case and the appearance in the system of free aliphatic amino-groups. The combination in the first stage of the acid chloride and anhydride "silylated polyamide formation reactions" made it possible to synthesise high-molecular-weight polyamidoimides based on 4-chloroformylphthalic anhydride:[117]



The single-stage method. Using Si-diamines of different nature and cyclic dianhyrides (including dithioanhydrides[119]), high-molecular-weight polyimides were obtained in a single stage in solution at elevated temperatures:[114,119,120]



where X = O or S. It was established that there is no appreciable difference between the reactivities of diamines and their silylated analogues both in the single-stage polyimide formation reactions and in the reactions involving the aminolysis of polyimides.[120]

§ The polymeric salt based on the dianhydride of oxydi(3,4-dicarboxybenzene) and dodecamethylenediamine is insoluble in polar solvents even after prolonged heating at 100 °C.

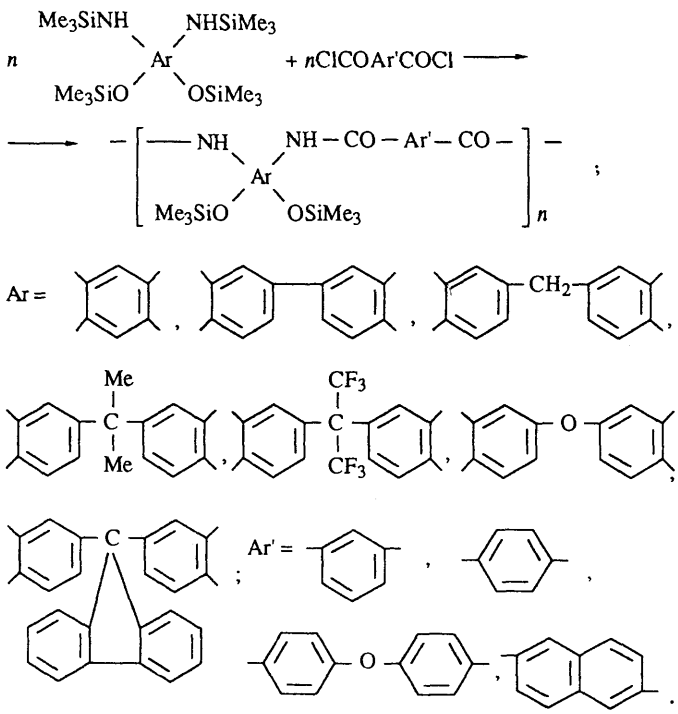
Acyclic linear polyimides. The "trimethylsilyl activation" of the amide nitrogen, which was discussed above, has been used successfully to acylate acid amides i.e. to synthesise acyclic analogues of polyimides:[62]

$$n(Me_3Si)_2NH + \tfrac{n}{2}ClCORCOCl \rightarrow \tfrac{n}{2}Me_3SiNHCORCONHSiMe_3 \rightarrow$$
$$\xrightarrow{\frac{n}{2}ClCORCOCl} -(-COR - CONHCO - R - CONH)_{n/2} - .$$

A characteristic feature of this reaction is that the primary amine behaves as a bifunctional reactant. Disilylated primary monoamines $(SiMe_3)_2NR'$ can apparently be used also under analogous conditions.

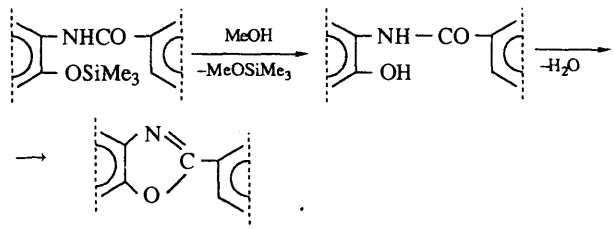
Like polyanhydrides,[121–123] the polyimides examined are of potential interest as rapidly degradable polymers for medical-biological purposes, especially since both R and R′ can carry different functional groups.

Polybenzazoles. The use of silylated monomers also for the synthesis of polybenzoxazoles by a two-stage method proved fruitful:[24,25,42,94,124–129]

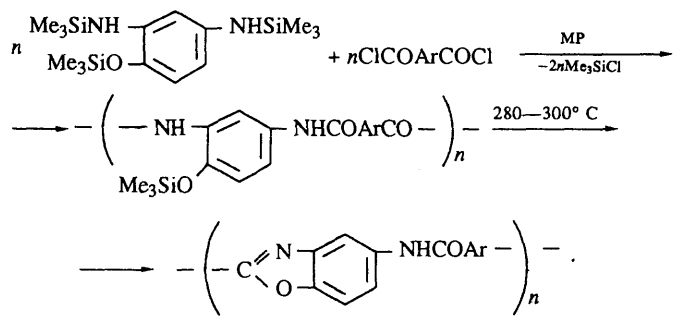


Higher-molecular-weight poly-*o*-hydroxyphenylamides ($\eta_{log} \leqslant 0.64$ dl g^{-1}) can be obtained from silylated bis-*o*-aminophenols[41] than from the free bases ($\eta_{log} \leqslant 0.33$ dl g^{-1}).[42] Here one can assume that the reaction proceeds with participation of the silylated amino-groups, because the silylated hydroxy-groups do not interact with acid chlorides under the conditions of low-temperature polycondensation (see below).

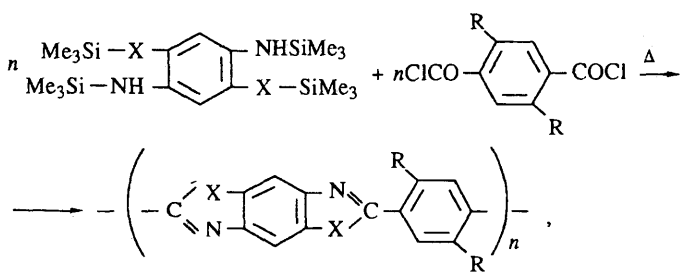
In order to facilitate the second reaction stage (cyclisation to the target benzoaxole), the hydroxy group is desilylated by treating the polymers with methanol:



Imai and co-workers[1] synthesised film-forming polyimidobenzoxazoles ($\eta_{log} \leqslant 1.49$ dl g^{-1}) in *N*-methylpyrrolidinone (MP) in accordance with the following scheme:

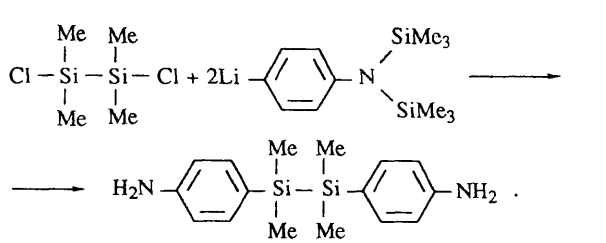


Kricheldorf and co-workers[24,25,128] obtained rod-like polybenzoxazoles and polybenzothiazoles with the aid of "silyated polycondensation":



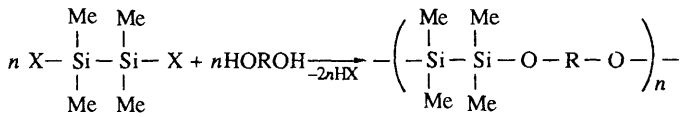
where X = O or S. According to the authors, the minimal contribution of side reactions is an advantage of this method.

Photosensitive polymers. An interesting study designed to create photo-sensitive (photodegradable) polymers has been carried out.[130–132] 1,2-Bis(*p*-aminophenyl)tetramethyldisilane was synthesised by the reaction of 1,2-dichlorotetramethyldisilane with 4-[*N*,*N*-bis(trimethylsilyl)amino]phenyl-lithium:

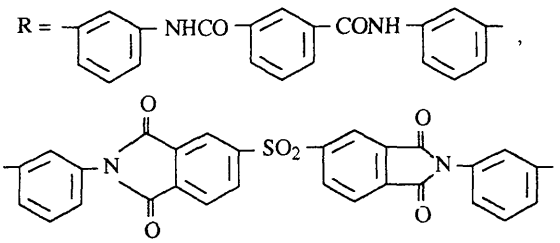


Polyamides ($\eta_{log} \leqslant 0.7$ dl g^{-1}) and polyimides ($\eta_{log} \leqslant 0.84$ dl g^{-1}), which undergo photodegradation on UV illumination, were synthesised by the polycondensation of the above diamine with dicarboxylic acid dichlorides[130] and the dianhydride of di(3,4-dicarboxyphenyl) sulphone[131] respectively.

The same workers proposed also an alternative method of synthesis of photo-sensitive polyamides and polyimides ($\eta \leqslant 0.59$ dl g^{-1}), in which the silylated amino-groups are directly involved in the chain propagation process:[132]

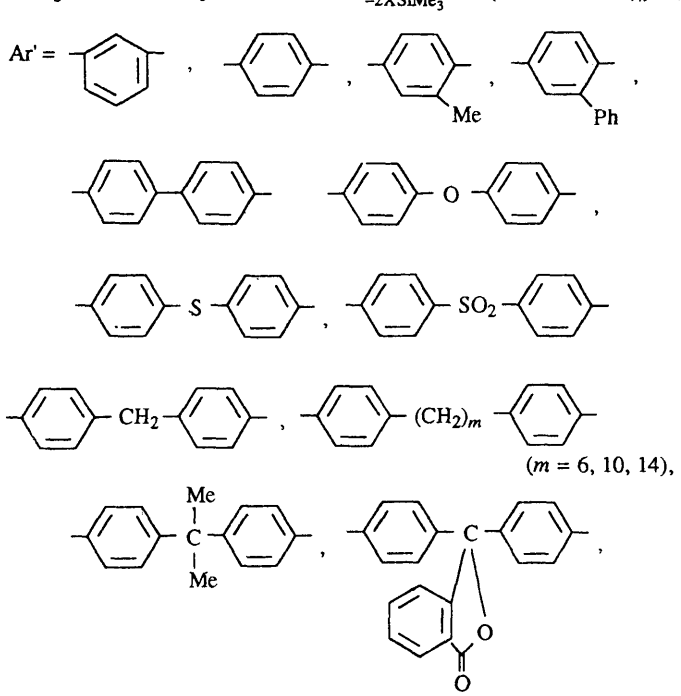


where X = NEt_2, HN−Ph;

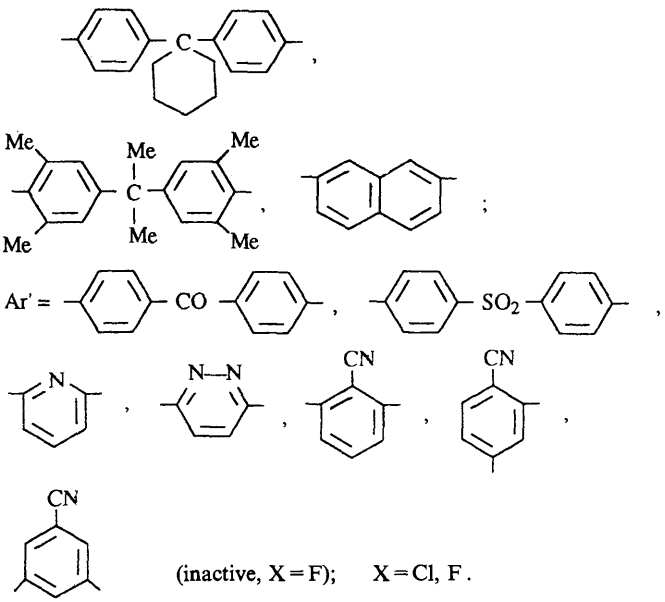


Polymers based on monomers with a O(S)−Si bond

Polyethers. Kricheldorf and co-workers obtained high-molecular-weight ($\overline{M}_W \leqslant 2 \times 10^5$) simple homopolymers and copolymers by the reaction of silylated bisphenols with activated (with the aid of a heterocycle or the electron-accepting CO_2 and SO_2 groups) aromatic difluoro(chloro)-compounds:[24,25,31,35,38,39,48,133–136]



(*m* = 6, 10, 14),



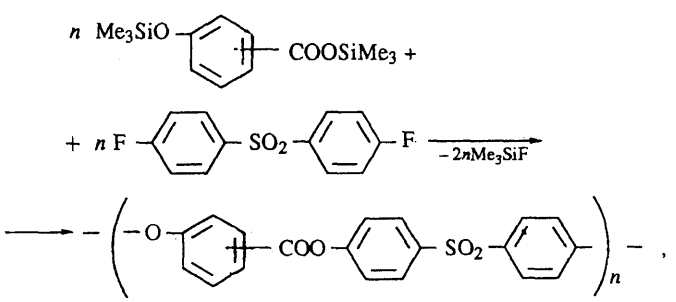
(inactive, X = F); X = Cl, F.

The polycondensation of silylated bisphenols with activated aromatic difluoro-compounds proceeds at elevated temperatures ($\leqslant$340 °C) in bulk. The silylated oxygen in bisphenols can be activated by inorganic anions (F^-, Cl^-, CO_3^{2-}), the use of fluorides (KF, CsF) producing the best results.

Polycondensation with participation of activated aromatic chloro-compounds also proceeds in solution in methylpyrrolidinone in the presence of K_2CO_3. On the whole, in the reactions indicated aromatic fluoro-compounds are much more reactive than their chloro-analogues, as in the reactions with alkali metal phenoxides.[137,138]

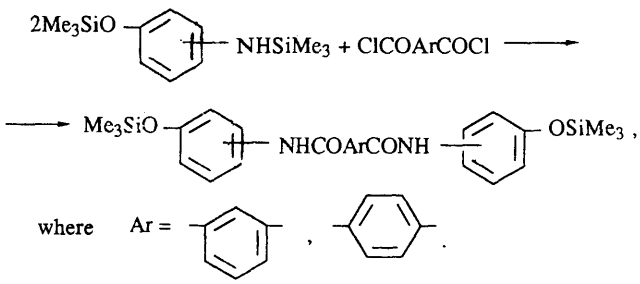
The proposed methods of synthesis of aromatic polyethers, involving the evolution of volatile products (Me_3SiF, Me_3SiCl), have advantages over the traditional method of their synthesis by the polycondensation of alkali metal bisphenoxides with activated aromatic dihalo-compounds in solution (in DMSO, methylpyrrolidinone, etc.).[137,138] The main disadvantage of the traditional method consists in the necessity to eliminate large amounts of metal salts (low-molecular-weight polycondensation side products) from the polyethers.

Polymers containing ether and ester linkages in the main macromolecular chains have been obtained by the reaction of silylated *m*- and *p*-hydroxybenzoic acids and di(4-fluorophenyl) sulphone:[48]



$\bar{M}_n \leq 20\,000$.

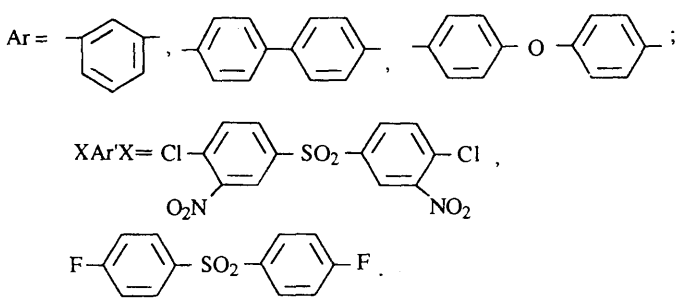
Using the different reactivities of *O*- and *N*-silylated functional groups, regular polyamides containing ether linkages have been synthesised.[139] Silylated diphenyldiamides were obtained initially by the reaction of *N,O*-bis(trimethylsilyl)-3-(or 4-)aminophenol with acid dichlorides under mild conditions. The diamides were then condensed with activated aromatic difluoro-monomers:



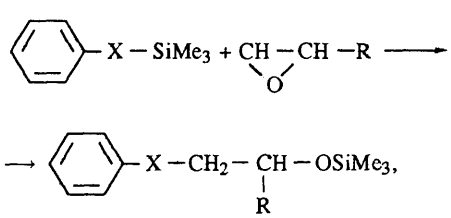
Polysulphides have also been synthesised by the reaction of *S,S'*-bistrimethylsilylated dithiophenols with aromatic dihalo-compounds:[140]

$$n\,Me_3Si-SArS-SiMe_3 + n\,XAr'X \xrightarrow[-2nMe_3SiX]{} -(-SArSAr'-)_n-,$$

where



We may note that silylated phenols and thiophenols may be alkylated also with the aid of epoxy-compounds. The oxiran ring is then inserted (and opened) between the Si and O(S) atoms:[68]



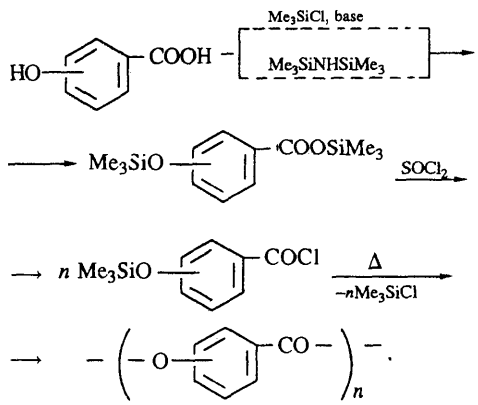
where X = O or S.

Polyesters. Kricheldorf and co-workers[30,32–34,49,141] developed a method of synthesis of polyarylates which serves as an alternative to the procedure for the arylation of silylated acids described above. It consists in the interaction of silylated phenols with acid chlorides at elevated temperatures in bulk or in a high-boiling solvent:

$$\sim ArOSiMe_3 + ClCOAr'\sim \xrightarrow{200-300^\circ C} \sim ArOCOAr'\sim ,$$

According to the authors, "silylated polyesterification" is especially useful in the synthesis of AB-polyesters, because monomers are partly volatilised in the AA–BB polycondensation, which leads to the breakdown of stoichiometry.

The silylated aromatic OH groups are inert to acid chlorides in a neutral medium and at moderate temperatures. This made it possible to synthesise the chlorides of trimethylsiloxybenzoic acids:

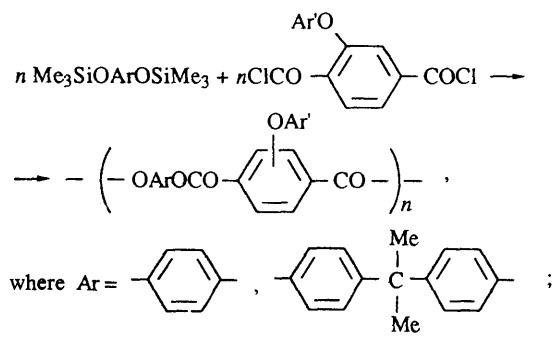


The polycondensation of trimethylsiloxybenzoic acid in bulk in the temperature range 200–300 °C leads to the synthesis of polyesters with $\overline{M}_n$ = 12 000–13 000; in solution in the presence of pyridine (a nucleophilic catalyst), much worse results are achieved ($\overline{M}_n \leqslant 2300$).[33]

The new scheme for the synthesis of aromatic AB-polyesters also has an advantage over the thermal polycondensation of acetoxybenzoic acids[30] and over direct polycondensation in the presence of phosphorus compounds as condensing agents.[33]

By selecting appropriate conditions (redistilled trimethylsilyl ester of *p*-trimethylsiloxybenzoic acid in the persence of an excess of $SOCl_2$, polycondensation in Marlotherm S), it was possible to increase $\overline{M}_n$ for the polyester to 200 000.[34]

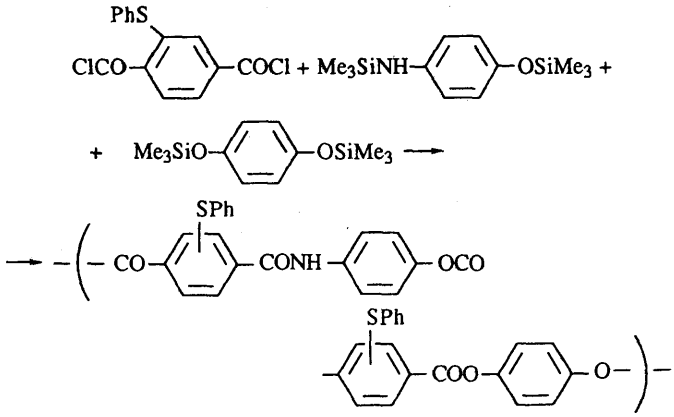
Using the silylated polyesterification method, thermotropic polyarylates were synthesised from aryloxyterephthalic acid:[52,72,146]



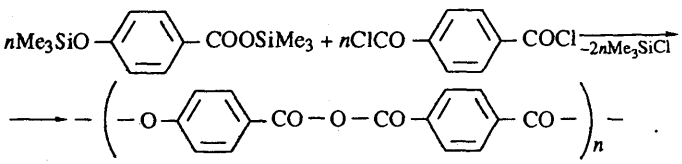
Ar' = Ph, PhOPh, $PhOC_6H_4Cl$, $PhOC_6Cl_5$.

Polyarylates with higher viscosities were obtained by the above method in many instances than in the traditional low-temperature polyesterification of bisphenols by acid dichlorides in the presence of pyridine or in the high-temperature polycondensation of aryloxy-terephthalic acids with acetylated bisphenols. The advantage of the new scheme is the small contribution of the anthrone formation side reaction.[24,49,141]

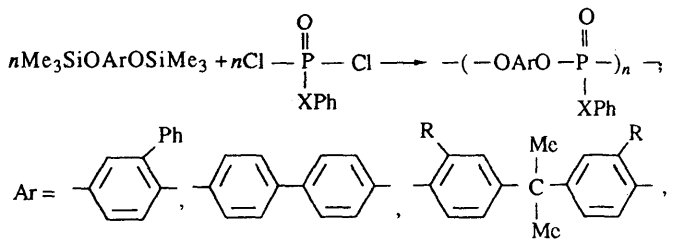
Using silylated 4-aminophenol as the comonomer, thermotropic polyamidoesters have been synthesised:[24]



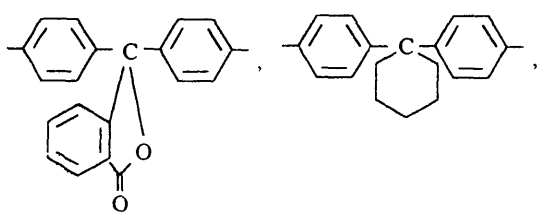
The polycondensation of terephthaloyl chloride with a silylated hydroxyacid afforded thermotropic polyester anhydrides:[24]



Stepwise heating of silylated bisphenols with phenyl phosphorodichloridate and phenyl phosphonodichloridate in the presence of benzyltriethylammonium chloride as the catalyst afforded fire-resistant poly(phenyl phosphates) and poly(phenyl phosphonates) with $M_n \leqslant 20\,000$:[36,37]

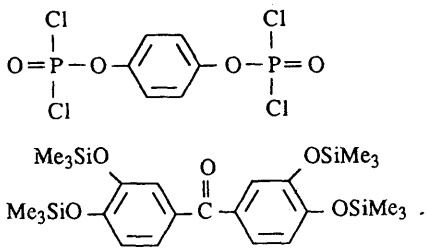


(R= H, Me, Cl, Br),



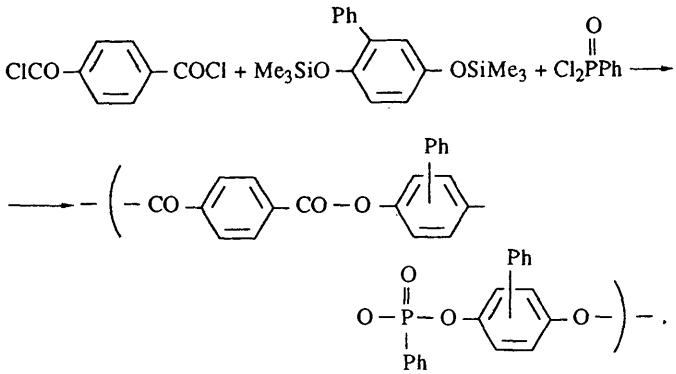
X = bond, O.

"Cross-linking" tetrafunctional compounds have also been used in the synthesis of phosphorus-containing polyesters, but the reaction yielded polymers with lower viscosity characteristics:

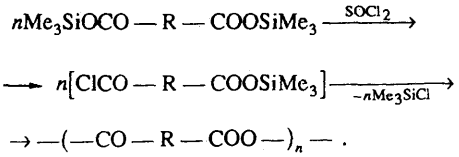


According to the author,[37] this is associated with the involvement of the tetrafunctional monomers in side reactions.

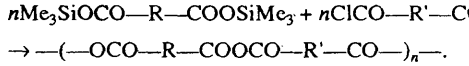
Thermotropic copolymers of terephthalic and phenylphosphonic acid have been synthesised:[24]



Polyanhydrides. The synthesis of polyanhydrides ($\eta_{int} \leqslant 0.6$ dl g^{-1} in chloroform) by the polycondensation of bistrimethylsilylated dicarboxylic acids with $SOCl_2$ in the presence of benzyltriethylammonium chloride as the catalyst has been described:[142]



Polyanhydrides can also be synthesised by the reaction of bistrimethylsilylated dicarboxylic acids with acid dichlorides, similarly to the synthesis of polyester anhydrides described above:

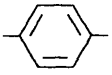


The "silylated polyanhydrides formation" reactions can be useful for the synthesis of new polyanhydrides promising as biodegradable polymers.[121–123]

Polyesterurethanes. Under certain conditions, silylated alcohols and phenols react with carboxylic acid chlorides whilst remaining inert to isocyanate groups. This feature has been used[29] to synthesise diesterdiisocyanates in accordance with the scheme

$$2OCN(CH_2)_mCOCl + Me_3SiOROSiMe_3 \longrightarrow$$

$$\longrightarrow OCN(CH_2)_mCOOROCO(CH_2)_mNCO;$$

R = $(CH_2)_4$,  ; m = 2, 3, 5.

Polyesterurethanes with a regular structure have been synthesised from diesterdiisocyanates. We may note that the above monomers are of interest for the synthesis of regular polyesterureas and polyamidoesters.

Polycondensation *in situ*

Polycondensation reactions in which the silylating agent is added directly to a mixture of the biselectrophile and bisnucleophile are examined below. Under these conditions, one of them gives rise to a silylated derivative, which then reacts *in situ* with the monomer of the opposite kind.

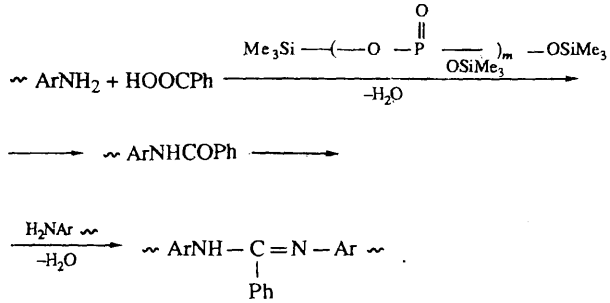
Modification of the bisnucleophile. Kaneda and co-workers[143,144] proposed a simplified method of synthesis of polyamides which does not require the preliminary synthesis and purification of silylated diamines. The diamine is subjected to polycondensation with an acid dichloride in amide solvents (HMPA, DMA, methylpyrrolidinone) at 0 °C in the presence of Me_3SiCl. This entails the silylation of the amino-groups of the diamine, which reacts *in situ* with the acid chloride. The addition of Me_3SiCl makes it possible to obtain polyamides with higher molecular weights ($\eta_{log} \leqslant 6.68$ dl g^{-1}) than in the case where salts such as LiCl ($\eta_{log} \leqslant 3.9$ dl g^{-1}) or $CaCl_2$ ($\eta_{log} \leqslant 4.48$ dl g^{-1}) (polyamides based on 3,9-diaminophenanthridinone and terephthaloyl chloride) are used.

Direct polycondensation. A method of synthesis of polyamides by the polycondensation of diamines and dicarboxylic acids or *p*-aminobenzoic acids in the presence of $SiCl_4$ as the condensing agent has been proposed (in this case both the biselectrophile and the bisnucleophile may be activated simultaneously):[145–147]

$$n H_2NArNH_2 + n HOOCAr'COOH + {}^n/_2 SiCl_4 \rightarrow$$
$$\rightarrow -(-NHArNHCOAr'CO-)_n- + (SiO_2)_{n/2} + 2n HCl.$$

It is of interest that SiO_2 is formed in these processes as a side product. This leads to the prospect of obtaining filled materials directly during synthesis.

Poly(trimethylsilyl phosphate) has also been used as the condensing agent:[148]



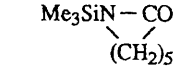
This agent exerts such a powerful dehydrating effect that an amidine bond is formed from the amide and amine groups. The interaction of diamines with benzoic acid (which behaves as a bifunctional monomer in the processes indicated) yielded polyamidines.

The syntheses described in this Section illustrate a variety of direct polycondensation—a new promising method of synthesis of heterochain polymers.[149,150]

(b) Polymerisation

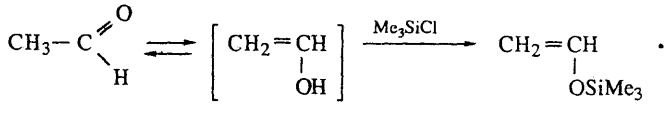
Polymerisation of heterocycles

The silyl protecting group has been used in the synthesis of polycarbohydrates by polymerisation with the opening of the ring in the corresponding anhydro-sugars. For example, the reaction of t-butylchlorodimethylsilane and 1,5-anhydro-β-D-xylofuranose afforded 1,5-anhydro-2,3-di-*O*-(t-butyldimethylsilyl)-β-D-xylofuranose, whose polymerisation in the presence of BF_3 or $SbCl_5$ yielded high-molecular-weight polymers containing the 1,5-α- and 1,5-β-furanose fragments.[151] A polysaccharide with free hydroxy-groups, capable of further polymer-analogue transformations, was obtained by the desilylation of the polymer indicated.

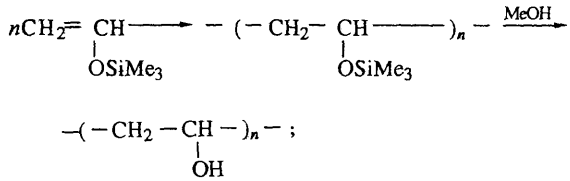
N-Trimethylsilylated lactams have also been used in the synthesis of polymers. In particular, it has been established that *N*-trimethylsilyl caprolactam  accelerates the anionic polymerisation of ε-caprolactam.[152]

Timethylsilated compounds are also effective as catalysts of the polymerisation of heterocycles. It has been shown[153] that trimethylsilylated acids, in particular, trimethylsilyl triflate ($CF_3{=}SO_3SiMe_3$) and bistrimethylsilyl sulphate ($Me_3SiOSO_2OSiMe_3$) initiate the polymerisation of lactones. Polycaprolactone with a molecular weight of 60 000 (degree of conversion 70–90%) has been obtained by treatment with trimethylsilyl triflate in 1,2-dichloroethane at 50 °C.

Polymerisation of silyl ethers of enols. An elegant method of synthesis of poly(vinyl alcohol) from acetaldehyde has been proposed.[154] The *O*-trimethylsilyl derivative of the enolic form of acetaldehyde was synthesised initially and then trimethylsiloxyethylene was obtained:

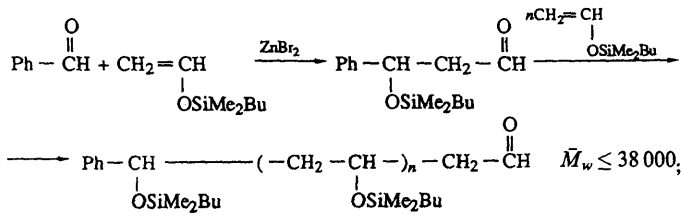


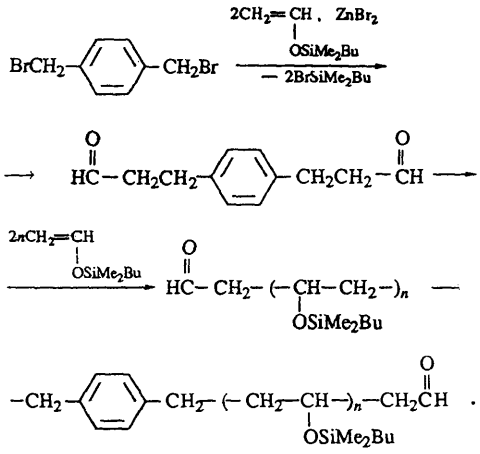
The polymersiation of the latter afforded silylated poly(vinyl alcohol). It was desilylated by adding methanol;



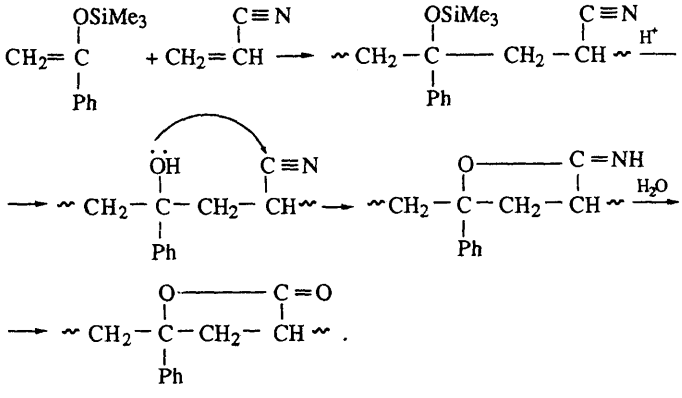
$$[\eta]^{30}_{H_2O} \leq 0.6 \text{ dl g}^{-1}.$$

This interesting procedure was developed in a study[53] whose authors achieved the synthesis of silylated poly(vinyl alcohols) in accordance with one of the schemes presented below (the polymer formation process proceeds via the mechanism of aldol condensation):



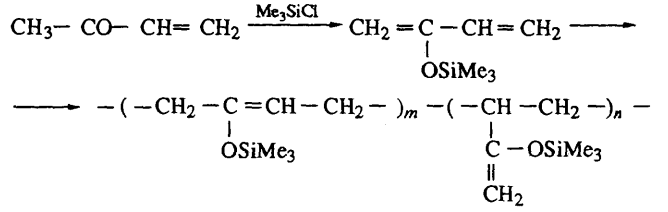


α-Trimethylsiloxystyrene, its polymers, and its copolymers with styrene[155] and acrylonitrile[156] were synthesised from acetophenone. In the latter case, in the presence of a proton, there is possibility of cyclisation with formation of a five-membered lactone:

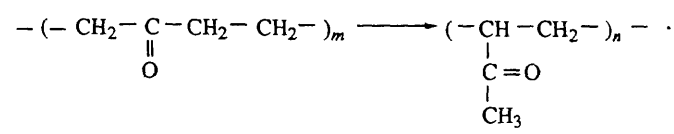


Lactone-containing polymers are of intereest, for example, as carriers for the covalent immobilisation of various substances. In this case, there is no need for the additional activation of the polymer, because it is known that five-membered lactones exhibit an enhanced reactivity and readily interact with aliphatic amino-groups.[157]

An interesting method of synthesis of polyolefins containing ketone groups in the main and side chains of the macromolecules has been proposed.[158] 2-Trimethylsiloxybuta-1,3-diene was obtained initially by silylating methyl vinyl ketone and its polymerisation or copolymerisation with unsaturated monomers led to polymers with 1,4- and 3,4-units:



Desilylation of the polymers by treatment with HCl or NBu_4F results in the formation of polyketones:



These are of interest, for example, as photodegradable materials.

Interesting examples of the use of silyl compounds as initiators of the polymerisation of unsaturated compounds exist. Thus metallo-derivatives of silylamines $(Me_3Si)_2NM$ (where M = Li or Hg) catalyse the polymerisation of vinyl monomers,[1] lithium derivatives exhibiting a high catalytic activity; the catalytic activity of the corresponding amide complex of mercury is less marked. Polymers resistant to fungi have been obtained using the above initiators.

Silyl compounds can also be used to protect catalytic systems. For example, silylamines having the general formula

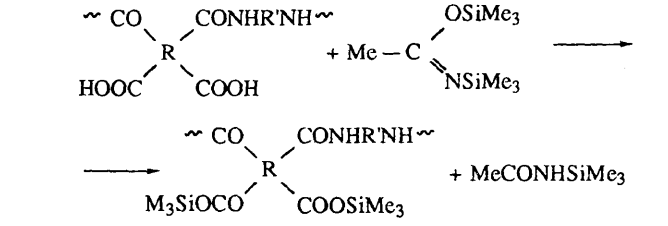
$$R_aSiH_b(NR^1R^2)_c,\ a=1,\ 2,\ 3;\ b=0.01;\ c=1,\ 2;\ a+b+c=4$$

are used as additive neutralising compounds which poison the anionic polymerisation of unsaturated compounds.[160]

Silylation is used to block functional groups (phenolic hydroxyls) present in the monomer itself and capable of inhibiting polymerisation, for example, the polymerisation of 4-allyl-2,6-dimethylphenol.[161]

IV. Reactions in polymer chains

An alternative method of synthesis of Si-PAA, by polymer-analogue reactions in accordance with the scheme



(apart from the silylating agent indicated in the scheme, other donors of the $SiMe_3$ group have been used) is of undoubted interest as regards the employment of the advantages of silylated polycondensation in the synthesis of polymides. Carboxylic acids are silylated more readily than the initial arylenediamines. However, such treatment of PAA at room temperature results in an effective

imide formation reaction.[75]¶ As can be seen from Table 2, best results are then achieved using *N,O*-bis(trimethylsilyl) acetamide.

An advantage of silylating agents in imide formation processes is that, in contrast to, for example, carboxylic acid anhyrides and tertiary amines, which are effective only when used in combination with one another, there is no need for a second agent when silazanes and silylamides are employed. In addition, the cyclisation of PAA takes place successfully in the presence of equivalent amounts of silazanes. Whereas the attainment of optimum results with mixtures of anhydrides and tertiary amines requires an appreciable excess of the components of the catalytic system. The silylation of polyamide chains has also been achieved.[163]

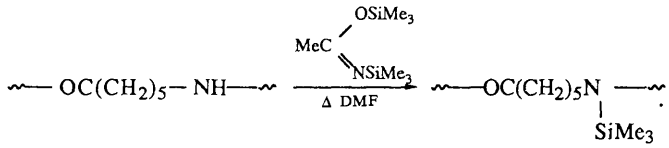


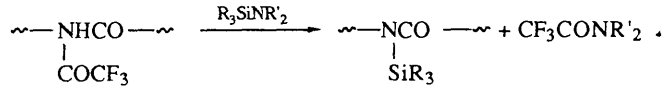
Table 2. Synthesis of polyimides by cyclising PAA in the presence of silylating agents.[75]

PAA base	η_{lg} for PAA, dl g^{-1}	Silylating agent	η_{lg} for the polymide dl g^{-1}
p-Phenylenediamine and 3,3-bis(3',4'-dicarboxyphenyl)phthalide	1.22	*N,O*-bis(trimethylsilyl)acetamide	0.95
	0.99	$Me_3SiCl+NEt_3$(1 : 1)	0.32
Anilinofluorene and bis(3,4-dicarboxyphenyl) oxide	1.10	*N,O*-bis(trimethylsilyl)acetamide	0.90
	0.64	$Me_3SiCl+NEt_3$ (1 : 1)	0.21

As a result of sharp decrease in the number of intermolecular hydrogen bonds, silylated polyamides are soluble in many organic solvents and are suitable for conversion into various articles and for studies by the gel-chromatographic methods. They can be regarded also as polymeric reagents—effective donors of the silyl group.

The conversion of polyamides into a soluble form by silylation has advantages over another known method—chain trifluoroacetylation, because certain *N*-trifluoroacetates, for example those of poly-α-aminoacids, are readily degraded.[164]

We may note that the polyamide derivatives indicated can undergo interconversions. For example, *N*-trifluoroacetyl derivatives of polyamides, which are effective trifluoroacetyl group transferring agents, can be converted into the corresponding silylated derivatives on treatment with silazanes:



¶ It is not clear why Greber and Darms[162] nevertheless obtained Si-PAA under analogous conditions, although they do note that the cyclisation of the latter takes place more readily than that of PAA.

Instances of the use of silylated amines instead of free bases in polymer-analogue reactions of polymers are known. Thus, in order to suppress aldol condensation, trimethylsilylated amines were used[165] to convert poly(methyl methacrylate) into the corresponding amide by the aminolysis of ester side groups.

V. Conclusion

There is evidently no need to conclude the review by listing anew and discussing the advantages and characteristics of the employment of the silylation method in polymer chemistry. One can only draw the reader's attention to the steady and extremely marked enhancement of interest in this approach, which has been expressed both by an increase in the number of publications and reviews on this question and also by the application of silylation to the synthesis of new poymers which are relatively difficult to obtain by means of traditional polymer formation reactions. At the same time, it is essential to note that so far the "silyl" method has not reached the stage of its industrial use as regards its application to polymers. This is apparently partly due to the fact that a successful compromise between the chemical, technological, economical, and ecological problems arising when silylated monomers and reagents are employed in the synthesis of polymers has not been found. However, one may assume that, as the process is improved and some kind of unique possibilities of the latter are discovered, it will become more than a purely preparative method for the synthesis of monomers and polymers with a specified combination of properties.

References

1. J F Klebe *Adv. Org. Chem.*, 1972, **8** 97
2. A E Pierce *Silylation of Organic Compounds*, Pierce Chem. Comp., Rockford, Illinois, 1968, 487 pp
3. W R Weber *Silicon Reagents for Organic Synthesis*, Springer, Berlin, 1983, 430 pp
4. E W Colvin *Silicon in Organic Synthesis*, Butterworth, Sevenoaks, 1981, 288 pp
5. M F Kashutina, S L Ioffe, V A Tartakovskii *Usp. Khim.*, 1975, **44**(9) 1620 [English translation in *Russ. Chem. Rev.*, 1975(9)]
6. S Itsuno, T Wakasugi, K Ito *Polymer Bull.*, 1988, **20** 435
7. S Funakoshi, H Tamamura, N Fujii, et al. *J. Chem. Soc., Chem. Commun.*, 1988, 1588
8. R Nakao, K Oka, T Fukumoto *Bull. Chem. Soc. Jpn.*, 1981, **54** 1267
9. W E Dennis *J. Org. Chem.*, 1970, **35** 3253
10. G A Tolstikov, M S Miftakhov, N S Vostrikov, et al. *Zh. Org. Khim.*, 1988, **24** 224
11. A Wissner, C V Grudzinskas *J. Org. Chem.*, 1978, **43** 3972
12. V F Mironov, V P Kozyukov *Zh. Obshch. Khim.*, 1984, **54** 1217
13. H R Kricheldorf *Chem. Ber.*, 1970, **103** 3353
14. V P Kozyukov, Vikt P Kozyukov, V F Mironov *Zh. Obshch. Khim.*, 1982, **52** 1386
15. S Djuric, J Venit, P Magnus *Tetrahedron Lett.*, 1981, 1787
16. P S Mason, F D Smith *J. Gas Chromatogr.*, 1966, **4** 398
17. K Bergström, J Gurtler *Acta Chem. Scand.*, 1971, **25** 175
18. J P Hardy, S L Kerrin *Analytical Chem.*, 1972, **44** 1497
19. Y Imai, Y Oishi *Progr. Polym. Sci.*, 1989, **14** 173

20. A L Rusanov *Usp. Khim.*, 1990, **59**(9) 1492 [English translation in *Russ. Chem. Rev.*, 1990(9)]
21. Y Imai, Y Oishi *Sen-I Gakkaishi*, 1987, **43** 435
22. Y Imai *Kagaku Koge. Chem. Ind.*, 1987, **38** 481
23. Y Imai *Kobunshi/High Polym. Jpn.*, 1988, **37** 892
24. H R Kricheldorf *Polymer Sci. Contemporary Themes, Vol. 1* (Edited by S Sivaram), Tata McGraw Hill Publ. Co. Ltd., New Delhi, 1991, p. 49
25. H R Kricheldorf *Polymer Preprints*, 1991, **32**(1) 395
26. J F Klebe *J. Polym. Sci.*, 1964, **A2** 2673
27. M Kakimoto, Y Oishi, Y Imai *Makromolek. Chem. Rapid. Commun.*, 1985, **6** 557
28. Y Oishi, M Padmanaban, M A Kakimoto, et al. *J. Polym. Sci., Polm. Chem. Ed.*, 1987, **25** 3387
29. W Normann, B Brahm *Makromolek., Chem. Rapid Commun.*, 1988, **9** 175
30. H R Kricheldorf, G Schwarz *Polym. Bull.*, 1979, **1** 383
31. H R Kricheldorf, G Bier, BRD P. 1 591 258 1982
32. H R Kricheldorf, G Schwarz BRD Appl. 2 907 613 1982
33. H R Kricheldorf, Q-Zh Zang, G Schwarz *Polymer* 1982, **23** 1821
34. H R Kricheldorf, G Schwarz *Makromol. Chem.*, 1983, **184** 475
35. H R Kricheldorf, G Bier *Polymer*, 1984, **25** 1151
36. H R Kricheldorf, H Koziel *J. Makromol. Sci.-Chem.*, 1986, **A23** 1337
37. H R Kricheldorf, H Koziel, E Witek *Makromol. Chem. Rapid. Commun.*, 1988, **9** 217
38. H R Kricheldorf, G Schwarz, J Erxleben *Makromol. Chem.*, 1988, **189** 2255
39. H R Kricheldorf, U Delius *Macromol.*, 1989, **22** 517
40. A Hara, Y Oishi, M A Kakimoto, et al. *Polymer Prepr. Jpn.*, 1987, **36** 316
41. Y Imai, M A Kakimoto, Y Oishi, et al., Japanese Appl. 62-283 124; *Ref. Zh. Khim.*, 1988, 24S620P
42. Y Maruyama, Y Oishi, M A Kakimoto, et al. *Macromol.*, 1988, **21** 1305
43. Z M Nagiev *The Synthesis and Study of Mixed Cardo-Polyimides*, Candidate's Thesis in Chemical Sciences, Moscow, 1983, 191 pp
44. R D Katsarava, D P Kharadze, N Sh Japaridze, et al. *Makromol. Chem.*, 1985, **186** 939
45. V V Korshak, G F Bondarevskii, A I Kalachev, et al., USSR P. 464 590; *Byull. Izobret.*, 1975(11) 67
46. G S Bonarevskii, P M Valetskii, A I Kalachev, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 920
47. A L Narkson, V I Bakhmutov, Sh A Karapet'yan *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1090
48. H R Kricheldorf, G Bier *J. Polymer Sci., Polymer Chem. Ed.*, 1983, **21** 2283
49. H R Kricheldorf, G Schwarz, F Ruhser *J. Polymer Sci., Polymer Chem. Ed.*, 1988, **26** 1621
50. L Birkofer, P Sommer *J. Organomet. Chem.*, 1972, **35** C15
51. L Birkofer, P Sommer *J. Organomet. Chem.*, 1975, **99** C1
52. Ya S Vygodskii, Yu A Davidovich, A S Pushkin *Tezisy XVIII Vsesoyuznoi Konferentsii po VMS, Kazan'* (Abstracts of Reports at the XVIIIth All-Union Conference on High-Molecular-Weight Compounds, Kazan), Kazan, 1973, p. 63
53. D Y Sogah, O W Webster *Macromol.*, 1986, **19** 1775
54. N A Makarova, E A Kirichenko, A I Ermakov *Zh. Anal. Khim.*, 1973, **28** 972
55. S E Skobeleva, A N Egorochkin, N S Vyazankin, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 644
56. Yu V Kolodyazhnyi, M G Grunfest, V A Bren', et al. *Zh. Obshch. Khim.*, 1975, **45** 1083
57. R R Tarasyants, O P Sakovets, M M Morgunova, et al. *Zh. Obshch. Khim.*, 1973, **43** 2428
58. S M Andreev, N V Mironova, Yu A Davidovich, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1789
59. M Rothe, T Toth, R Daser *Chem. Ber.*, 1966, **99** 3820
60. L Birkofer, P Richter, A Ritter *Chem. Ber.*, 1960, **93** 2804
61. Y Oishi, M A Kakimoto, Y Imai *Macromol.*, 1988, **21** 547
62. J R Bowser, P Williams, K Kurz *J. Org. Chem.*, 1983, **48** 4111
63. N M Oleinik, L M Litvinenko, Yu S Sadovskii, et al. *Zh. Org. Khim.*, 1980, **16** 1469
64. R Yu Katskarava *Usp. Khim.*, 1991, **60**(7) 1419 [English translation in *Russ. Chem. Rev.*, 1991(7)]
65. Y Kawazoe, M Nomura, Y Kondo, et al. *Tetrahedron Lett.*, 1987, **28** 4307
66. Y Oishi, M Padmanaban, H A Kakimoto, et al. *Polymer Prepr. Jpn.*, 1987, **36** 318
67. M Padmanaban, Y Oishi, M Kakimoto, et al. *IUPAC 32nd Int. Symp. Macromol. Kyoto 1–6 Aug. 1988. Prepr.* Kyoto, 1988, p. 476; *Ref. Zh. Khim.*, 1990, 13S507
68. L I Komarova, S N Salazkin, Ya S Vygodskii, et al. *Vysokomol. Soedin., Ser. A*, 1990, **32** 1571
69. I H Shulz, C G Zike US P. 3 072 594; *Chem. Abs.*, 1963, **58** 6988
70. E M Khrustaleva, G E Golubkov, D E Zhinkina, et al. *Plastmassy*, 1970, (1) 12
71. T Munetoh, K Miyazawa, T Matsumoto, et al. *Polymer Prepr. Jpn.*, 1987, **36** 325
72. K Miyazawa, T Munetoh, T Matsumoto, et al. *Polymer Prepr. Jpn.*, 1987, **36** 324
73. S Hara, Japanese Appl. 62-235 008
74. S Ramakrishnan, J C W Chien *J. Polym. Chem. Ed.*, 1987, **25** 1433
75. Yu A Davidovich, Ya S Vygodskii, A S Pushkin, et al., USSR P. 412 212; *Byull. Izobret.*, 1974, (3)
76. Y Oishi, M A Kakimoto, Y Imai *Macromol.*, 1987, **20** 703
77. R W Taft, D Gurka, L Joris, et al. *J. Am. Chem. Soc.*, 1969, **91** 4801
78. R D Katsarava, D P Kharadze, L M Avalishvili *Chimia Stosowana (Polish J Appl. Chem.)*, 1986, **3** 187
79. Y Oishi, M A Kakimoto, Y Imai *J. Polym. Sci., Polm. Chem. Ed.*, 1987, **25** 2493
80. Y Imai, M Kakimoto, N Hamaoka *J. Polym. Sci., Polym. Chem. Ed.*, 1984, **22** 1981
81. R D Katskarava *Vysokomol. Soedin., Ser A*, 1989, **31** 1555
82. Y Oishi, S Harada, M A Kakimoto, et al. *LIII Chem. Soc. Jpn. Annual Meeting. Preprints*, 1986, 25
83. Y Oishi, S Harada, M A Kakimoto, et al. *Polymer Prepr. Jpn.*, 1987, **36** 313
84. C K Ingold *Structure and Mechanism in Organic Chemistry* (Translated into Russian), Mir, Moscow, 1973, 1056 pp
85. Y Takahashi, M Tuima, K Inagawa, et al. *LIV Chem. Soc. Jpn. Annual Meeting. Preprints*, Kyoto, 1987, p. 1549
86. S L Kwolek, P W Morgan *J. Polym. Sci.*, 1964, **2A** 2693
87. R D Katsarava, D P Kunchuliya, L M Avalishvili, et al. *Vysokomol. Soedin., Ser. B*, 1979, **21** 643
88. R D Katsarava, D P Kharadze, L M Avalishvili, et al. *Vysokomol. Soedin., Ser. A*, 1984, **26** 1537

89. R D Katsarava, D P Kharadze, L M Avalisvili, et al. *Makromol. Chem. Rapid. Commun.*, 1984, **5** 585
90. A Rodriguez-Galan, J J Bou, S Munoz-Guerra *Int. Symp. Honour Prof. P Sigwalt 65th Birthday, Paris, Sept.9–13*, 1990. *Prepr. SYMPOL'90*, Paris, 1990, p. 341
91. H R Kricheldorf, E Stengele, W Regel *Liebigs Ann. Chem.*, 1975, **718** 1379
92. R D Katsarava *Kompozitsionnye Polimernye Materialy (Kiev)*, 1986, (29) 70
93. R D Katsarava, D P Kharadze, L M Avalishvili, et al. *Soobsch. Akad. Nauk. Gruz. SSR*, 1989, **134** 121
94. Y Imai *Polymer Science Contemporary Themes*, Tata McGraw Hill Publ. Co. Ltd., New Delhi, 1991, Vol. 1, p. 3
95. R D Katsarava, D P Kharadze, L I Kurmelashvili, et al. *Makromolek. Chem.* (in press)
96. F W Harris, R P Eury *197th ACS Nat. Meet. Dallas, Texas, Apr.9–14, 1989. Abstr. Pap.*, Washington DC, 1989, p. 876
97. V P Kozyukov, N V Mironova, V F Mironov *Zh. Obshch. Khim.*, 1978, **48** 2541
98. V P Kozyukov, N V Mironova, V F Mironov *Zh. Obshch. Khim.*, 1979, **49** 784
99. Z M Nagiev, N Sh Rasulov, Sh A Amirov *Materialy 3 Respublikanskoi Konferentsii Molodykh Uchenykh-Khimikov, Posvyashchennoi 80-Letiyu Akad. M F Nagieva, Baku* (Proceedings of the 3rd All-Republic Conference of Young Research Chemists Commemorating the 80th Birthday of Academician M F Magiev, Baku), Baku, 1988, p. 88; *Ref. Zh. Khim.*, 1988, 24S604
100. R D Katsarava, T M Kartvelishvili *Vysokomol. Soedin.*, 1986, **28** 377
101. P W Morgan *Condensation Polymers: By Interfacial and Solution Methods* (Translated into Russian), Khimiya, Leningrad, 1970, 448 pp
102. C S Cleaver, B C Pratt *J. Am. Chem. Soc.*, 1955, **77** 1544
103. R D Katsarava, T M Kartvelishvili, D P Kharadze, et al. *Vysokomol. Soedin., Ser. A*, 1987, **29** 2069
104. R D Katsarava *Kompositsionnye Polimernye Materialy (Kiev)*, 1986, (29) 77
105. J F Klebe *J. Polymer. Sci.*, 1964, **2B** 1079
106. T N Sentsova, V I Butaeva, Yu A Davidovich, et al. *Dokl. Akad. Nauk SSSR*, 1977, **232** 335
107. Y Oishi, M A Kakimoto, Y Imai *J. Polym. Sci., Polym. Chem. Ed.*, 1987, **25** 2185
108. R D Katsarava, T M Kartvelishvili, Yu A Davidovich, et al. *Dokl. Akad. Nauk SSSR*, 1982, **266** 363
109. R Yamadera, M Murano *J. Polym. Sci., A1*, 1967, **5** 2259
110. R D Katsarava, D P Kharadze, P L Toidze, et al. *Acta Polymerica*, 1991, **42** 95
111. R D Katsarava, T M Kartvelishvili, M M Zaalishvili *Soobshch. Akad. Nauk Gruz. SSR*, 1984, **113** 533
112. E M Boldebuck, J F Klebe, US P. 3 303 157; *Chem. Abs.*, 1967, **66** 96 125
113. Ya S Vygodskii *Studies on the Synthesis and Properties of Cardo-Polyimides*, Doctoral Thesis in Chemical Sciences, Moscow, 1980, 585 pp
114. V V Korshak, S V Vinogradova, Ya S Vygodskii, et al. *Makromol. Chem., β*, 1983, **184** 235
115. S G Alekseeva, S V Vinogradova, V D Vorob'ev, et al. USSR P. 790 725; *Byull. Izobret.*, 1983, (3)
116. R D Katsarava, D P Kharadze, T M Avalishvili, et al. *Izv. Akad. Nauk Gruz. SSR, Ser. Khim.*, 1984, **10** 156
117. Y Oishi, M Kakimoto, Y Imai, *STEPI-2 Conference*, 1991, Montpelier, pp. 1a–3
118. S V Vinogradova, Ya S Vygodskii, N A Churochkina, et al. *Vysokomol. Soedin., Ser A*, 1971, **13** 1146
119. Y Oishi, M Kakimoto, Y Imai *IUPAC 32nd Int. Symp. Macromol. Kyoto 1–6 Aug. 1988. Prepr. Kyoto*, 1988, p. 204; *Ref. Zh. Khim.*, 1990, 13S398
120. Ya S Vygodskii, Z M Nagiev, V V Korshak, et al. *Acta Polymerica*, 1984, **35** 690
121. K W Leong, B C Brott, R Langer *J. Biomed. Mater. Research*, 1985, **19** 941
122. K W Leong, V Simonte, R Langer *Macromol.*, 1987, **20** 705
123. A Ch Albertson, S Lundmark *Polym. in Medical Devices*, 1989, **18** 134
124. S V Vinogradova, V V Korshak, G S Bondarevskii, et al., USSR P. 477 177; *Byull. Izobret.*, 1975, (26)
125. G S Bondarovskii, A I Kalachev, P M Valetskii *IV Mezhdunarodnyi Simpozium po Khimii Kremniiorganicheskikh Soedinenii, Moskova* (The IVth International Symposium on the Chemistry of Organosilicon Compounds, Moscow), Moscow, 1975, Vol. 2, Part 1, p. 81
126. V P Semenov, G M Tseitlin, P M Valetskii, USSR P. 663 699; *Byull. Izobret.*, 1979, (19)
127. Y Imai, M Kakimoto, Y Oishi, et al., Japanese Appl., 62-283 127; *Ref. Zh. Khim.*, 1988, 24S621P
128. H R Kricheldorf, J Engelhardt *Makromol. Chem.*, 1989, **190** 2939
129. Y Imai, M Kakimoto, Y Oishi, et al., Japanese Appl. 1-292 034; *Ref. Zh. Khim.*, 1991, 5S627P
130. M Padmanaban, M Kakimoto, Y Imai *J. Polym. Sci., Polym. Chem. Ed.*, 1990, **28** 1569
131. M Padmanaban, M Toriumi, M Kakimoto, et al. *Makromol. Chem. Rapid Commun.*, 1990, **11** 15
132. M Padmanaban, M Kakimoto, Y Imai *Polymer J.*, 1990, **22** 587
133. H R Kricheldorf, J Meier, G Schwarz *Makromol. Chem., Rapid Commun.*, 1987, **8** 529
134. H R Kricheldorf, U Delius *Makromol. Chem., Rapid. Commun.*, 1989, **10** 41
135. H R Kricheldorf, D Lübbers *Makromol. Chem., Rapid. Commun.*, 1990, **11** 303
136. H R Kricheldorf, P Jahnke *Makromol. Chem.*, 1990, **191** 2027
137. J W Rose *High Performance Polymers: Their Origin and Development* (Edited by R B Seymour, G S Krichenbaum), Elsevier, New York–Amsterdam, 1986, p. 187
138. M J Mullins, E P Woo *J. Macromol. Sci. Rev. Chem. Phys.*, 1987, **27C** 313
139. H R Kricheldorf, B Schmidt, U Delius *Eur. Polym. J.*, 1990, **26** 791
140. A Hara, Y Oishi, M Kakimoto, et al. *Polymer Prepr. Jpn.*, 1987, **36** 316
141. H R Kricheldorf, J Engelhardt *J. Polym. Sci., Polymer Chem. Ed.*, 1990, **23** 2335
142. H R Kricheldorf, D Lübbers *Makromol. Chem., Rapid Commun.*, 1990, **11** 261
143. T Kaneda, S Ishikawa, H Dainan, et al. *Makromol. Chem.*, 1981, **183** 417
144. T Kaneda, S Ishikawa, H Dainan, et al. *Makromol. Chem.*, 1981, **183** 433
145. W Heitz, P Strohriegl, BRD P. 3 400 236
146. W Heitz, P Strohriegl, BRD P. 3 400 237

147. P Strohriegl, W Heitz, G Weber *Makromol. Chem., Rapid Commun.*, 1985, **6** 111
148. S Ogata, M Kakimoto, Y Imai *Makromol. Chem., Rapid. Commun.*, 1985, **6** 835
149. V A Vasnev, A L Rusanov, M L Keshtov, et al. *Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii* (The Chemistry and Technology of High-Molecular-Weight Compounds), Moscow, 1987, p. 3 [*Itogi Nauki i Tekhniki* (Advances in Science and Engineering), Vol. 23]
150. R D Katsarava *Usp. Khim.*, 1989, **58**(9) 1549 [English translation in *Russ. Chem. Rev.*, 1989(9)]
151. T Yoshida, T Arai, Y Mukai, et al. *Carbohydr. Res.*, 1988, **177** 69
152. H S-I Chao, P P Policastro *J. Polym. Sci., Polym. Lett. Ed.*, 1986, **24** 253
153. R Dunsing, H R Kricheldorf *Eur. Polym. J.*, 1988, **24** 145
154. S Murahashi, S Nozakura, M Sumi *J. Polym. Sci.*, 1965, **3B** 245
155. K Nagai, K Asada, K Chiba, et al. *J. Polym. Sci., Polym. Chem. Ed.*, 1989, **27** 3779
156. K Nagai, K Chiba, K Asada, et al. *Polym. Sci., Polym. Chem. Ed.*, 1990., **28** 2195
157. R D Katsarava, D P Kharadze *Usp. Khim.*, 1992, **61**(1) 161 [English translation in *Russ. Chem. Rev.*, 1992(1)]
158. K Nagai, K Asada, N Kuramoto *J. Polym. Sci., Polym. Chem. Ed.*, 1990, **28** 2845
159. S B Shustov, L M Bochkarev, S M Zhil'tsov, et al. *Biokhimicheskie Osnovy Zashchity Promyshlennykh Materialov ot Biopovrezhdenii* (Biochemical Principles of the Protection of Industrial Materials from Biological Damage), Gorky, 1987, p. 45; *Ref. Zh. Khim.*, 1988, 5S533
160. J D Citron, US P. 4 771 116 1988
161. G G Brownell, M K Hays, A J Sivak, US P. 4 916 248; *Chem. Abs.*, 1990, **113** 232 235
162. G Greber, R Darms, Swiss. P. 549 068; *Chem. Abs.*, 1972, **77** 2165 517
163. S V Rogozhin, Yu A Davidovich, S M Andreev, et al., USSR P. 449 082; *Byul. Izobret.*, 1974, (41)
164. E Jacobi, H Schuttenberg, R C Schulz *Makromol. Chem., Rapid. Commun.*, 1980, **1** 397
165. T F DeRosa, R Jennejahn *J. Polym. Sci., Polym. Chem. Ed.*, 1990, **28** 2445

Translated from *Uspekhi Khimii* **61** 1185–1223 (1992) U.D.C. 541.124; 541.127

Modern theories of chemical reactions in condensed phases

M V Bazilevskii, V I Faustov
Karpov Physicochemical Institute, Moscow
Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow

ABSTRACT. The review is devoted to theoretical studies of the dynamics of chemical reactions in condensed phases. The fundamental differences in the description of the kinetics of gas-phase and liquid-phase reactions are demonstrated. The principal approaches, developed in the theory of liquid-phase reactions, are examined in detail: numerical modelling by Monte Carlo and molecular dynamics methods; numerical and analytical study of stochastic Langevin equations, the Fokker–Planck equation, and the kinetic Bohm–Gross equation. The possibilities and limitations of the modern theory are demonstrated in relation to examples of calculations of rate constants for specific isomerisation, substitution, addition, and electron transfer reactions.

The bibliography includes 114 references.

Contents

I. Distinctive features of the dynamics of liquid-phase reactions 651
II. Numerical modelling methods 653
III. Stochastic dynamics 659
IV. Examples of the application of stochastic models 663
V. Dynamics of multidimensional stochastic systems, Non-equilibrium solvation and its kinetic consequences 668
VI. Certain problems and prospects 670

The dynamics and kinetics of elementary chemical processes in condensed media constitute an important aspect of theoretical chemistry. It has developed vigorously during the last decade. The methodology for and calculations of potential energy surfaces and gas-phase reaction rate constants as well as dynamic calculations were developed in the previous decade on the basis of powerful computational techniques. Towards the end of the 1970's, the principal methodological aspects and problems of the gas-phase theory were exhausted and the interest of investigators shifted to the region of liquid-phase and solid-phase reactions.

This article deals with the present state of the problem. Without aiming at a complete survey of the literature, we concentrated attention on key factors in order to give the reader an idea, at an elementary level, about the advances in the theory and in its applications at the present time. Several reviews dealing with reactions in the condensed phase from current theoretical standpoints have been published.[1–7] Together with more specialised reviews, which will be quoted in the course of further exposition, they contain a complete bibliography.

Our exposition is restricted to reactions in non-ordered condensed media, primarily in molecular liquids, and only to those reactions whose dynamics can be adequately described within the framework of classical mechanics. Only processes occurring in the kinetic regime are described, i.e. diffusion kinetics are excluded. This in fact represents the situation, of fundamental importance for chemistry, where the medium influences directly the chemical step. New approaches and concepts, which are the subject of the present article, have been developed in this field.

I. Distinctive features of the dynamics of liquid-phase reactions

Under the influence of the medium, the rates of reactions can vary within a wide range. There exist fairly numerous chemical systems in which the interaction with the medium is weak. As a rule, these are reactions which occur in non-polar solvents under the usual conditions (room temperature, normal pressure). As a typical example, we shall quote data on the dimerisation of cyclopentadiene. Table 1 shows that different solvents hardly alter the Arrhenius parameters determined for the gas phase. There exist extensive experimental data also for other reactions. The established point of view is that, in the absence of polar effects, the liquid-phase reactions are usually faster by a factor of 2–5 compared with the gas phase and these slight differences between the rate constants are insufficient to detect reliably differences between the Arrhenius parameters in the gas phase and in solution and also when different non-polar solvents are compared.

One may quote an example of the opposite kind. For ionic reactions in polar solvents, i.e. for systems with a strong interaction, the rate constant is sometimes smaller by 10–20 orders of magnitude compared with the gas phase. There are well known S_N2 nucleophilic substitution reactions (Fig. 1) where the unusual gas-phase two-well PES profile is converted for an aqueous solution into a potential curve with a barrier (free energy profile),[10] which is familiar to chemists, while the activation energy increases from several units to 10–20 kilocalories per mole. However, the last example illustrates merely a change in the energetics of the elementary chemical process and at first sight does not require a revision of the principles governing its theoretical description. This aspect is not very interesting from the standpoint of the present review, whose subject is new approaches and concepts. S_N2 reactions will be examined below from new idealogical standpoints.

The transition state (TS) theory provides the standard method for the theoretical description of gas-phase reactions. The expression for the rate constant is

$$K = \kappa \frac{kTF^{\neq}}{hF^{(0)}} \exp(-\Delta U^{*}/kT), \qquad (1.1)$$

where k and h are the Boltzmann and Planck constants, T is the absolute temperature, $F^{\neq}$ and $F^{(0)}$ are the partition functions of the transition state and the reactants, and $\Delta U^{\neq}$ is the activation energy, usually identified with the height of the potential barrier on the PES.

Table 1. Experimental Arrhenius parameters and rate constants for the dimerisation of cyclopentadiene.

Medium	T, K	lg A (litre mol^{-1} s^{-1})	E_a, kcal mol^{-1}	lg$K$ (25 °C)
Gas phase	353–423	6.11	16.7	
	393–467	4.93	14.9	
	405–455	6.77	16.9	
Non-polar solvents				
C_6H_6	258–358	6.10	16.4	6.06
CCl_4	273–328	6.70	17.1	6.15
	273–295	5.90	16.2	6.00
paraffin	273–445	7.10	17.4	6.31
CS_2	273–308	6.20	16.9	7.80
	273–295	5.57	17.7	7.43
cyclopentadiene	271–308	5.80	16.2	7.90
	273–331	5.57	16.8	7.82

Note. The original literature on gas-phase reactions is quoted by Hynes[1] and the literature on liquid-phase reactions is quoted by Denisov.[9]

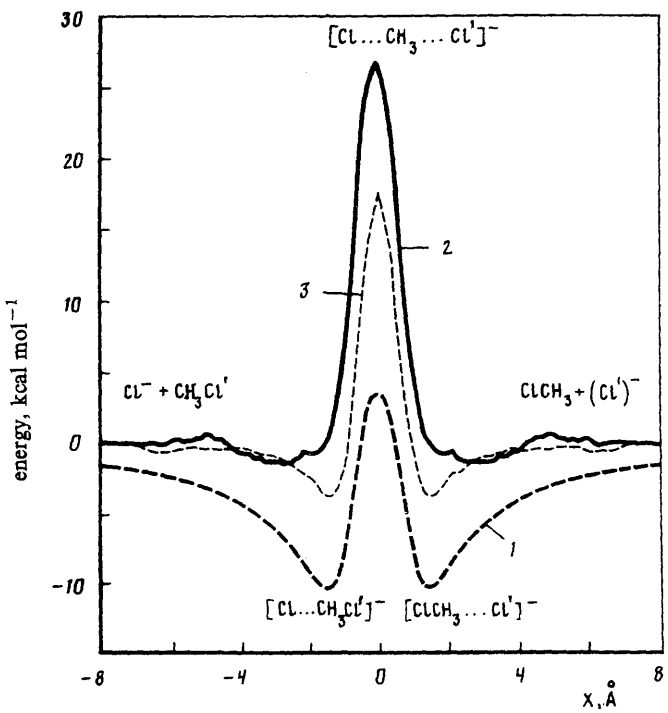


Figure 1. The calculated potential energy profile in the gas phase (curve *1*) and the free energy profile in water (curve *2*) and dimethylformamide (curve *3*) for an S_N2 reaction: $Cl^- + CH_3Cl'$.[10] The difference between the C–Cl and C–Cl′ distances is the reaction coordinate X.

The transmission factor $\varkappa$ cannot be calculated within the framework of the transition state theory and is usually assumed to be unity. The partition function is as a rule calculated in terms of the "harmonic oscillator–rigid rotator" approximation. It is useful to examine specially the isomerisation reactions (transition in a two-well system). Only the oscillator degrees of freedom change significantly in such reactions and, in terms of the classical approximation, the ratio of the partition functions is equal to the ratio of the products of the vibration frequencies ω at the minima for the reactants ($\omega_\nu^{\neq}$) and in the transition state (ω_ν^0) (ν = 0, 1, 2, ..., N):

$$K = \varkappa \frac{\Omega}{2\pi} \prod_{\nu=0}^{N} \frac{\omega_\nu^0}{|\omega_\nu^{\neq}|} \exp\left(-\Delta U^{\neq} / kT\right). \qquad (I.2)$$

The transition state frequencies include the purely imaginary frequency $\omega_0^{\neq} = i\Omega$. The modulus in the denominator of Eqn. (I.2) is necessary in order to eliminate the imaginary unity. A decomposition mode is known to correspond to the imaginary frequency, such modes being found by solving a standard vibrational problem in the vicinity of the saddle point on the PES.

For liquid-phase reactions with strong interaction, the harmonic approximation is inapplicable in principle.

We shall consider the S_N2 reaction already mentioned, for example:

$$\underset{\text{reactants}}{Cl^- + CH_3Cl} \rightarrow \underset{\text{TS}}{[Cl \cdots CH_3 \cdots Cl]^-} \rightarrow \underset{\text{products}}{ClCH_3 + Cl^-}. \qquad (I.3)$$

It is assumed that the reaction proceeds in the kinetic regime, i.e. the reactants in Eqn. (I.3) are in a solvent cage, their diffusion into the cage constituting a fast stage which does not affect the kinetics. Thus the reacting system is surrounded by a solvation shell consisting of a large number of molecules, the influence of which on the reaction has to be taken into account. The orientation motion of each solvent molecule is relatively free. It is found that the solvation shell has a multiplicity of configurations which correspond to different orientations of the solvent molecules. A minimum on the PES corresponds to each configuration; there is a set of minima with approximately equal energies separated by a low barrier (of the order of kT at room temperature). Rapid transitions occur between them and there are no grounds for differentiating any one of them as the "reactants minimum". Likewise in the region of the transition state there exists a set of first-order saddle points separated by higher-order saddle points whose relative height is of the order of kT and they must all be considered on an equal basis. This fundamentally anharmonic situation entails the breakdown of the usual ideas of the gas-phase theory, according to which its single minimum on the potential energy surface corresponds to the reactants and a single saddle point corresponds to the transition state.

Detailed study of each of the configuration minima of the solvation shell loses significance. The local frequencies corresponding to them have no direct bearing on the rate of the chemical reaction. An average description of the influence of the entire assembly of the configurations of the solvation shell on the reaction in the chemical subsystem (I.3) is necessary. This is formally achieved by a transition from the PES to the free energy surface (FES) with the corresponding modification of Eqn. (I.1):

$$K = \varkappa \frac{kT}{h} \exp(-\Delta G^{\neq}/kT), \qquad (I.4)$$

where $\Delta G^{\neq}$ is the height of the barrier on the FES. The use of Eqn. (I.4) presupposes the calculation of the anharmonic partition functions in Eqn. (I.1). The method for the theoretical description is then radically altered. For a gas-phase reaction, the central feature was the quantum-chemical calculation of the PES and the search for stationary points on the latter: the minima for the reactants and products as well as the saddle point corresponding to the transition state. This was sufficient to determine the activation energy as the height of the potential barrier and to establish the reaction mechanism. The dynamic calculations necessary for the evaluation of the pre-exponential factor reduced to the solution of the standard vibrational problem. After this, the dynamic calculation of the transmission factor, which is possible in principle, was assumed to be superfluous in the majority of applications. In order to find the activation energy and to establish the mechanism of reaction (I.3) in a polar medium, one has to construct the free energy profile. Thus the calculation of the anharmonic partition functions comes to the fore. As a rule this is a calculation by the Monte Carlo method.

The next stage is the calculation of the transmission factor $\varkappa$ by the method of molecular dynamics. One has to bear in mind that for a liquid-phase reaction the calculation of the transmission factor is more fundamental than for a gas-phase reaction. In the latter case, the decomposition mode, along which the reaction coordinate is directed at the saddle point on the PES, is chosen by the optimisation procedure as a result of the solution of the vibrational problem. On the other hand, the FES profile for a liquid-phase reaction is constructed as a rule along the reaction coordinate for the chemical subsystem found without taking into account the medium. When there is a strong interaction between the chemical subsystem and the medium, there are no grounds for the assumption that the coordinates of the medium (i.e. the orientation motions of the solvent molecules) do not contribute to the decompositon mode. Thus in the calculation of the FES profile the mode is not chosen by the optimum method. This constitutes an additional cause of the decrease in the transmission factor, which is characteristic only of a liquid-phase calculation.

II. Numerical modelling methods

The development of the computer technique, has made possible the direct modelling of systems comprising several hundreds of particles interacting in accordance with the laws of classical mechanics. The required values are calculated as averages over a large number of instantaneous configurations. Under certain conditions, such a model system describes successfully the properties of real microscopic objects. This is the essential feature of the method of molecular dynamics (MD).[11] The second approach in numerical modelling—the Monte Carlo (MC) method[11,12]—starts with the fundamental postulates of classical equilibrium statistical mechanics. It represents a procedure for calculating the average values $<A>$ of the observed quantity $A(\mathbf{r})$ for an equilibrium ensemble comprising n particles. Here $\mathbf{r}$ is the vector of the coordinates of the particles (r_1, r_2, r_3, ..., r_N). For example, in the case of a canonical ensemble, we have

$$<A> = \frac{\int A(\mathbf{r})\exp[-U(\mathbf{r})/kT]d\mathbf{r}}{\int \exp[-U(\mathbf{r})/kT]d\mathbf{r}}, \qquad (II.1)$$

where $U(\mathbf{r})$ is the potential function of the interaction.

A common feature of the method of molecular dynamics and the Monte Carto method is the absence of conceptual differences betweem them in the description of the interaction within the chemical subsystem, the interactions of the chemical subsystem with the molecules of the medium, and the interactions between the molecules of the medium themselves. The entire information about the system is included in the parameters of the classical particle interaction potentials and also in the masses of the particles in the method of molecular dynamics. By virtue of this factor, both methods are suitable, in principle, for the investigation of reactions occurring in any state of aggregation (gas, liquid, or solid) and for any densities and temperatures.

The test system is placed in a cell, which is frequently cubical or octahedral in shape. The system consists of molecules of the reactants and the solvent and their number ranges from several tens to several hundreds. Periodic boundary conditions are imposed on the cell, i.e. it is assumed that it is surrounded on all sides by exact copies. If in the course of modelling any one particle leaves the cell through one of its walls, then a similar particle from a neighbouring cell enters it through the opposite wall in the same direction (and with the same momentum in the method of molecular dynamics). This approach reduces to a minimum the edge effects and when the calculations are performed for a comparatively small number ($\sim 10^2$) particles, makes it possible to model successfully the properties of macroscopic systems containing $\sim 10^{23}$ particles.

The observed quantities are calculated as averages over a large number ($\sim 10^5 - 10^6$) of instantaneous configurations of this system. In the Monte Carlo method, the configuration is determined by the set of coordinates $\mathbf{r}$, while in the method of molecular dynamics it is determined by the set of coordinates $\mathbf{r}$ and the momenta $\mathbf{p}$ of the particles (the molecules of reactants and the medium) in the cell. Both methods were developed and have been widely used in relation to equilibrium chemical systems and have begun to be employed only recently in the study of the dynamics of chemical reactions. Studies on equilibrium chemical systems have shown that, despite the serious simplifications characteristic of the molecular dynamics and Monte Carlo methods (the ergodic hypothesis and the restrictions imposed on the number of particles in the cell and on the modelling time), both methods make it possible to calculate with satisfactory accuracy, using only the microscopic characteristics of the system (the interparticle interaction potentials and the masses of the particles), the equilibrium macroscopic characteristics of real chemical systems (heat capacity, density, equilibrium constants, etc.). Calculations by the Monte Carlo method are more economical as regards computer time than modelling of the same system by the method of molecular dynamics. On the other hand, the Monte Carlo method is applicable, because of its very nature, only to equilibrium systems. Therefore, in the study of the dynamics of chemical reactions in condensed phases the FES characteristics are calculated in the first stage by the Monte Carlo method and the rate constant is determined within the framework of the equilibrium transition state theory, while the transmission factor $\varkappa$ is calculated (but not always) in the second stage by the method of molecular dynamics. We shall consider both methods in greater detail, emphasising their applications to the dynamics of chemical reactions.

1. The Monte Carlo method

A random sequence of configurations of the system $\{\mathbf{r}_j\}$ is used in the Monte Carlo method.[11,12] Their energies obey the Boltzmann distribution $\exp[-U(\mathbf{r}_j)/kT]$ and Eqn. (II.1) is replaced by the average over the configurations realised:

$$<A> = \frac{1}{M}\sum_{j=1}^{M} A\{\mathbf{r}_j\}, \qquad \text{(II.2)}$$

where M is the number of configurations. The random sequence $\{\mathbf{r}_j\}$, sometimes called the trajectory of the Monte Carlo method, is generated with the aid of the Metropolis algorithm. The Metropolis algorithm and the details of the Monte Carlo method in relation to equilibrium chemical systems have been described in detail.[7,11,12] The texts of the Fortran and Basic programs, which employ the Monte Carlo method for equilibrium[13,14] and non-equilibrium[12] systems, have been published.[12–14] We shall consider below only the versions of the Monte Carlo method applicable to calculations for chemical reactions. The majority of the points on the Monte Carlo trajectory correspond to the configurations with energies close to the minimum value, precisely the configurations which make the main contribution to the partition functions used in the calculations of the equilibrium characteristics of the system. This approach is relatively ineffective in the calculation of the free energy of activation $\Delta G^{\neq}$.

We are interested in the free energy changes along the reaction coordinate x. In principle, they can be determined by averaging the probability of realising different values of x along the Monte Carlo trajectory. The distribution function $g(x)$, which yields the dependence of the free energy on x to within an additive constant C, is usually calculated:

$$G(x) = -kT\ln[g(x)] + C. \qquad \text{(II.3)}$$

The quantity $G(x)$ defined in this way is sometimes referred to as the average force potential. In order to achieve satisfactory statistics of the values in the vicinity of the transition state with a coordinate $x = x^{\neq}$ and a relative potential energy $\Delta U^{\neq}$, the Monte Carlo trajectory must pass fairly frequently through regions of the configuration space whose energies relative to the reactants minimum are close to $\Delta U^{\neq}$. The probability of the occurrence of such configurations for points on the Monte Carlo trajectory is proportional to $\exp(-\Delta U^{\neq}/kT)$ i.e. it is negligible when $\Delta U^{\neq} \gg kT$. In the usual version of the Monte Carlo method, it would therefore be either necessary to generate an extraordinarily long sequence of configurations or to be content with a very rough estimate of $G(x)$. There are two main ways of obviating this difficulty. The first is called the method of importance sampling[10,12] and the second is referred to as the statistical theory of perturbations.[10,13]

The method of importance sampling involves the imposition of an artificial external potential V, which "forces" the Monte Carlo trajectory to remain for most of the time in the region with the value of x in which we are interested. The potential V usually has a constant negative value within the range $(x - \Delta/2, x + \Delta/2)$ and is zero outside it. A sequence of configurations with a non-Boltzmann distributon of probabilities $\exp[-(U + V)/kT]$ is then generated and most of the points on the resulting Monte Carlo trajectory correspond to the range $(x - \Delta/2, x + \Delta/2)$. Within the range indicated, the relative probabilities of different values of V obey the Boltzmann distribution.

The imposition of the external potential V creates, as it were, a "window" which makes it possible to see the distribution of the probabilities of the values of x along the given section of the reaction coordinate. By carrying out a series of Monte Carlo calculations with window potentials V_j centred on different sections of the reaction coordinates which must partly overlap, we find for each window i its own distribution function $g_i'(x)$. The true distribution function $g(x)$ in the ith interval $(x - \Delta/2, x + \Delta/2)$ is related to distribution function in the corresponding window by the formula $g(x) = C_i g_i'(x)\exp(V_i/kT)$, where C_i is a normalised constant. The constants C_i are determined from the condition of the continuity of $g(x)$. By joining together the functions $g_i'(x)$ calculated for different intervals i, we obtain a single function $g(x)$ embracing the entire range of variation of x—from the reactants to the transition state.

An alternative to the importance sampling method is the statistical perturbation theory.[10,12,15] It is based on the formula:

$$G(H_0 + H_1) - G(H_0) = -kT\ln <\exp(-H_1/kT)>_0, \qquad \text{(II.4)}$$

where H_0 is the Hamiltonian of the initial system, H_1 is the perturbation, and the averaging $<\ldots>_0$ is carried out with respect to the distribution of the initial system. When applied to the Monte Carlo method, this means that trajectories corresponding to the Hamiltonian H_0 are generated. The expansion of the exponential function $\exp(-H_1/kT)$ in Taylor's series corresponds to the thermodynamic perturbation theory. In the calculation of the free energy profile, the configuration of the reactants minimum might be adopted as the initial system assuming that the non-equilibrium configurations along the reaction coordinate up to the transition state are perturbed systems. Eqn. (II.4) yields the exact computational algorithm, but, if the perturbation H_1 is large, the calculations converge slowly. The calculation is therefore carried out by scanning along x in several stages, so that in each step an acceptably small perturbation is achieved. The calculation requires careful optimisation of the length of the step and is refined in each step by the alternate replacement of the initial and final configurations.

The practical execution of the program for the evaluation of the free energy of activation in solution throughout the entire volume has been achieved for the simplest S_N2 substitution reaction [Eqn. (I.3)][16] and for the nucleophilic addition of OH^- to $H_2C{=}O$.[17] We shall consider the principle stages in the calculations and we shall discuss the results in relation to reaction (I.3).

1. The gas-phase reaction pathway corresponding to the potential energy minimum in the cross-section, i.e. the gas-phase reaction coordinate, was determined in the first stage with the aid of non-empirical quantum-chemical calculations. The parameters of the empirical analytical potential, describing the interaction in the chemical system along the reaction coordinate x, were selected.

2. Quantum-chemical calculations for the interaction of the reacting system with a single solvent molecule were carried out in the second stage for different values of x and the parameters of the solvent–reacting system interaction potentials were evaluated as functions of x. The potentials of the interaction between the solvent molecules had been calibrated previously.

3. The one-dimensional average force potential was calculated in the third stage by the importance sampling method and the activation energy $\Delta G^{\neq}$ was calculated with its aid.

Specific calculations have been carried out for two polar solvents—water and dimethylformamide (DMF).[16] The potential and free energy curves obtained are presented in Fig. 1. Evidently the section through the FES calculated for an aqueous medium has little in common with the gas-phase potential energy curve. On passing from the gas phase to the aqueous solution, the minima corresponding to the pre-reaction and post-reaction ion–dipole complexes vanish almost completely and the height of the activation barrier increases from 4 to 26 kcal mol^{-1}. For the reaction in DMF, the differences from the gas phase are not so large. The activation barrier increases to 18 kcal mol^{-1} and, in addition, in DMF there are distinct although not quite so deep as in the gas phase, minima for the ion–dipole complexes. The latter factor is important, since it requires a revision of the traditional ideas concerning the single-stage mechanism of the S_N2 reactions in solutions occurring without the formation of intermediates.

Similar results have been obtained[18,19] for the S_N2 reaction in a polar medium using semiempirical quantum-chemical approaches in the stage involving calculations for the interactions in the chemical subsystem and partly the interactions between the chemical subsystem and the solvent molecules in combination with the statistical perturbation theory in the stage involving the calculation of the free energy.

2. The method of molecular dynamics

Despite the apparently self-evident nature of the molecular dynamics method and the simplicity of the underlying idea, the theoretical aspects of its numerical application merit examination. It is known[20] that the differential equations of motion in the method of molecular dynamics with the intermolecular interaction potentials normally employed are locally unstable. This means that the solutions corresponding to similar initial conditions can differ very greatly. The numerical solution of the equations of motion inevitably introduces an error, which can be treated as a change in the initial conditions. It is therefore important to analyse the dependence of the results of the modelling on the characteristics of the system and on the selected algorithm for the solution of the dynamic equations. In estimating the errors of numerical methods, one usually compares the results of computer calculations carried out with the accuracy of the arithmetical operations and with twice such accuracy.

In the case of molecular dynamics, it is possible to estimate directly the accuracy of the method on the basis of the invariance of Newton's equations relative to changes in the sign of the time. The calculated trajectories for a specific time interval with subsequent inversion at the final point of the signs of the momenta of all the particles and the calculation of the trajectory of the reverse motion should lead to the initial point in the phase space. In reality, numerical calculation does not lead to the return to the exact starting point and the differences obtained between the initial and final points constitute an estimate of the accuracy of solving the equations of motion.

Systematic studies[20] on the forward and reverse trajectories for systems with a short-range interaction potential (Lennard-Jones) have led to a series of important conclusions concerning the errors in numerical modelling by the method of molecular dynamics. Analysis of the accumulated errors led to the conclusion that the results of the molecular dynamic experiment resemble in many respects the solutions of the stochastic Langevin equation, which will be examined in detail in the next Section. For short modelling times, the standard errors of the coordinates and momenta of the particles vary linearly with time, the duration of the linear interval depending on the algorithm for the solution of the differential equations, in particular on the degree of the equation fitted to the function to be integrated. With increase in the modelling time, the system becomes stochastic and the error of the calculation is found to depend solely on its physical characteristics and not on the numerical application of the method of molecular dynamics. The error is expressed in this case in terms of the entropy of the system by the Krylov–Kolmogorov procedure.[20]

The existence of errors in the method of molecular dynamics leads to a randomly migrating trajectory in a layer with a thickness ΔE resembling the trajectory of the Monte Carlo method. This means that the modelling in the method of molecular dynamics, formally carried out for a microcanonical ensemble taking into account the random scatter of the values of ΔE, possesses features of averaging with respect to a canonical ensemble. Thus the numerical application of the method of molecular dynamics introduces a series of fundamental factors which infringe the deterministic nature of the initial equations and which render the method of molecular dynamics similar to other approaches used in the modelling of multiparticle systems—the Monte Carlo method and stochastic equations. It is useful to bear these considerations in mind in comparing the results of various approaches to the description of the kinetics of chemical reactions in a condensed phase.

3. Calculation of the transmission factor by the reaction flux method

We shall consider how the complete dynamic theory, free from the limitations of the approximation of the transition state theory, is formulated within the framework of classical dynamics.[12,21] The idea of a "critical surface" in the configuration space, separating regions of the reactants and products, is introduced as a basis. The reaction coordinate x is normal to the surface. If this coordinate is known, then the equation of the surface in the vicinity of the transition state can be formulated as follows:

$$x = x^{\neq}. \tag{II.5}$$

The simplest and commonest is the selection of the top of the barrier on the FES profile as the coordinate $x^{\neq}$.

Another important factor is the introduction of the characteristic function

$$\eta[x(t)] = \begin{cases} 1 \text{ when } x(t) > x \\ 0 \text{ when } x(t) < x^{\neq} \end{cases} \tag{II.6}$$

i.e. η is a power function. It is a function of time and a functional of the classical trajectory $x(t)$. The starting point of the trajectory at $t = 0$ is selected on the critical surface. The distribution of the initial conditions is assumed to correspond to equilibrium. In particular, the initial rates $\dot{x}(t = 0)$ are taken from the equilibrium (Maxwell) distribution. In the course of dynamic evolution, the trajectory can intersect repeatedly the critical surface but ultimately, at $t \to \infty$, it always remains either in the reactants region or in the products region. In the former case

$$\eta[x(t)] = 1 \text{ when } t \to \infty, \tag{II.7}$$

while in the latter

$$\eta[x(t)] = 0 \text{ when } t \to \infty. \tag{II.8}$$

The conditions (II.7) and (II.8) can hold only in a multidimensional system (strictly speaking a macroscopic system), since otherwise even at $t\to\infty$ transitions from the reactants to the products region and conversely are inevitable on a two-well FES.

The classical rate constant is calculated from the equation

$$K = \lim_{t\to\infty}\left\langle \delta\left(x - x^{\neq}\right)\dot{x}(t=0)\,\eta\left[x(t) - x^{\neq}\right]\right\rangle. \qquad \text{(II.9)}$$

The angular brackets denote averaging with respect to the equilibrium distribution i.e. correspond to the equilibrium initial conditions on the critical surface. It can be shown that in the limit $t\to 0$ this average value reduces to the rate constant in terms of the approximation of the transition state theory:

$$K_{TS} = \lim_{t\to 0}\langle \delta(x^{\neq} = x)\,\dot{x}(t=0)\eta[x(t) - x^{\neq}]\rangle =$$

$$= \langle \delta(x = x^{\neq})\,\dot{x}(t=0)\eta\,\dot{x}(t=0)]\rangle .$$

We used the fact that $x(t) - x = t\dot{x}(t = 0)$ when $t\to 0$. Consequently the transmission factor $\varkappa$ is

$$\varkappa = \frac{\lim_{t\to\infty}\langle \delta(x = x^{\neq})\dot{x}(t=0)\eta[x(t) - x^{\neq}]\rangle}{\langle \delta(x - x^{\neq})\dot{x}(t=0)\eta[\dot{x}(t=0)]\rangle} . \qquad \text{(II.10)}$$

In fact, the calculation of the transmission coefficient reduces to studying an ensemble of the trajectories $x_i(t)$ with equilibrium initial conditions on the critical surface. In calculating the contributions of the trajectories to the transmission factor, one should take into account correctly their direction and the sign of the initial rate. Various recipes have been proposed for this purpose.[5,21–25] We shall consider one of them. For all the trajectories, the initial rate $\dot{x}(t = 0) = \dot{x}$ is positive. The trajectories extend both into the future ($t > 0$, $t\to\infty$) and into the past ($t < 0$, $t\to-\infty$). The evolution of each trajectory can be traced for a fairly long time (in practice for ~3 ps). After this, a characteristic multiplier Q_i is attributed to each trajectory $x_i(t)$:

$$Q_i = 1, \text{ when } t>0 \;\; x_i > x^{\neq} \text{ at } t\to\infty ,$$

$$Q_i = -1, \text{ when } t<0 \;\; x_i > x^{\neq} \text{ at } t\to-\infty , \qquad \text{(II.11)}$$

$$Q_i = 0 \begin{cases} \text{when } t>0 \; x_i < x^{\neq} \text{ at } t\to\infty , \\ \text{when } t<0 \; x_i < x^{\neq} \text{ at } t\to-\infty . \end{cases}$$

The trajectories with $Q_i = 1$ are reaction trajectories, while those with $Q_i = 0$ are non-reaction trajectories. The trajectories with $Q_i = -1$ may be called anti-reaction trajectories since their contribution is subtracted from the total reaction flux. One can write for the transmission factor

$$\varkappa = \frac{\Sigma_i W_i \dot{x}_i Q_i}{\Sigma_i W_i \dot{x}_i} , \qquad \text{(II.12)}$$

where W_i is the Maxwellian weighting factor.

4. Examples of calculations by the method of molecular dynamics

The first reaction in a condensed phase for which it was possible to carry out direct calculations of the rate constant by the method of molecular dynamics was the *gauche–trans* isomerisation of n-butane in liquid CCl_4.[26] The molecular dynamics calculations were performed for a unit cell containing a n-butane molecule and 122 CCl_4 molecules. The modelling conditions corresponded to a temperature of ~300 K. The interactions of the solvent molecules with one another and with the solute were described by the Lennard-Jones potentials. The CCl_4 molecules were assumed to be spherically symmetrical, while the n-butane molecule was assumed to consist of a chain of four Lennard-Jones spheres rotating about the central axis.

The calculations were performed for two models of the medium: a liquid solvent with moving CCl_4 molecules and a "frozen" vitreous solvent, in which the positions of the CCl_4 molecules were fixed in one of the equilibrium configurations obtained by the Monte Carlo method. The time variation of the rate of reaction $K(t)$ and the transmission factor $\varkappa = K(t)/K(0)$ were calculated by the reaction flux method using the formula (II.12).[21] Here $K(0)$ is calculated in the initial instant and, as shown above, agrees with the rate constant in the transition state theory.

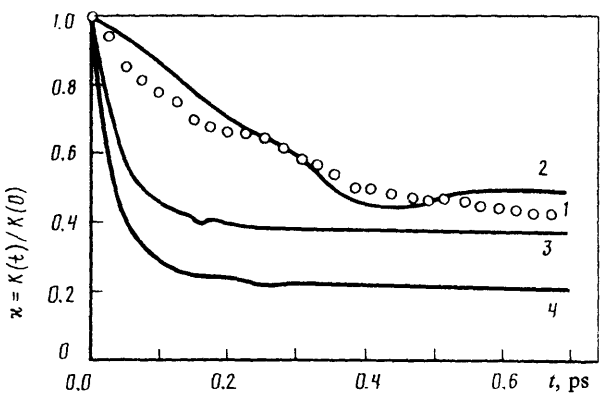


Figure 2. Time variation of the transmission factor $\varkappa = K(t)/K(0)$ calculated from Eqn. (II.12) by the method of molecular dynamics (curve *1*) and the method of stochastic dynamics (curves *2–4*) based on the kinetic Bohm–Gross equation (see text) for the isomerisation of n-butane in liquid CCl_4:[28] (*2*) $\nu = 0.2 \times 10^{13}$ s^{-1}; (*3*) $\nu = 4.0 \times 10^{13}$ s^{-1}; (*4*) $\nu = 10.0 \times 10^{13}$ s^{-1}.

The calculated relations are presented in Fig. 2. The points were obtained by numerical modelling and the continuous lines are a result of the solution of the stochastic equation (subsection II.5). The form of the curves obtained for the liquid and vitreous solvents is completely analogous. In both cases the $K(t)/K(0)$ curve reaches a plateau almost at the same time. The existence of the plateau makes it possible to consider the existence of a rate constant for the given reaction. The transmission factor in the region of the plateau for the liquid solvent ($\varkappa = 0.361$) does not differ greatly from the value $\varkappa = 0.276$ obtained for the vitreous solvent. This can be

partly explained by the fact that the mass of the solvent molecules is much greater than the mass of the n-butane units: $m_{CH_4}/m_{CCl_4} = 0.11$. The small molecules therefore move much more slowly than the methyl groups of n-butane.

One of the problems for the solution of which the application of the method of molecular dynamics is most fruitful is that of testing the applicability of the approximate models describing the influence the medium on the rate of reaction. Calculations for the chair–boat type of isomerisation of cyclohexane are instructive in this sense.

It was observed at the beginning of the 1980's[28,29] that the rate of isomerisation of cyclohexane increases with increase in pressure. The experimental pressure dependence of the free energy of activation, which determines the pressure dependence of the rates within the framework of the transition state theory, proved to be too weak to account for the observed relation. Calculation[30] by the method of molecular dynamics within the framework of the stochastic model (see the next Section) reproduced the observed effect.

The reason for the discrepancy between the predictions of the transition state theory and the stochastic calculation was elucidated by the Monte Carlo and molecular dynamic methods.[31] The modelling was carried out for the cyclohexane molecule in a cell containing 250 CS_2 molecules. An empirical intermolecular potential, which satisfactorily reproduced the geometry and conformational properties of the cyclohexane, was used. The solvent–solvent and solvent–cyclohexane intermolecular interactions were described by Lennard-Jones potentials. The energy of the system corresponded to a temperature of 300 K and the density (ρ = 1.0, 1.3, 1.4, and 1.5 g cm^{-3}) corresponded to the experimental pressure range. The calculations of the free energy of activation $\Delta G^{\neq}$ by the Monte Carlo method using window potentials showed that an increase in density from 1.0 to 1.5 g cm^{-3} does not alter $\Delta G^{\neq}$ to within the accuracy determined by the statistical scatter. A more detailed allowance for the influence of the medium at ρ = 1.5 g cm^{-3} yielded a positive contribution of solvation to the activation barrier, amounting to 0.08 $\pm$ 0.02 kcal mol^{-1}. This means that, according to the transition state theory, the rate of reaction should diminish only slightly with increase in pressure. The molecular dynamic calculation demonstrated that, on the contrary, the transmission factor $\varkappa$ increases from 0.34 to 0.47 with increase in density, which in fact produces an increase in the rate of reaction.

The establishment of the theory of gas-phase reactions, in particular the transition state theory, was in many respects based on theoretical and experimental studies of the substitution reaction:

$$A + BC \rightarrow AB + C, \qquad (II.13)$$

which is the simplest chemical reaction in which bonds are simultaneously ruptured and formed. Reactions (II.13) proved to be suitable for the elucidation of the mechanism of the elementary chemical step and the fundamental concepts of theoretical chemical kinetics were in fact first formulated in relation to these processes as an example. An enormous amount of experimental data, obtained in the gas and liquid phases, has accumulated for substitution reactions, indicating a wide variety of their mechanisms. These factors explain the interest in the study of reactions (II.13) by various theoretical methods, including the method of molecular dynamics.[32–34]

In the initial version,[32] the hypothetical reaction

$$X + X_2 \rightarrow X_2 + X \qquad (II.14)$$

was modelled in a cell containing 100 atoms of the medium [an inert gas (He, Ar, or Xe) with the density corresponding to the liquid state]. The interaction in the chemical subsystem X_3 was described by the London–Eyring–Polanyi–Sato (LEPS) potential, usually employed in theoretical studies on the gas-phase reactions involving triatomic sytems.

Three series of calculations were performed with the parameters of the LEPS potential corresponding to barrier heights of 20, 10, and 5 kcal mol^{-1} and frequencies of the decomposition mode at the top of the barrier of 419, 288, and 168 cm^{-1} respectively. The chemical subsystem–solvent and solvent–solvent interactions were described by the Lennard-Jones potentials. In calculations with high gas-phase activation barriers (20 and 10 kcal mol^{-1}), not one case of a repeated intersection of the critical surface by trajectories was observed. All the trajectories starting from the critical surface at velocities directed towards the reactants appeared at the reactants minimum, while all the trajectories with initial velocities directed towards the products appeared at the products minimum. This is a result of the weakness of the interaction of the X_3 system with a medium comprising a liquid inert gas. Only for a low barrier (5 kcal mol^{-1}) with a small curvature in the vicinity of the transition state did individual trajectories reintersect with the critical surface. In this case transmisison factors $\varkappa$ of 0.97, 0.91, and 0.91 were obtained respectively for the reactions in He, Ar, and Xe. Thus calculations by the method of molecular dynamics for reaction (II.14) in a system interacting weakly with the medium showed that, for sufficiently high barriers, the transition state theory constitutes a satisfactory approximation for the calculation of the rate constant. This estimate agrees with the conclusion known from the gas-phase theory.

In order to elucidate the limits of the applicability of the transition state theory, it is desirable to investigate chemical reactions by the method of molecular dynamics under the conditions of strong interaction with the medium. A good example is provided by the ionic version of the substitution reaction (II.14)–an S_N2 (I.3) reaction occurring in a polar medium.

The $Cl^- + CH_3Cl$ reaction in an environment comprising 64 H_2O molecules has been modelled[33,34] by the method of molecular dynamics. A potential of the LEPS type was adopted for the $Cl^- + CH_3Cl$ system. In the one-dimensional case, it reproduced the principal characteristics of the potential used in a study[16] of this reaction by the Monte Carlo method. The potential of the interaction of the solvent molecules with the chemical system depended on the charge distribution in the latter, which varied continuously along the reaction coordinate. The calculations yielded a transmission factor $\varkappa$ = 0.55.

The main qualitative result consisted in the description of the dynamic events occurring in the vicinity of the barrier. The outcome of the reaction is usually determined in the course of the first 0.02 ps after the start of the trajectory from the top of the potential barrier. This period is much shorter than the reorientation time of the solvent molecules. For a sufficiently high potential barrier, the reaction in the vicinity of the transition state is determined by the potential generated by the configuration of the solvent "frozen" in this state, which was the equilibrium configuration at an earlier stage but is a non-equilibrium configuration in relation to the transition state.

The presence or absence of ternary points on the trajectory depends on the configuration of the solvation shell in the initial instant. Having been selected at random this configuration makes an additional contribution to the potential barrier which is

asymmetric relative to the gas-phase top of the barrier. Whether the reaction occurs or not depends on the direction in which the given trajectories starts relative to this fluctuation barrier. The average picture corresponds to an effective decrease in the curvature of the potential barrier in the vicinity of the transition state, which reduces the transmission factor.

The situation described can be reproduced at the phenomenological level with the aid of the stochastic theory, which will be examined in detail in the succeeding Sections of the present review. Using the trajectories calculated by the method of molecular dynamics, the correlation function for a random external force acting on the variable reaction coordinate has been determined.[34] The principal dynamic characteristic of the corresponding generalised Langevin equation (GLE)—the friction kernel—is expressed directly in terms of this correlator.[33,34] The transmission factor, obtained as a result of the solution of the GLE by a standard approximate method (The Grote—Hynes method), agrees satisfactorily with the result of the direct dynamic calculation.

The dynamic study considered above constitutes undoubtedly an outstanding computational achievement. It demonstrates not only the possibilities of modern methods of the computer modelling of reactions but also their limitations. Thus the qualitative picture of the dynamics of the trajectories in the vicinity of the barrier, described in detail above, is incorrect or at least is only partly correct. The point is that in the method of molecular dynamics, which is applied using simplified potentials (atom—atom potentials) because of computational limitations, one cannot take into account the polarisation of the electrons of solvent molecules caused by the dynamic charge redistribution in the chemical subsystem in the course of evolution along the molecular dynamic trajectory. This, so called non-inertial polarisation, is almost instantaneously adjusted to the current charge distrubution, in contrast to the orientation polarisation associated with the motion of heavy molecular fragments, which, as shown above, remains frozen in the course of the reaction. Since the non-inertial polarisation is known to constitute not less than 40% of the total polarisation of the medium by the chemical subsystem, one may conclude that the inference concerning the "frozen" medium, which is undoubtedly valid within the framework of the given molecular dynamic study, cannot be extended to the real development of events in an S_N2 reaction.

In conclusion we may note that the problem of calculating the absolute rate constant for reaction (I.3) has not been fully exhausted. The point is that the calculation by the Monte Carlo method described above (subsection II.1) was carried out for a one-dimensional set of rigid configurations of the chemical subsystem located along the reaction coordinate. The corresponding free energy profile takes into account only the contribution of solvent molecules to the partition function. The contribution of the motions of the chemical subsystem to the pre-exponential factor has not so far been calculated. Thus the Arrhenius exponential function (the calculation of $\Delta G^{\neq}$ [16] yields the activation energy) and the transmission coefficient $\varkappa$ have been found,[33,34] but the contribution to the pre-exponential factor, calculated within the framework of the usual transition state theory, has not been determined. The difficulty is associated with the estimation of the corresponding partition functions for the chemical subsystem in solution. A well-founded solution of the problem requires an extremely complex calculation by the Monte Carlo method taking into account the configurations of the reactants with complete allowance for their interactions (and their internal structure) with solvent molecules on different bases.

5. Application of the method of molecular dynamics in the modelling of chemical kinetics by stochastic equations

The stochastic theory, which provides the most general and natural methods for the description of many-particle systems, is widely used in the study of the influence of the medium on chemical reactions. In the subsequent Sections of the present review, it is discussed in detail at a qualitative level. The direct numerical solution of stochastic equations constitutes a more complex problem, which can be solved by the method of molecular dynamics within a certain range of dynamic parameters. Calculations of the trajectories (the reaction flux method) have been used[35–39] to extract kinetic information from the Langevin equation (LE) and the generalised Langevin equation.

Here we shall describe in greater detail an alternative stochastic model based on the kinetic Bohm—Gross equation.[41] In this model, the phase point $(\mathbf{r}, \dot{\mathbf{r}})$ of a system comprising N particles evolves subject to the potential $U(\mathbf{r})$ in conformity with Newton's equations. At a random instant t', the velocity of the ith particle $\dot{r}_i$ changes abruptly to $\dot{r}'_i$. The evolution then continues until the time t'', when the velocity of the jth particle (this can be any particle including the ith particle) changes abruptly to $\dot{r}''$, and so on. The velocities $\dot{r}'$, $\dot{r}''$, ... are selected at random from the Maxwell distribution. The time intervals t' after which the velocities of the particles become stochastic are statistically independent and obey the Poisson distribution:

$$P_n(t) = \frac{(\nu t)^n}{n!} \exp(-\nu t),$$

where ν has the significance of the collision frequency. This algorithm is equivalent to the solution of the kinetic Bohm—Gross (BG) equation[36] for the distribution function $f(\mathbf{r}, \dot{\mathbf{r}}; t)$

$$\left[\frac{d}{dt} + \hat{L}\right] f(\mathbf{r}, \dot{\mathbf{r}}; t) = \hat{D}(\nu) f(\mathbf{r}, \dot{\mathbf{r}}; t), \qquad \text{(II.15)}$$

where $\hat{L}$ is the Liouville operator describing the evolution of the system in the absence of collisions and $\hat{D}(\nu)$ is an integral operator taking into account the influence of collisions. One may point to the relation between this approach and the stochastic theories discussed below. The Langevin equation can be reduced by a standard procedure to the Fokker—Planck equation.[42] On the other hand, the latter differs from Eqn. (II.15) only by its right-hand side: the corresponding collision operator describes the diffusion process subject to the external forces potential.

The solution of the Bohm—Gross equation (II.15) with the aid of the Laplace transformation makes it possible to write formal expressions for the correlaton functions in terms of which the rate of the chemical reaction is expressed.[40,43] Analytical studies on the expressions obtained have been carried out for two limiting cases corresponding to low and high collision frequencies ν. In the diffusional limit for high values of ν, Eqn. (II.15) reduces to the Smoluchowski equation with a coefficient of friction ν/m [the equivalent of the intense friction limit in the Langevin equation (see sub-section III.2).

Within the framework of this technique, the reaction flux method (see sub-section II.3) was first applied to the study of chemical reaction kinetics.[40] The simplest unimolecular reactions were considered—conformational isomerisation of alkanes in a non-polar solvent.[27,40] The interaction with the medium was described by a single parameter—the collision frequency ν. In specific calculations a value with the same order of magnitude as the average collision

frequency in the modelling of the solvent by the method of molecular dynamics using the hard sphere potential was adopted as ν. The dependence of the result of the calculations on ν when the latter was varied in the range $(2-300) \times 10^{12}$ s^{-1} has been studied in detail.[27,40]

Fig. 2 presents the time variations of the rate constant $K(t)$ for the *trans–gauche* isomerisation of n-butane obtained by the reaction flux method[21] within the framework of the Bohm–Gross model[27] and by the method of molecular dynamics.[26] The values of $K(t)/K(0)$, where $K(0)$ is the rate in the initial instant equal exactly to the rate constant in the transition state theory, were plotted along the ordinate axis. After the initial transition period, the duration of which depends on the parameter ν, the value of $K(t)$ reaches a plateau, as in the usual molecular dynamics calculation. The quantity $K(t)/K(0)$ in the region of the plateau represents the transmission factor $\varkappa$. With increase in the collision frequency ν, the system reaches the plateau sooner and there is a simultaneous decrease in the transmission factor $\varkappa$, in agreement with the result derived from the Kramers theory in the high friction limit (see subsection III.2).

Fig. 2 shows that the results of calculations by the methods of stochastic and molecular dynamics agree best for $\nu = 2 \times 10^{12}$ s^{-1}, which agrees in terms of order of magnitude with the collision frequency in liquid CCl_4 for which the molecular dynamics calculation was carried out. Using certain assumptions, it is possible to determine for specific systems the $\nu(p, T)$ relation (p is the pressure and T the temperature) and thus to determine the dependence of the rate of reaction on the thermodynamic parameters of the system. It has been found[14] that, in the isomerisation of n-butane under normal conditions (T = 300 K, p = 1 atm), the change in the activation barrier $\Delta E^{\neq}$ owing to collisions is very small, while the contribution of collisions to the change in the activation volume $\Delta V^{\neq}$ is approximately an order to magnitude higher than follows from the transition state theory. Several calculations have been devoted to the study of the influence of pressure on the isomerisation of cyclohexane.[27–30]

III. Stochastic dynamics

1. Simplest stochastic equations

In the dynamic theory, an enormous number of coordinates of the medium have to be studied. An effective way of obviating this difficulty is to eliminate most of them from the equation of motion, leaving only significant dynamic variables. Among "significant variables", one includes the internal coordinates of the chemical subsystem and in the first place the reaction coordinate. It is sometimes necessary to examine explicitly one or several coordinates of the medium. This happens in those cases where the reorganisation of the medium is an important or even fundamental condition for the chemical reaction, as happens, for example, in electron transfer processes. The examples presented below illustrate the choice of significant coordinates.

The coordinates which have not been taken into account explicitly (these usually include all the coordinates of the medium with a few possible exceptions) are referred to as the thermostat. The explicitly considered significant coordinates interact (exchange energy) with the thermostat, forming a thermodynamically open system. The dynamics of open systems is described by stochastic equations. The simplest of these, the Langevin equation, deals explicitly with a single dynamic variable:

$$m\frac{d^2x}{dt^2} + \gamma\frac{dx}{dt} = -\frac{dU(x)}{dx} + (\text{random force}). \qquad \text{(III.1)}$$

The first terms on the left-hand and right-hand sides of this equation represent the usual Newtonian contributions: the kinematic term proportional to the acceleration (m is the mass) and the regular force $-dU(x)/dx$. The frictional force added to the left-hand side is proportional to the velocity (γ is the coefficient of friction)†. It describes the dissipation of energy as a result of the interaction of the dynamic variable x with the thermostat. The random force describes the irregular effect of the thermostat on the variable x. In the modelling of a chemical reaction by Eqn. (III.1), the random force ensures the thermal activation of the substrate which is necessary to overcome the potential of the barrier. Its intensity is related to the coefficient of friction in such a way that the joint effect of the random and dissipative forces leads to the establishment of the Boltzmann equilibrium for the variable x during a time significantly exceeding its relaxation period.

For chemical applications, it is necessary to examine a more complex stochastic equation—the so called generalised Langevin equation:[44,45]

$$m\frac{d^2x}{dt^2} + \int_{-\infty}^{t} f(t-\tau)x(\tau)d\tau = -\frac{dU(x)}{dx} + (\text{random force}). \qquad \text{(III.2)}$$

It differs from the Langevin equation (III.1) by a more complex structure of the term describing the dissipative force. The corresponding integral expression depends in each instant t on the entire preceding evolution of the dynamic variable $x(t)$. The quantity $f(t-\tau)$ is called the relaxation kernel or the memory kernel. Dynamic systems with such properties are referred to as non-Markov systems in contrast to the Markov systems in which the frictional force is local in terms of time, i.e depend only on the current instant t. Eqn. (III.2) is obtained when the linear response theory is applied to continuous dynamic models of the medium.[46]

An alternative form of the formulation of the generalised Langevin equation, where the integral term contains the velocity $\dot{x}(t)$ and not the coordinate $x(t)$, is also commonly used:[44]

$$m\frac{d^2x}{dt^2} + \int_0^t \beta(t-\tau)\,\dot{x}(\tau)d\tau = \frac{d\,\bar{U}(x)}{dx} + \text{random force}. \qquad \text{(III.3)}$$

The quantity $\beta(t)$ is called the friction kernel. The different lower integration limit compared with Eqn. (III.2) is in most cases insignificant. To within this difference, Eqns. (III.2) and (III.3) are mathematically equivalent and the integral kernels $f(t-\tau)$ and $\beta(t-\tau)$ as well as the potentials $U(x)$ and $\bar{U}(x)$ are linked by the relations:[44]

$$f(t) = d\beta/dt;\ \bar{U}(x) = U(x) + \frac{\beta(0)x^2}{2}. \qquad \text{(III.4)}$$

The Langevin equation (III.1) can be obtained both from Eqn. (III.2), when the memory kernel is the derivative of the Dirac delta function:

$$f(t) = \gamma\delta'(t), \qquad \text{(III.5)}$$

† The quantity γ/m is sometimes referred to as the coefficient of friction.[42–45]

and from Eqn. (III.3) if

$$\beta(t) = \gamma\delta(t). \tag{III.6}$$

The intensity of the random force on the right-hand side of Eqn. (III.2) is linked to the kernel $f(t)$ by the relation called the fluctuation-dissipative theorem (FDT). We shall designate the random force by $F(t)$ and its autocorrelation function by $<F(t)F(0)>$ [the averaging is over instances of the random process $F(t)$]. The Fourier transform of the autocorrelation function is designated by

$$\left(F^2\right)_\omega = \int_{-\infty}^{+\infty} \langle F(t)F(0)\rangle \exp(i\omega t)\mathrm{d}t.$$

Then FDT assumes the form[45–47]

$$(F^2)_\omega = -\frac{2kT}{\omega}\,[\mathrm{Im}f(\omega)], \tag{III.7}$$

where $f(\omega)$ is the Fourier transform of the kernel $f(t)$:

$$f(\omega) = \int_{-\infty}^{+\infty} f(t)\exp(i\omega t)\mathrm{d}t. \tag{III.8}$$

It can be shown that the imaginary component of $f(\omega)$ is always negative.

In the case of Eqn. (III.3), the FDT is written in the following form:[44,45]

$$<F(t)F(0)> = kT\beta(t). \tag{III.9}$$

The two forms of the FDT, namely Eqns. (III.7) and (III.9), are equivalent, which can be readily established using Eqn. (III.4). The FDT ensures the establishment in the system of a Boltzmann equilibrium for times exceeding the relaxation period. The analogous relation for the Langevin equation (III.1) mentioned above is a special case of the FDT.

Henceforth we shall always assume that the random force $F(t)$ is Gaussian.[43–45] In this case, it is fully determined by its autocorrelation function. If the friction kernel has been specified, then the FDT fully determines the Gaussian random force. This factor permits the description of the dynamics of the medium by only one friction kernel in a phenomenological study of reactions in a condensed medium. The Langevin equation was first used for the description of Brownian motion of colloidal (i.e. macroscopic) particles. In applying it in the theory of elementary chemical processes, it is essential to remember that the coordinate x in Eqn. (III.1) characterises the changes in the chemical subsystem and is a microscopic variable. Therefore the interpretation of γ as a macroscopic coefficient of friction is illegitimate although it is frequently used. The quantity γ as well as the integral kernels $f(t)$ and $\beta(t)$ should be regarded as phenomenological characteristics of the interaction between the chemical subsystem and the medium. Their microscopic interpretation is discussed below.

2. Extraction of kinetic information from stochastic equations

If the potential (more precisely the free energy profile) is represented by a two-well curve, then such equations decribe the dynamics of the transition through the barrier and can model the chemical reaction (Fig. 3). The corresponding frequencies (the frequency at the top of the barrier $\omega^{\neq}$ is imaginary) are:

$$\omega_0^2 = \lambda_0/2m, \qquad (\omega^{\neq})^2 = -\lambda^{\neq}/2m.$$

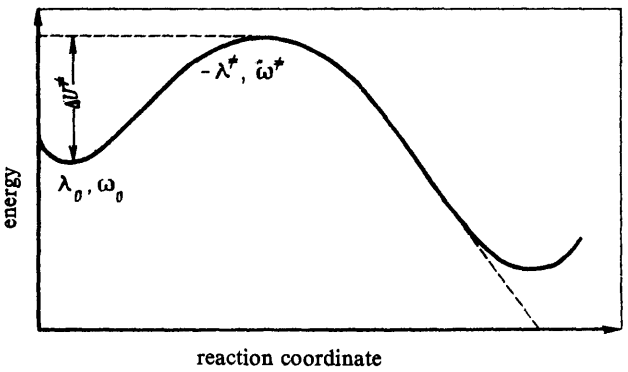


Figure 3. Potential curve (free energy profile) for a chemical reaction in a condensed medium; $\Delta U^{\neq}$ is the height of the barrier, λ_0 and $-\lambda^{\neq}$ are the force constants at the reactants minimum and at the top of the barrier ($\lambda_0 > 0$, $\lambda^{\neq} > 0$) and ω_0 and $\omega^{\neq}$ are the corresponding frequencies. In the Kramers theory, the presence of the second well is ignored (dashed straight line).

The rate constant in Eqn. (III.1) has been calculated by Kramers.[48] If the condition

$$\gamma/m\omega_0 >> 1, \tag{III.10}$$

has been fulfilled, then

$$K = \frac{\Omega}{2\pi}\sqrt{\lambda_0/\lambda^{\neq}}\exp(-\Delta U^{\neq}/kT),$$
$$\Omega = \sqrt{(\gamma/2m)^2 + (\omega^{\neq})^2} - \gamma/2m. \tag{III.11}$$

When

$$\gamma/2m\omega^{\neq} >> 1 \tag{III.12}$$

the expression for the rate constant assumes a simpler form:

$$K = \frac{\omega_0\omega^{\neq}m}{2\pi\gamma}\exp\left(-\frac{\Delta U^{\neq}}{kT}\right). \tag{III.13}$$

This is the so called high friction limit in the Kramers theory, where the rate constant is inversely proportional to the coefficient of friction. If Eqn. (III.11) is extended to the region of low friction, formally ignoring the limitation (III.10), then the well known result

$$K = \frac{\omega_0}{2\pi}\exp(-\Delta U^{\neq}/kT) = K_{\mathrm{TS}}, \tag{III.14}$$

is obtained, which is equivalent to the application of the transition state theory without taking into account the influence of the medium.

The condition (III.10) defines the regions of intermediate and high friction. In the region of very low friction, where

$$\gamma/m\omega_0 << kT/\Delta U^{\neq}, \tag{III.15}$$

a different expression is valid for the rate constant. It differs from Eqn. (III.11) by the pre-exponential factor, which is directly proportional to the coefficient of friction. In this region the kinetics are limited by the thermal activation of the chemical system. The rate constant increases in proportion to the intensity of the random force ensuring activation, which is proportional to γ according to the FDT.

The overall dependence of the rate constant on γ, predicted by the Kramers theory, is presented in Fig. 4. Between its two-branches, corresponding to the increase and decrease in K, there is a transition region; in order to find the solutions in this region, use is made of numerical methods for the solution of the generalised Langevin equation.[3,5–39] The exact value of the constant K is always less than that calculated by Eqn. (III.14) obtained in the primitive transition state theory without taking into account the influence of the medium.

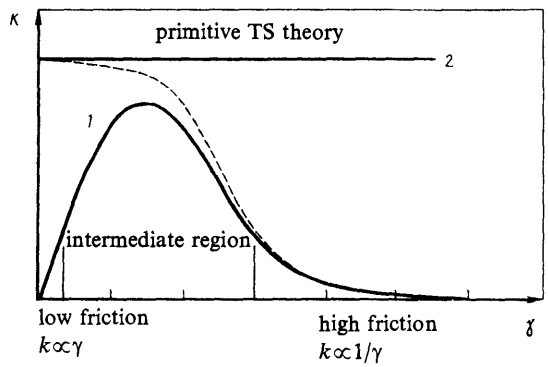


Figure 4. Dependence of the rate constant K on the coefficient of friction γ in the Kramers theory (curve *1*) and in the primitive transition state theory (curve *2*). The regions of high and low friction are described by simple formulae. Dashed curve—calculation by Eqn. (III.11). Upper horizontal line (primitive transition state theory)—calculation by Eqn. (III.14).

It is sometimes assumed that the quantity γ is proportional to the hydrostatic viscosity of the medium. The Kramers theory stimulated the experimental search for the relation between the reaction rates and the viscosity‡.[49,50] The decrease in K with increasing viscosity has been observed in a number of cases. On the other hand, the question of the existence of a kinetic regime for which the rate of reaction increases with increasing viscosity still remains open. The point is that the thermal activation of a fairly complex chemical subsystem can be achieved not only through the interaction with the medium but also as a result of energy exchange within the subsystem itself. This effect, which is not taken into account within the framework of the simple model (III.1), is independent of the viscosity and can render the Kramers model insignificant in the region of very low friction [Eqn. (III.15)].

‡ This concerns the effect of the viscosity on the kinetics of an elementary chemical process and not its trivial effect, which is always observed for diffusion-controlled reactions.

For the generalised Langevin equation (III.3), the rate constant for a system with a two-well potential was calculated by Grote and Hynes.[51] It has the form of Eqn. (III.11) with a modified expression for the decomposition frequency Ω. This quantity is determined as the single positive root of the characteristic equation

$$m\Omega^2 + \Omega\beta(\Omega) + \lambda^{\neq} = 0,$$

where

$$\beta(\omega) = \int_0^{\infty} \beta(t)\exp(-\omega t)dt$$

represents the Laplace transformation of the kernel $\beta(t)$.

The characteristic equation for the generalised Langevin equation (III.2) assumes the form:[2,9]

$$m\Omega^2 + f(i\Omega) + [\lambda^{\neq} - f(\omega = 0)] = 0, \qquad \text{(III.17)}$$

where $f(\Omega)$ is the Fourier transform of the kernel $f(t)$ defined in Eqn. (III.8). If Eqn. (III.4) holds, then Eqns. (III.16) and (III.17) yield the same decomposition frequency Ω and the same rate constant K. The Grote–Hynes equation for the rate constant is obtained on the same assumptions as those underlying the derivation of the Kramers formulae (III.11). For the reactions occurring in complex chemical subsystems, these postulates are found to be justified in many cases. Eqns. (III.11), (III.16), and (III.17) are widely used in modern literature and are known as the Kramers–Grote–Hynes (KGH) approximation.

An alternative formulation of the KGH theory, in which the characteristic equation (III.17) plays a key role, is also possible. It can be conveniently rewritten by introducing the notation $\omega = i\Omega$:

$$\begin{aligned} -m\omega^2 + f(\omega) + [\lambda^{\neq} - f(\omega = 0)] = 0, \\ -m\omega^2 + f(\omega) + [\lambda_0 - f(\omega = 0)] = 0. \end{aligned} \qquad \text{(III.18)}$$

The second equation analogous to the first, was formulated for the reactants minimum. We shall consider all the roots of these equations, designating them by $\Omega_{\nu}^{\neq}$ and $\Omega_{\nu}^{(0)}$ (ν = 0, 1, ..., N) respectively. For the first equation, the decomposition frequency is

$$\Omega_0^{\neq} = i\Omega; \quad \Omega > 0. \qquad \text{(III.19)}$$

All the remaining roots $\Omega_{\nu}^{\neq}$ and $\Omega_{\nu}^{(0)}$ are complex and have negative imaginary components. This fact implies that the characteristic equations (III.18) describe decaying oscillations, whose energy is dissipated. It follows from the property of causality of the core $f(t)$.[45,47] The rate constant can now be represented in the form[52]

$$K = \frac{\Omega}{2\pi}\left(\left|\prod_{\nu=0}^{N}\frac{\Omega_{\nu}^{0}}{\Omega_{\nu}^{\neq}}\right|\right)^{1/2}\exp\left(-\Delta U^{\neq}/kT\right). \qquad \text{(III.20)}$$

This formulation corresponds to the generalised transition state theory, because, as in the usual harmonic transition state theory [Eqn. (I.2)], it uses only the energies and characteristic frequencies at stationary points. It also has a deeper significance, based on the equivalence of the KGH and transition state theories, which is discussed in the next Section. Here one considers of course the transition state theory taking into account the influence of the medium, in contrast to the primitive version of this theory which completely ignores the medium [see Eqn. (III.14)].

3. Relation between the dynamic and stochastic descriptions. Generalised transition state theory as a multidimensional extrapolation of the KGH approximation

Hitherto, in speaking of dynamics, we had in mind the study of equations of motion, both classical Newtonian and stochastic Langevin equations. In this Section, the dynamic systems will be understood as conservative systems retaining the total energy and obeying the equations of classical mechanics. In contrast to them, stochastic systems, being open, dissipate energy, exchanging it with the thermostat.

Stochastic systems permit an abbreviated description of dynamic systems with a large number of degrees of freedom (ideally a macroscopically large number). They can be obtained rigorously from Newtonian equations formulated for the complete dynamic system, differentiating one or several "significant" variables for explicit examination, excluding all others in succession. The exclusion of "insignificant" variables represents a mathematical procedure, the application of which results in the subdivsion of the initial dynamic system into a subsystem having a small number of dynamic degrees of freedom and the thermostat interacting with it.[44,45,53] We shall consider the result of the application of this procedure to the model dynamic system "coordinate x + set of harmonic oscillators q_j with linear interaction in terms of q_j. The system Hamiltonian is

$$H = \frac{p_x^2}{2m} + U(x) + \sum_{j=1}^{N}\left\{\frac{p_j^2}{2\mu_j} + \frac{\mu_j}{2}\left[\omega_j q_j + \frac{C_j}{\mu_j\omega_j}x\right]^2\right\}, \quad \text{(III.21)}$$

where m is the mass of a "one-dimensional particle" x, $U(x)$ its potential, and p_x its momentum. The oscillator variables q_j are characterised by masses μ_j, frequencies ω_j, and momenta p_j ($j = 1, 2, ..., N$). The interaction of the dynamic variable x with the oscillator variables q_j has the form of the linear combination $x\sum_{j=1}^{N} C_j q_j$, where C_j are coupling constants. In essence one considers harmonic oscillators the equilibrium positions of which depend linearly on x.

The equation of motion for the variable x, obtained as a result of the exclusion of the oscillator variables,[54] reduces to the generalised Langevin equation (III.3) with the friction kernel.

$$\beta(t) = \sum_{j=1}^{N}\frac{C_j^2}{\mu_j\omega_j^2}\cos(\omega_j t). \quad \text{(III.22)}$$

The random force is determined by the initial conditions for oscillator variables and satisfies the FDT.

For a continuous medium, $N\to\infty$ and the set of oscillators is characterised by a spectral density defined as follows:[55]

$$J(\omega) = \frac{\pi}{2}\sum_{j=1}^{N}\frac{C_j^2}{\mu_j\omega_j}\delta(\omega - \omega_j), \quad \text{(III.23)}$$

$$\beta(t) = \frac{2}{\pi}\int_{-\infty}^{+\infty}\frac{J(\omega)}{\omega}\cos(\omega t)d\omega. \quad \text{(III.24)}$$

Eqns. (III.23) and (III.24) specify the mutually single-valued correspondence between the phenomenological generalised Langevin equation, specified by the friction core $\beta(t)$, and the dynamic system described by Eqns. (III.21) and (III.23). This correspondence permits a deeper understanding of the significance of the KGH approximation. If $U(x)$ is a one-dimensional two-well potential, then the Hamiltonian (III.21) describes transitions in a model two-well system. By applying to it the canonical transition state theory, it is possible to calculate the rate constant defined by Eqns. (I.2). Here one observes that, if the friction core satisfies Eqns. (III.22) and (III.24), the result agrees with the rate constant based on the KGH theory. Thus the following general assertion is valid:[56–59] the KGH approximation for the generalised Langevin equation (III.3) is equivalent to taking into account the medium within the framework of the dynamic model (III.21) to which the canonical transition state theory has been applied.

However, as mentioned in Section I, the medium is in principle anharmonic. The application of the oscillator model therefore requires explanation. We shall consider a completely different method for the microscopic modelling of the generalised Langevin equation (III.3) on the basis of a dynamic system of equations. For a real medium, having a PES with a complex anharmonic structure with a multiplicity of shallow (with a depth of $\sim kT$) minima, it is possible to construct a smooth free energy profile along a "significant" variable, which we designate by x. It corresponds to the two-well curve of stochastic models. Then, on the basis of the complete system of dynamic equations, it is possible to calculate the friction kernel for the generalised Langevin equation, which is achieved by statistical mechanical methods within the framework of the linear response theory.

The molecular-dynamic calculation permits the study of the fluctuating force $F(t)$ acting on the variable x and, in particular, permits the calculation of the autocorrelation function $\langle F(t)F(0)\rangle$. Then, having identified $F(t)$ with the random force included in the generalised Langevin equation, and applying the FDT [Eqn. (III.9)], we obtain the friction kernel $\beta(t)$ for the generalised Langevin equation (II.9).[33,34,60] Thus, when the methods of molecular dynamics and the FDT are used jointly, the generalised Langevin equation can be fully reproduced for a specific dynamic model reaction in the given medium. Having compared the Hamiltonian (III.21) with the generalised Langevin equation obtained, one can now show that the oscillator variables included in it have no direct microscopic interpretation. They arise on transition, within the framework of the linear response theory, from the strongly anharmonic microscopic PES to the smooth FES, because the dissipative force in the generalised Langevin equation is linear in x. This is only one of the indirect methods for describing the influence of the medium on the variable x. It is not essential to resort to it, because all the results are obtained by studying the phenomenological generalised Langevin equation without employing a particular interpretation.

We obtained two important corollaries from the above discussion. Firstly a practical recipe has been formulated for the microscopic evaluation of the friction kernel. Secondly, the assertion that the KGH approximation is a version of the transition state theory with allowance for the medium has acquired a profound significance. We demonstrated that the KGH method permits the extrapolation of the harmonic version (I.2) of the transition state theory to the description of fundamentally anharmonic models within the framework of the linear response theory.

In chemical applications, one cannot restrict the treatment to one-dimensional stochastic equations (III.1)–(III.3). It is frequently necessary to examine explicitly several "significant" variables, whose dynamics are described by a system of stochastic equations. An equivalent of the Kramers theory for a system of Markov–Langevin

equations of type (III.1) as well for a system of non-Markov equations of type (III.3) is known.[63–66] An alternative solution of the problem[52] is provided by employing the generalised transition state theory in the form defined by Eqn. (III.20). This universal expression for the rate constant is independent of the dimensions of the system. It can be obtained by applying the canonical transition state theory to the oscillator Hamiltonian of type (III.21) containing any number of oscillator variables $x_1, x_2, \ldots$ At the phenomenological level, these variables evolve on a multidimensional two-level FES $U(x_1, x_2, \ldots)$ in conformity with the specified system of generalised Langevin equations.

In order to apply the generalised transition state theory, it is necessary to find initially the reactants minimum and the saddle point on the FES. The difference between their energies yields the activation energy $\Delta U^{\neq}$ in Eqn. (III.20). The force constants matrices are then calculated at both points. The linearisation of the system of generalised Langevin equations in the vicinity of the stationary points makes it possible to obtain two systems of linear integrodifferential equations, whose coefficients are the matrices of masses, friction kernel (they are assumed to be known), and the calculated force constants. Two characteristic equations are derived from these quantities by a standard method. They are analogous to Eqn. (III.18), whose roots are the characteristic frequencies for the reactants and the transition state. The roots are complex and have the same properties as the roots in the one-dimensional case. The pre-exponential factor in Eqn. (III.20) is derived from the frequencies obtained. This method makes it possible to obtain the rate constant in terms of an approximation analogous to the one-dimensional KGH approximation for systems of any complexity.

An alternative method of calculating the rate constant in a multidimensional stochastic system is also known.[63–66] It reduces the calculation to the one-dimensional expression (III.11), the ratio of the two force constants is replaced by the ratio of the corresponding determinants, and the decomposition frequency Ω is calculated from the multidimensional characteristic equation. The result is equivalent to the calculation by Eqn. (III.20).

IV. Examples of the application of stochastic models

1. Charge transfer reactions. Formulation of the continuous model of the medium in relation to outer-sphere electron transfer

The electron transfer between the donor D and the acceptor A in a polar solvent

$$D^- + A \rightarrow D + A^- \qquad \text{(IV.1)}$$

is the simplest chemical process in which the specific features of the influence of the medium are fully manifested. The kinetics of a multiplicity of reactions (IV.1), in which D and A are transition metal complexes, organic substrates, and fragments of biomolecules, have now been investigated. The term "outer-sphere electron transfer" presupposes that the internal coordinates of the chemical subsystem do not change in the rate-limiting stage of the reaction. Changes occur in the configuration of the solvation shell surrounding the reaction complex. The solvation shell is adjusted to the charge distribution in the chemical subsystem, which changes significantly during the reaction. The rearrangement of the solvation shell for a fixed geometry of the chemical subsystem occurs mainly as a result of the orientation motions of the solvent molecules. The study of reaction (IV.1) makes it possible to investigate in relation to a specific example and in a pure form the dynamic behaviour of the coordinates of the medium in the chemical process.

We shall designate the coordinates of the solvent by Q_v. It is necessary to examine the dependence of the free energy $G(Q_v)$ on these coordinates. In the continuous model of the medium, one introduces as Q_v not the elementary orientation motions of individual solvent molecules but collective modes describing concerted combinations of a large number of elementary displacements. This approach permits, in principle, the differentiation of one or several collective coordinates significant for the description of the reaction and the restriction of the treatment to their explicit study.

In a purely electrostatic interaction of the medium with a donor–acceptor pair, the inertial polarisation $P(r)$, i.e. the part of the total polarisation of the medium from which the polarisation due to electrons has been excluded, may be conveniently adopted as the variable.[67,68] The inertial polarisation varies from point to point in the three-dimensional space. Its values at each point are independent variables. Such quantities are referred to as field variables. A field variable actually represents a three-dimensional continuum of variables of the usual type. For a given charge distribution $\rho_a(r)$ in the pair $[D + A]^-$, one may consider the dependence of the FES on the variable $P(r)$ modelling the collective motions of the solvent molecules. This dependence is quadratic: the FES represents a paraboloid, with an infinite number of dimensions, in the polarisation space. Its minimum corresponds to the polarisation $P^{(a)}(r)$ adjusted by an equilibrium procedure to the charge ρ_a. For a different charge distribution $\rho_b(r)$, the minimum in the FES paraboloid shifts to another point in the polarisation space $P^{(b)}(r)$. If, during the reaction, the charge distribution in the substrate changes from ρ_a to ρ_b, then the FES has the form of two intersecting paraboloids. It describes the reorganisation of the polar solvent taking into account only electrostatic forces and has an activation barrier whose height is

$$\Delta U^{\neq} = (E_r + Q)^2/4E_r. \qquad \text{(IV.2)}$$

This is the familiar Marcus formula,[67,68] where Q is the difference between the free energies of the products and the reactants (it is assumed that $Q < 0$ for exothermic reactions) and E_r is the so called solvent reorganisation energy (an important parameter characterising the change in the FES on passing from the ρ_a to the ρ_b charge distribution). It is assumed that $|Q| \leqslant E_r$.

The interaction between the donor and the acceptor is introduced into the theory within the framework of the two-level model. A matrix Hamiltonian of the following type is considered:

$$H = \begin{pmatrix} H_{aa} & H_{ab} \\ H_{ba} & H_{bb} \end{pmatrix}. \qquad \text{(IV.3)}$$

The diagonal matrix elements depend parametrically on the polarisation $P(r)$:

$$H_{aa} = \alpha_a - \frac{1}{2} f_0 \int [P_a^2 - (P - P_a)^2] \mathrm{d}^3 r,$$
$$H_{bb} = \alpha_b - \frac{1}{2} f_0 \int \left[P_b^2 - (P - P_b)^2\right] \mathrm{d}^3 r. \qquad \text{(IV.4)}$$

The electronic matrix elements α_a and α_b characterise the intrinsic energy of the chemical subsystem in the states "a" and "b" without taking into account the interaction with the inertial polarisation. The effects of the polarisation of the electrons of the medium (non-inertial) are assumed to be implicitly included in α_a and α_b. The non-diagonal matrix element is a parameter of the electronic interaction:

$$H_{ab} = H_{ba} = \beta. \tag{IV.5}$$

The coefficient $1/f_0$ is called the Pekar multiplier:[69]

$$\frac{1}{f_0} = \frac{1}{4\pi}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right), \tag{IV.6}$$

where ε_0 and ε_∞ are the static and optical dielectric constants. The quantity f_0 is the coefficient of the linear response for the inertial polarisation (response)—induction field (external force) pair:

$$f_0 P(r) = D(r). \tag{IV.7}$$

In particular, one may consider the equilibrium induction fields D_a and D_b related to the charges ρ_a and ρ_b by the Poisson equation.

We shall consider the adiabatic theory in greater detail. The lowest eigenvalue of the matrix H plays the role of the FES in it:

$$U[P] = -\sqrt{\alpha^2/4 + \beta^2} + \alpha/2 + H_{aa}. \tag{IV.8}$$

Here $\alpha = H_{bb} - H_{aa} = Q + E_r - X$, where

$$Q = \alpha_b - \alpha_a - \frac{1}{2}f_0\int(P_b^2 - P_a^2)\mathrm{d}^3r, \qquad E_r = \frac{1}{2f_0}\int(D_b - D_a)^2\mathrm{d}^3r,$$
$$X = X[P] = \int(P - P_a)(D_b - D_a)\mathrm{d}^3r. \tag{IV.9}$$

The free energy of the reaction Q and the reorganisation energy E_r were discussed above. The quantity X is a variable of the usual type (a non-field variable), which is a functional of the field variable $P(r)$.

The quantity $U[P]$ is called the free energy functional. It depends on $P(r)$ solely via the usual variable X, which makes it possible to obtain a closed dynamic equation for this variable.

The dynamic properties of the continuous model are specified phenomenologically through the complex dielectric constant $\varepsilon(\omega)$.[70,71] This function of the frequency ω is determined experimentally from the relation between the variable periodic electric field $E(\omega)$ and the induction $D(\omega)$. The form of $\varepsilon(\omega)$ usually employed in practice is the Debye approximation:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\tau_D\omega}, \tag{IV.10}$$

where the parameter τ_D (the Debye time) characterises the time scale of the relaxation processes determined by the polarisation of the medium. The renormalised quantity

$$\tau_L = \tau_D(\varepsilon_\infty/\varepsilon_0), \tag{IV.11}$$

called the longitudinal relaxation time, is frequently employed subsequently.

The dynamic theory starts with the equation of motion for polarisation. In the absence of external charges, it assumes the following form for the Debye model:[71]

$$(\tau_L f_0 \frac{\mathrm{d}}{\mathrm{d}t})P = -f_0 P + \text{random force}, \tag{IV.12}$$

where $f_0 P$ is a regular force generated by the change in the intrinsic energy of the polarisation field. In the presence of external charges, the regular force is modified. It can be found[46] as the variational derivative of the functional $U[P]$ [Eqn. (IV.8)]. The following equation is obtained as a result:[72]

$$\tau_L f_0 \frac{\mathrm{d}}{\mathrm{d}t}(P - P_a) = -f_0(P - P_a) + G(X)(D_b - D_a) + \text{random force}, \tag{IV.13}$$

where

$$G(x) = \frac{1}{2}[1 - \alpha/\sqrt{\alpha^2/4 + \beta^2}\,].$$

We have to determine the reaction rate constant from Eqn. (IV.13).

2. Kinetics of the outer-sphere electron transfer within the framework of the stochastic continuous model

The principal concepts of the continuous model of a polar solvent in relation to the simplest charge transfer reaction—the outer-sphere electron transfer—were introduced in the previous subsection. This is an essential preparatory stage before proceeding to the kinetic problems proper. For a number of reasons, the theory of such processes has nowadays advanced further than others and is essentially complete. It is useful to trace, in relation to this example, the logical structure of the complete dynamic theory of an elementary chemical process in a condensed phase.

A simplifying factor, characteristic of the two-level model described by Eqns. (IV.8) and (IV.9), is the dependence, mentioned above, of the free energy functional $U[P]$ on the field variable P through the coordinate X of the usual type. By virtue of this, the stochastic equation (IV.13) for the field variable P reduces to the incomparably simpler equation of X:[72,73]

$$\tau_L f_0 \frac{\mathrm{d}}{\mathrm{d}t} X = -X + 2E_r G(X) + \text{random force}. \tag{IV.14}$$

In this equation it is easy to recognise the generalised Langevin equation (III.1), from which the kinematic term, containing the acceleration (mass equal to zero), has been omitted. The first two terms on the right-hand side of the equation are functions of X representing the regular force. The corresponding one-dimensional potential $U(x)$ is represented by a two-well curve over a wide range of parameters§. The positions of the reactants minima and of the top of the barrier as well as the force constants are calculated for this potential. After this, it is possible to apply immediately the Kramers formula (III.11). Furthermore, since the inequality (III.12) is valid for $m = 0$, it is sufficient to use the high friction approximation (III.13). In this case the rate constant is given by:[46,72,73]

$$K = \frac{1}{2\pi\tau_L}\left(\frac{E_r}{2|\beta|}\right)^{1/2}\left(1 - \frac{Q^2}{E_r^2}\right)^{3/4}\exp(-\Delta U^*/kT), \tag{IV.15}$$
$$(E_r >> |\beta| >> kT;\ |Q| \leqslant E_r).$$

§ More precisely, the condition $2|\beta|/E_r < 1$ should hold. If it is infringed, the two-well potential becomes a one-well potential.

The activation energy $\Delta U^{\neq}$ is given by Eqn. (IV.2) in the zeroth approximation; it can be refined by subtracting $|\beta|$ from it. An important feature of Eqn. (IV.15) is the presence in the pre-exponential factor of a dynamic characteristic of the medium—the relaxation time τ_L.

Hitherto we have considered the adiabatic theory. It is valid subject to the condition

$$2|\beta|/kT \gg 1. \qquad \text{(IV.16)}$$

The numerator contains the minimal energy splitting of the two electronic terms of the two-level model described by Eqns. (IV.3)–(IV.5). The condition (IV.16) means that thermal fluctuations (i.e. the random force in the stochastic model are incapable of populating effectively the electronically excited state. If the condition (IV.16) has broken down, it is necessary to solve the electronic-non-adiabatic problem, which involves the consideration of a coupled system of two stochastic equations.[74] The dynamics of the outer-sphere electron transfer was first considered by Levich and Dogonadze[4,68,75] precisely within the framework of the non-adiabatic approach. Their calculations were based on perturbation theory. Current studies[74,76,77] were able to overcome this serious limitation. [It is noteworthy that the collective variable X, defined by Eqn. (IV.9), first appeared as a significant element of the dynamic theory in Zusman's study[74] within the framework of the non-adiabatic approach.] The expression recommended on the basis of the modern non-adiabatic theory for the rate constant has the Arrhenius form with an activation energy described by Eqn. (IV.2). The pre-exponential factor is usually formulated thus:

$$A = \frac{\beta^2}{\hbar}\sqrt{\frac{\pi}{E_r kT}}\,\frac{1}{1+\beta^2\tau_L B}. \qquad \text{(IV.17)}$$

The quantity B differs somewhat in the studies of different workers.[74,76–81] We shall quote the simplest (albeit not the best founded) version of the definition of B:[79]

$$B = 4\pi/\hbar E_r. \qquad \text{(IV.18)}$$

If the electronic matrix element β is sufficiently small in absolute magnitude, then the well known result based on perturbation theory in the classical limit is obtained from Eqn. (IV.17).[4,75] However, one can show directly that in the opposite limiting case where $\beta^2\tau_L B \gg 1$, Eqn. (IV.17) does not reduce to the correct Eqn. (IV.15) of the adiabatic theory. The approximate non-adiabatic theory, underlying Eqn. (IV.17), describes only cases of weak and intermediate linkages between the diabatic terms H_{aa} and H_{bb} in the two-level mode (IV.3). Thus Eqns. (IV.15) and (IV.17) supplement one another.

In conformity with the criterion (IV.16), the question of the mechanism, adiabatic or non-adiabatic, involved in electron transfer reduces to the estimation of the matrix element β. On the basis of the results of published calculations and their discussion,[82–83] one may conclude that the adiabatic condition in intermolecular electron transfer holds in many cases, while in intramolecular transfer it holds in all cases. In the study of more complex charge-transfer reactions, where internal motions of the chemical subsystem play a significant role (see subsection IV.3), the application of the adiabatic theory is natural and promising.

The scheme described for the outer-sphere electron transfer involves simplifications which are undesirable in the solution of specific problems. The most serious of them is the homogeneous medium approximation, on which the electrostatic formulae of subsection (IV.1) are based. A more realistic approximation is called the Born–Kirkwood–Onsager (BKO) model, it involves the cutting out of a cavity in the continuous medium in which the chemical subsystem is placed. The dielectric constants within and outside the cavity are different. In the dynamic theory, the complex dielectric constant has two values:

$$\varepsilon = \begin{cases} 1 \text{ (within the cavity)}, \\ \varepsilon(\omega) \text{ (outside the caivity)}. \end{cases} \qquad \text{(IV.19)}$$

In the static theory $\varepsilon(\omega)$ outside the cavity is replaced by the static constant ε_0.

The introduction of an inhomogeneity in the form of a cavity complicates the theory, but its structure remains the same as before.[84] The inhomogeneity leads to the renormalisation of the parameters: the expressions for the energy effect Q, the reorganisation energy E_r, and the principal dynamic variable X in Eqn. (IV.9) are altered. In particular, the reorganisation energy is[4,67,85]

$$E_r = \frac{1}{2f_0}\int_{V_e}(\nabla\varphi_b - \nabla\varphi_a)^2 d^3r, \qquad \text{(IV.20)}$$

where V_e is the volume outside the cavity and $\varphi_a(r)$ and $\varphi_b(r)$ are the vacuum potentials ($\varepsilon = 1$) generated by the diabatic charge distributions $\rho_a(r)$ and $\rho_b(r)$ and calculated from the Poisson equation. The general expressions (IV.15) and (IV.17) for the rate constant remain in force.

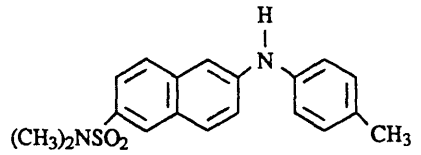
On going outside the framework of the Debye model of the solvent described by Eqn. (IV.10), a dynamic equation is arrived at in the adiabatic approximation,[46] which differs from Eqn. (IV.13) by its left-hand side: instead of the derivatives dP/dt, a linear integral operator acting on the polarisation variable P appears. This dynamic equation is the generalised Langevin equation (IV.2). A similar rate constant, defined by Eqn. (IV.15), can be calculated in terms of the KGH theory [Eqns. (III.11), (III.17), and (III.20)]. A non-adiabatic version of the non-Debye theory has also been formulated.[76,77,86]

Allowance for the internal degrees of freedom of the chemical subsystem, i.e. the extension of the treatment outside the framework of the outer-sphere model, means in essence that electron transfer is regarded as a reaction with charge redistribution in the chemical subsystem. We shall consider such processes in the next Section. Finally, the question of the extension of the treatment outside the framework of the two-level model (IV.3)–(IV.5) by improving the wave function describing the chemical subsystem has been discussed recently.[84,87,88] The wave function of the two-level model is linear and consists of two terms, i.e. contains only one variational parameter. In many cases this is insufficient. The problem is of current interest in applications of the theory to intramolecular processes in complex chemical substrates.

Experimental kinetic studies have confirmed the dependence of the rate constant for the outer-sphere electron transfer on the longitudinal relaxation time τ_L [see Eqns. (IV.11) and (IV.15)]. The distinct inverse proportionality observed for organic radical-ion donors and acceptors[89,90] constitutes convincing evidence in support of the adiabatic process mechanism. For a reaction involving

ruthenium complexes in different aliphatic alcohols and glycerol, a weaker relation $K \propto \tau_L^{-0.6}$ was observed.[91] This result can be explained in different ways: either on the basis of the non-adiabatic formula (IV.17),[92,93] or within the framework of the non-Debye approximation for $\varepsilon(\omega)$,[93,94] or by including in the dynamics the internal degrees of freedom of the chemical subsystem.[52]

The correlation between the kinetic measurements and the quantity τ_L is complicated by the fact that, together with τ_L, other factors change in different solvents, and their effect on the kinetics cannot be excluded. We may mention in the first place the change in solvent polarity, which is capable of altering the potential barrier in the reaction. In this respect, the study of intramolecular electron transfer in systems of the type



is instructive. The reaction was investigated in aliphatic alcohols in the temperature range 168–338 K.[95] Comparison of the temperature variations of the reaction rate constants and of the quantity τ_L itself in the same solvent (the influence of the change in polarity is excluded) demonstrated quite convincingly the transition of the kinetics from the regime in which there is no dependence on τ_L to one where it does obtain. The authors identified these two regimes as "non-adiabatic" and "adiabatic". However, we may note that, for the systems investigated, the electron transfer is accompanied by an appreciable change in intramolecular geometry, i.e. can be hardly classified as a purely outer-sphere process. Allowance for the internal degrees of freedom would make it possible to describe both regimes within the framework of the two-dimensional adiabatic model examined in the next subsection.

Thus the uncertainty in the interpretation of the experimental results within the framework of stochastic theories is difficult to overcome at the present time.

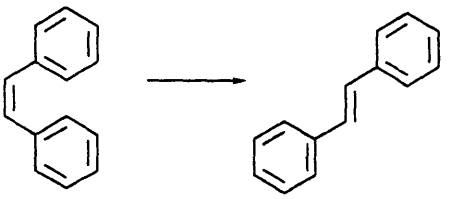
3. Reactions in polar and non-polar media

Transition to chemical reactions implies explicit study of the variables of the chemical subsystems together with the variables of the medium. For example, for charge transfer reactions in a polar solvent, one introduces the free energy functional $U[x_i, P(r)]$, which is a functional in relation to the variables of the medium [i.e. the polarisation $P(r)$] and is a normal function of the chemical variables x_i. We shall formulate the corresponding system of dynamic equations for the case of a single coordinate x[52] and the Debye approximation for $\varepsilon(\omega)$:

$$\tau_L f_0 \mathrm{d}P/\mathrm{d}t = -\delta U/\delta P + \text{random force}, \qquad m\mathrm{d}^2x/\mathrm{d}2t = -\mathrm{d}U/\mathrm{d}x. \tag{IV.21}$$

The functional $U[x_i, P(r)]$ plays the same role in the adiabatic theory of reactions in a condensed medium as the potential energy surface in the theory of gas-phase electronically adiabatic reactions. The variational derivative $\delta U/\delta P$ plays the role of the regular force. The rate constant for the system of Eqns. (IV.21) can be calculated on the basis of the generalised transition state theory [Eqn. (III.20)].[52]

Such a consistent theoretical programme of study, ranging from the construction of the energetic functional to the calculation of the rate constants for specific reactions in the medium, has not so far been realised. Fully phenomenological models are commonly used nowadays. The simplest of these arises from the Kramers Eqn. (III.1) and the corresponding expressions (III.11) and (III.13) for the rate constant. The isomerisation of cyclohexane[29,30] and the *cis–trans* isomerisation of stilbene and of its analogues in an excited state[49,50,96] have been frequently discussed at this theoretical level:



(IV.22)

In reaction (IV.22), the coordinate x of the Kramers model is identified with rotation about the central bond and a macroscopic quantity, directly proportional to the viscosity of the medium η and inversely proportional to the diffusion coefficient D, is used as the coefficient of friction γ. In order to observe the dependence of the rate constant on the viscosity, systematic studies have been carried out on the reaction kinetics in the gas phase and in non-polar liquids over a wide pressure range.[49,50] The observed relation is illustrated in Fig. 5. The right-hand side of this figure reveals a decrease in the rate constant with increasing viscosity, which is slower than would follow from the Kramers relation in the region of high friction. Considerable efforts have been made to observe the branch of the Kramers solution which ascends with increasing viscosity. Fig. 5 shows that its presence has not been convincingly confirmed. In this connection, one must recall the limitations of the Kramers model in the region of low friction when it is applied to complex molecular systems which were discussed in Section III.

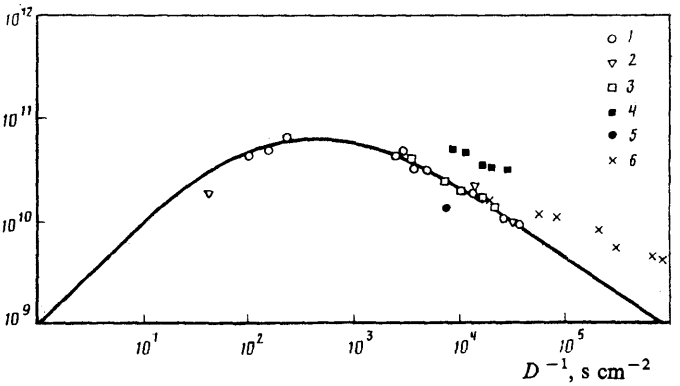


Figure 5. Correlation between the rate constant K for the photochemical isomerisation of stilbene and the reciprocal of the diffusion coefficient D^{-1}.[49] Experimental points obtained in the gas and liquid phases over a wide pressure range at 298 K: *1*, ethane; *2*, propane; *3*, CO_2; *4*, xenon; *5*, SF_6; *6*, n-hexane. Continuous curve — calculation based on the Kramers theory.

The phenomenological approach based on the Kramers equation encounters fundamental difficulties. We have seen that the role of the medium does not reduce only to the introduction of stochastic elements (the dissipative and random forces) into the description but

also involves the modification of the regular force. The interaction of the chemical system with the medium, superimposed on the intrinsic potential surface of the latter can distort appreciably both the height of the potential barrier and its shape (see, for example, Fig. 1). In the study of the role of friction, this side effect must be excluded, which requires accurate calculation of the interaction potential. For systems of type (IV.22), serious calculations have never been performed and the change in barrier height has been taken into account using an empirical method.[49]

Finally, in many cases the application of the one-dimensional generalised Langevin equation (III.1) as a model of the reaction in the given medium cannot be regarded as justified. In particular, using the hydrodynamic viscosities as a means of estimating the coefficient of friction γ, one frequently postulates a macroscopic description of the interaction in the spirit of the hydrodynamic Stokes formula

$$\gamma \sim \eta l, \qquad \text{(IV.23)}$$

where l is the characteristic distance over which the benzene rings migrate in reaction (IV.22).

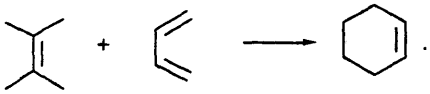
An attempt has been made to refine the dynamic description of isomerisation reactions with the aid of a two-dimensional stochastic model.[97,98] It was postulated that the process actively involves two angular variables with two different coefficients of friction. A study was made of the dynamic behaviour of the system as a function of the ratio of these parameters. The corresponding system of stochastic equations was solved in the high friction limit for both variables, where the kinematic contributions to the dynamics (proportional to the acceleration) are insignificant.

A consistent microscopic description of reactions in a given medium leads to a different two-dimensional dynamic model, in which the roles of both dynamic variables are fundamentally different:

$$m\mathrm{d}^2x/\mathrm{d}^2t + \mathrm{d}U/\mathrm{d}x = 0,$$
$$\gamma\mathrm{d}Q/\mathrm{d}t + \mathrm{d}U/\mathrm{d}Q = \text{random force}. \qquad \text{(IV.24)}$$

The chemical coordinate x, obeying Newtonian dynamics, and the medium coordinate Q, the dynamics of which are introduced at the level of the simplest version of the Kramers theory (the high friction limit in which the kinematic term, proportional to the mass, has been omitted), are considered explicitly. The two variables are linked by the interaction included in the regular two-well potential $U(x, Q)$. By specifying this potential, it is possible to take into account the microscopic interaction explicitly. The significant factor is that in the two-dimensional model the coefficient γ characterises the interaction of the differentiated medium coordinate Q with the remaining degrees of freedom of the medium (thermostat) and its interpretation in the spirit of Eqn. (IV.23) is not open to objection.

We shall illustrate the application of the model (IV.24) in relation to the study of the pressure dependence of the Diels–Alder reaction.[8] For a typical reaction of this type



(IV.25)

dienophile diene adduct

The distance between the reactants is adopted as the chemical coordinate x. This leads to the simple model illustrated in Fig. 6. The chemical subsystem x is placed at the centre of a cylindrical cavity with a cross-section σ_0 and a length L. The medium coordinate Q is identified with the quantity L. During the reaction, the distance x diminishes and this entails also the diminution of the cavity. The dynamics is described by Eqns. (IV.24). An advantage of the two-dimensional model is the possibility of taking into account non-equilibrium solvation, i.e. the situation in which there is insufficient time for the medium coordinate Q to become adjusted to the change in the coordinate x, which is assumed to be faster. This effect can be described only by considering explicitly both coordinates—x and Q. The corresponding kinetic theory goes beyond the framework of the KGH approximation and the generalised transition state theory. It will be examined in Section V.

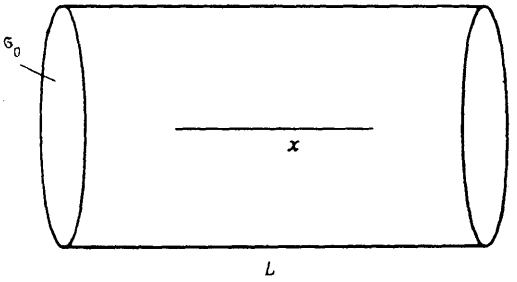
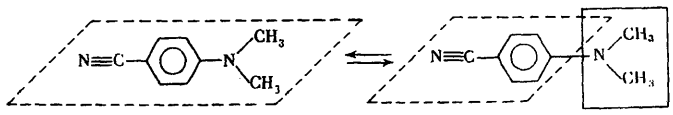


Figure 6. Model of the addition reaction in a condensed medium. x = distance between reactant molecules (reaction coordinate), L = coordinate of the medium; σ_0 = cross-section.

The experimental kinetic characteristics obtained for reaction (IV.25), investigated in the pressure range 0–6 kbar, have been interpreted[8] in terms of the non-equilibrium theory based on Eqns. (IV.24) and the reaction scheme adopted in Fig. 6. It was found that the majority of reactions can be regarded as reversible and that the rare anomalies in the pressure dependence of the rate constant could be interpreted as non-equilibrium effects.

Adopting the two-dimensional theory [Eqns. (IV.24)], we emphasised the difference between isomerisation reactions (IV.22) and addition reactions (IV.25). In the former case, the volume of the cavity hardly changes but its shape is altered. The latter case is characterised by a sharp decrease in the volume of the cavity during the elementary process. Accordingly, pressure affects addition reactions to an incomparably greater extent than isomerisation reactions. In the latter, the influence of the pressure is manifested mainly indirectly—through a change in the coefficient of friction γ.[28,29] The construction of a two-dimensional theory of isomerisation reactions would require the specification of a special medium coordinate the changes in which should model the change in the shape of the cavity. Without an explicit representation of coordinates x and Q, it is impossible to derive the energetic functional $U(x, Q)$.

Among charge-transfer reactions in polar media, photochemical isomerisation and nucleophilic substitution processes have been discussed in the literature. In the typical isomerisation reaction,[99]



planar structure perpendicular structure

(IV.26)

the molecule is excited to the first singlet state and there is rotation about the central C–C bond by 90° with alteration of the relative orientations of the terminal fragments. This conformational transition is accompanied by a strong polarisation of the molecule: according to a quantum-chemical calculation, its dipole moment increases from 6 to 16 D. A consistent dynamic description of reaction (IV.26) must include at least the angle of the conformational rotation and the polarisation of the medium as the dynamic variables.

It would also be necessary to examine the photochemical *cis–trans* isomerisation of non-polar conjugated molecules of the type of stilbene [reaction (IV.22)] when the latter occurs in a polar solvent, because it is known that the corresponding intermediate structures are highly polarised. However, all such reactions have been discussed theoretically hitherto at the elementary level of the one-dimensional Kramers model.[96,99,100] As in the electron transfer reaction, the coefficient of friction γ was assumed to be proportional to the relaxation time τ_L.

Methods for the explicit introduction of the medium coordinates into the two-dimensional model have been discussed in connection with the S_N2 reaction (I.3). In this case the antisymmetric motion in the complex

$$[Cl \cdots CH_3 \cdots Cl]^-$$

in the vicinity of the transition state is assumed to be the reaction coordinate. The form of the medium coordinate is determined by the form of the functional $U(q, P]$. One can imagine two limiting versions of the structure of this functional in the vicinity of the saddle point. In the first case, the section along x contains a barrier, while the section along the medium coordinate in the polarisation space consists of a paraboloid. This version corresponds to an insignificant modification of the gas-phase reaction coordinate in the presence of the polar solvent. A discrete coordinate corresponds to it:[101]

$$Y = \frac{\int D'(r)[f_0 P - D(r,\tilde{x})]d^3r}{\int [D'(r)]^2 d^3r}. \qquad (IV.27)$$

It is postulated that the regular electrostatic force $D(r,x)$, (the induction field which depends on the chemical coordinate x), has been linearised in the vicinity of the point $x = \tilde{x}$—for example, $\tilde{x}$ can correspond to the reactants minimum or to the saddle point of the potential $U[x, P(r)]$:

$$D(r, x) = D(r, \tilde{x}) + D'(r)(x - \tilde{x}),$$

$$D'(r) = \left.\frac{\partial D(r, x)}{\partial x}\right|_{x=\tilde{x}}.$$

In the second case, the section along x is a fragment of a parabola and that in the polarisation space is a two-well curve. In the vicinity of the transition state, the reaction proceeds mainly as a rearrangement of the medium, i.e. via the same mechanism as the outer-sphere electron transfer discussed above. The use of the variable X [Eqn. (IV.9)], which occurs in the electron transfer theory, as the reaction coordinate is most justified. Both variables, X and Y, correspond to the homogeneous medium approximation. The improvement of this simplest model by introducing a cavity would require the modification of both variables.[84]

Yet another procedure for the introduction of the medium variable, designed for a two-level electron transfer model, is possible. We designate by $P_a(r)$ and $P_b(r)$ the equilibrium polarisation of the medium corresponding to the reactants and reaction products. The current polarisation $P(r)$ can be specified by a linear interpolation:[67]

$$P(r) = \lambda P_a(r) + (1 - \lambda)P_b(r), \quad 0 < \lambda < 1. \qquad (IV.28)$$

This relation defines λ as the medium coordinate. It has been used for an S_N2 reaction[102] on the assumption of a one-well parabolic dependence of the free energy on λ. Such a scheme is not free from contradictions, since Eqn. (IV.28) was initially designed for a two-well model of the potential of the type which occurs in the electron transfer reaction.

The examples quoted in this Section show that theoretical studies on chemical reactions in a solvent are in their initial stage. The importance of the explicit consideration of the coordinates of the medium and their specific character has now been recognised. For reactions in non-polar media, these coordinates characterise the size or shape of the cavity in which the chemical subsystem is enclosed. In a polar solvent, the medium variables are represented by a particular functional of the inertial polarisation. In any version, such variables are collective modes, i.e. are concerted combinations of elementary motions of a large number of solvent molecules. The specific form of such a collective variable is defined within the framework of a particular model. Ultimately it follows from the concrete form of the energetic functional, just as the form of the usual vibrational modes is determined by the nature of the PES in the vicinity of its stationary points. In particular, in order to achieve a consistent solution of the problem of the medium coordinate in charge-transfer reactions, one has to establish the form of the cross-section of the functional $U[x, P]$ in the vicinity of the transition state. This requires the development of a method for quantum-chemical calculations with allowance for the effect of the medium.

V. Dynamics of multidimensional stochastic systems. Non-equilibrium solvation and its kinetic consequences

We shall consider in greater detail the equation of motion (IV.24) describing the stochastic dynamics of a system with two degrees of freedom. One of them, the Newtonian coordinate x, refers to the motion within the chemical subsystem. The second, the stochastic coordinate Q, is one of the modes of the medium. These variables are related via the potential $U(x, Q)$, which corresponds to the simplest version to a harmonic model with a quadratic term containing a linear combination of x and Q:

$$U(x, Q) = V(x) + \frac{\lambda}{2}(Q - ax)^2, \qquad (V.1)$$

where $V(x)$ is a one-dimensional two-well potential characterising a gas-phase reaction. The second term of Eqn. (V.1), containing the coordinates Q, corresponds to a harmonic oscillator with a force constant λ and an equilibrium position which depends linearly on x.

The two-dimensional equation (IV.24) is the simplest model suitable for the description of non-equilibrium solvation. In order to extend the treatment beyond kinetics under non-equilibrium conditions, it is necessary to abandon the KGH approximation. We shall introduce two characteristic periods τ_x and τ_Q related to the time scales of the motions of the corresponding variables. The period τ_x is assumed equal to the reciprocal of the frequency for two reactant wells subject to the one-dimensional potential $V(x)$. In certain cases, τ_x is determined in terms of the residence time of the system near the barrier. The period τ_Q characterises the relaxation of the variable Q; it is proportional to the coefficient of friction γ. If the time scales for τ_x and τ_Q are comparable in magnitude, then the non-equilibrium effects are insignificant and the multidimensional KGH theory yields a satisfactory approximation for the rate constant. Another situation arises if τ_x and τ_Q are quantities of the same order of magnitude. We shall assume that Q is the slow coordinate, having put

$$\tau_x/\tau_Q << 1. \qquad (V.2)$$

Then in the course of an elementary process, there is insufficient time for the coordinate Q to become adjusted to the changes in the faster coordinate x, which in fact entails non-equilibrium effects.[86,103] The mathematical situation described by the inequality (V.2) is treated by averaging the system of Eqns. (IV.24) over the period of fast motion ν_x.[103–105] As a result of the averaging, the two-dimensional potential function is converted into a one-dimensional effective potential $\tilde{U}(Q)$, which governs the motion of the slow variable of the medium Q. The kinetic evolution of Q is expressed in terms of the Fokker–Planck equation for the distribution function $R(Q, t)$:[103–107]

$$\frac{\partial R}{\partial t} = D_Q \frac{\partial^2 R}{\partial Q^2} + \frac{D_Q}{kT}\frac{\partial}{\partial Q}\left[R\frac{\partial}{\partial Q}\tilde{U}(Q)\right] - K(Q)R. \qquad (V.3)$$

Here the first two terms on the right-hand side describe diffusion subject to a potential U with a diffusion coefficient D_Q. The last term on the right-hand side describes the departure of the particles from the reactants region at each point Q with a rate constant $K(Q)$, i.e. a chemical reaction subject to a two-well potential, which is represented by the section along the variable x through the two-dimensional potential $U(a, Q)$ [Eqn. (V.1)] parametrically dependent on Q. The local rate constant is given by

$$K(Q) = \frac{\omega(Q)}{2\pi}\exp\left(-\frac{\Delta U(Q)}{kT}\right). \qquad (V.4)$$

The frequency in the pre-exponential factor and the height of the barrier are functions of Q. Under these conditions, the diffusion coefficient D_Q is proportional to τ_Q^{-1} and the frequency $\omega(Q)$ is proportional to τ_x^{-1}. Eqn. (V.3) gives rise to a range of kinetic regimes.[107–109] Even more varied kinetics are generated by the initial system of Eqns. (IV.24), from which Eqn. (V.3) is obtained in the limit represented by Eqn. (V.2). Each kinetic regime operates in a different range of parameters of Eqn. (IV.24) and can be derived within the framework of a particular approximate model.

Fig. 7 represents the regions of applicability of different approximate descriptions of the kinetics of reaction (IV.24) as a function of the ratio τ_Q/τ_x. For a fixed τ_x, the above parameter increases with increase in τ_Q and is therefore proportional to the coefficient of friction γ and inversely proportional to the diffusion coefficient D_Q. The exact solution of Eqn. (IV.24) would make it possible to cover the entire range of values of the parameter τ_Q/τ_x.

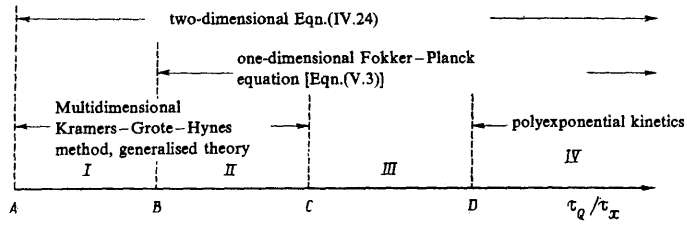


Figure 7. Schematic illustration of the changes in kinetics with increasing viscosity of the medium in the two-dimensional model of the reaction (IV.24). Points *A*, *B*, *C*, and *D* represent the conventional boundaries of different kinetic regimes.

The point B constitutes the left boundary of the region of applicability of the average quasi-one-dimensional equation (V. 3). To the left of this point, the solution is significantly two-dimensional (region I). Here τ_x and τ_Q are of the same order of magnitude and the two-dimensional KGH theory[94] or, what amounts to the same thing, the generalised transition state theory [Eqn. (III.20)] is applicable in this case. The next section of the horizontal axis (region II) corresponds to the situation where the quantity τ_Q/τ_x is now so large that the averaging of Eqn. (IV.24) is legitimate, but the KGH theory is still applicable. The rate constant in this region constitutes the quasi-one-dimensional limit of the two-dimensional KGH theory, is independent of γ, and is given by the simple Arrhenius expression

$$K_e = \frac{\omega_e}{2\pi}\exp\left(-\Delta U^{\neq}/kT\right), \qquad (V.5)$$

where ω_e is the frequency determined by the parameters of the two-dimensional potential.

The approximate solution of Eqn. (V. 3), which represents the equilibrium distribution $R_e(Q)$ and is obtained for fixed values of τ_Q and D_Q in the limit $\Delta U^{\neq}/kT \gg 1$, also corresponds to Eqn. (V. 5). The maximum in the reaction flux, described in Eqn. (V.3) by the term $K(Q)R(Q)$, is then found at the point $Q = Q^{\neq}$, i.e. the saddle point on the surface specified by the function (V.1). At the point $Q^{\neq}$, the quantity $K(Q)$ is a maximum and the reaction passes through the saddle point.

On passing to the region III, the distribution $R(Q)$ ceases to correspond to equilibrium. Movement along the coordinate Q becomes so slow that it has insufficient time to compensate for the decrease in the density of particles owing to the reaction in the vicinity of the point $Q^{\neq}$. The maximum in the reaction flux therefore shifts to the region $Q < Q^{\neq}$, the shift being extended further the greater the ratio τ_Q/τ_x. This increases the effective

potential barrier, which now depends on the coefficient of friction and temperature. A viscosity-dependent rate constant K with a non-Arrhenius temperature variation is thus obtained[103,104] and we then always have

$$\kappa = K/K_e < 1. \quad (V.6)$$

The non-equilibrium rate constant is always smaller than the equilibrium constant and there exists a range of parameters of the potential where the ratio (V.6) is extremely small ($\kappa \simeq 10^{-3}$ and less).[104,109]

Region IV is particularly interesting. Here the kinetics are of a polyexponential type; in other words, they cannot be described with the aid of a single rate constant.[107,108] The extreme case of polyexponential kinetics represents the "frozen" medium limit ($\tau_x/\tau_Q \to \infty$, $D_Q \to 0$) in which the rate of reaction is

$$Q(t) = \int \exp[-K(y)]R(y, 0)dy,$$

where $R(y, 0)$ is the distribution in the initial instant (it is determined by the conditions in the preparation of the reaction system). The dependence of the rate of reaction on the initial distribution is a distinctive property of the polyexponential regime. Eqn. (V.7) means that at each point on the Q axis a chemical reaction is generated with its own rate constant $K(Q)$ and the initial concentration of the reactants at each point is specified by the initial distribution $R(y, 0)$. Polyexponential kinetic regimes, especially the limit (V. 7), have been frequently observed in media with a low mobility. For example, they are typical for low-temperature chemistry.[110] Thus the simple two-dimensional model (IV.24) gives rise to a whole range of kinetic regimes, which are observed experimentally. In this respect, it is incomparably more elaborate than the primitive one-dimensional model (III.1). It can apparently be usefully employed as the phenomenological basis of the description of reactions in condensed media.

The description of effects due to the non-equilibrium nature of the medium is possible in a highly simplified form within the framework of a unique generalised Langevin equation.[34,60,111] We shall consider the dissipative term of Eqn. (III.3):

$$\int_0^t \beta(t - \tau)\dot{x}(\tau)d\tau.$$

Suppose that the time interval $\bar{\tau}$ during which the friction kernel $\beta(t)$ decays is sufficiently long compared with the reciprocal of the decomposition frequency Ω^{-1} [Ω is the solution of the characteristic equation for (III.3)]:

$$\bar{\tau}\Omega >> 1. \quad (V.8)$$

The multiplier $\beta(t-\tau)$ can then be taken outside the integral sign at the point $\tau = t$. This yields the additional term $\beta(0)x(t)$ in the expression for the regular force $(-\partial U/\partial x)$ in Eqn. (III.3), which effectively diminishes the absolute magnitude of the negative force constant in the transition state region. Such description is fully equivalent to the "frozen" medium picture mentioned in Section II.4 in connection with the calculation for the S_N2 reaction by the reaction flux method. Indeed, according to the inequality (V.8), the characteristic relaxation time of the medium $\bar{\tau}$ is much longer than the characteristic time of the motion of the chemical system in the vicinity of the barrier Ω^{-1}. In the other limiting case $\beta(t-\tau) = \delta(t-\tau)$, one obtains the usual Kramers equation; the intermediate case is characterised by a gradual change in the type of kinetics as a function of the ratio of the characteristic times indicated. In this abbreviated description many important results of the more complete two-dimensional theory are lost—for example the polyexponential kinetic regime.

VI. Certain problems and prospects

According to standard textbooks of chemical kinetics concerned with gas-phase reactions,[112,113] the calculation of the reaction rate constant is preceded by three stages:

1. calculation of the potential energy surface;
2. dynamic calculation on this surface;
3. calculation of the distribution function of the initial conditions in the reactants region with the aim of incorporating such conditions in the dynamic calculation.

After this, the rate constant is obtained by averaging the reaction flux in the reactant region on the basis of the initial conditions found.

The transition state theory eliminates the last two stages (dynamic and statistical) using the reaction flux in the region of the saddle point (i.e. the transition state) with the equilibrium distribution function. Modern gas-phase dynamic calculations involve as a rule the first two stages using the hypothesis of the equilibrium Boltzmann distribution in order to average the initial conditions.

Theoretical studies on the kinetics of reactions in condensed media have introduced significant modifications into the programme of operations indicated. In its numerical application, all its three stages are closely intertwined and their artificial separation is undesirable. Thus the calculation of the FES by the Monte Carlo method already involves the equilibrium estimate of the rate constant, which is more or less consistent with the transition state theory. In the stage involving the calculation of the transmission coefficient (i.e. the correction to the Monte Carlo calculation) by the method of molecular dynamics, the dynamic (calculation of reaction trajectories) and statistical (correction of the equilibrium distribution function) stages are virtually inseparable.

A similar situation occurs also in stochastic models: the search for the distribution function for a system of stochastic dynamic equations (we have in mind classical theories) reduces to the solution of the corresponding Liouville (or Fokker–Planck) equation, in which the dynamic and statistical aspects have merged into one.

Research has confirmed the striking vitality of the transition state theory. It was unexpectedly reborn in a generalised form, taking into account the medium, as the multidimensional KGH theory. After such radical modification, its application to a wide variety of kinetic chemical and biological problems promises to be fruitful.

From the standpoint of the development of the theory of chemical kinetics, it is of interest to go beyond the framework of the transition state and KGH methods, i.e. to investigate non-equilibrium effects. This concerns the small transmission factors $\kappa \ll 1$ in classical systems where tunnelling effects are ruled out. The search for the corresponding chemical objects constitutes a special task and this confirms yet again the advantages of the transition state theory in relation to reactions with thermal activation.

At the microscopic level, highly non-equilibrium situations have not so far been observed under thermal conditions. It is sufficient to point out that the calculation for an S_N2 reaction,[33,34] described in subsection II.4, which constitutes a record as regards the thoroughness and volume of computations, yielded only $\kappa = 0.55$ as

the transmission factor. However, even this quantity can be almost completely reproduced within the framework of the KGH theory,[34,60] i.e. it has no bearing on true non-equilibrium effects.

A general study of a model microscopic chemical system[114] showed that it is hardly possible to obtain $\varkappa < 10^{-1}$ retaining the hypothesis, usual for gas-phase reactions, that the initial distribution function in the reactants region corresponds to equilibrium. However, pronounced non-equilibrium effects arise naturally in the phenomenological description of the kinetics in the language of stochastic equations. Two examples were examined above: the region of low friction in the one-dimensional Kramers theory (subsection III.2) and the region of high friction in the two-dimensional stochastic model [Eqn. (IV.24)] (Section IV). Both cases are characterised by the breakdown of the Boltzmann distribution in the reactants zone, which is in fact the source of the disequilibrium.

Thus the next task to be tackled involves the calculation of the distribution functions for thermal reaction systems, under conditions where they deviate markedly from the Boltzmann equilibrium, and the experimental search for the corresponding natural objects. In this connection, we may note that the existing versions of the molecular dynamics calculations are unsuitable for such purposes. They are designed specially for the calculation of transmission factors close to unity under the conditions of small deviations from equilibrium in the transition state region. A converging (i.e. attaining a plateau) calculation of a low transmission factor within the framework of this method is impossible.

An evident aspect of theoretical studies is the application of the approaches already developed to specific chemical and biological systems. The next task on these lines is the development of continuous stochastic models for systems with non-electrostatic interaction by analogy with electron transfer theory. A promising procedure involves the combination of continuous models with numerical approaches: with Monte Carlo and molecular dynamic methods for the determination of the parameters of stochastic equations and with quantum-chemical methods for the calculation of interaction potentials. Finally, it is essential to develop quantum stochastic theories and their numerical application. Without such an instrument, it is impossible, for example, to investigte seriously electron transfer in a polar environment. Studies in this field are nowadays developing vigorously,[55,59] but their discussion is outside the framework of the present review.

References

1. J T Hynes *Theory of Chemical Reaction Dynamics,* Vol. IV (Edited by Baer), CRC Press Inc., Florida, 1985, p. 171
2. P Hanggi *J. Stat. Phys.*, 1986, **42** 105
3. P Hanggi, P Talkner, M Borkovec *Rev. Mod. Phys.*, 1990, **62** 251
4. J Ulstrup *Charge Transfer in Condensed Media,* Springer, Berlin, 1979, 419 pp
5. C H Bennett *Algorithms for Chemical Calculations* (ACS Symp. Ser.) (Edited by R G Christoffersen), Washington, D.C., 1977, Vol. 46, p. 63
6. M V Evans (Editor) *Dynamical Processes in Condensed Matter* (Advances in Chemical Physics), 1985, Vol. 63, 866 pp
7. B Ya Simkin, I I Sheikhet *Kvantovokhimicheskaya i Statisticheskaya Teoriya Rastvorov. Vychislitel'nye Metody i Ikh Primenenie* (Quantum-chemical and Statistical Theory of Solutions. Computational Methods and Their Application), Khimiya, Moscow, 1989, 252 pp
8. M V Basilevsky, V M Ryaboy, N I Weinberg *J. Phys. Chem.*, 1991, **95** 5533
9. E T Denisov *Konstanty Skorosti Gomoliticheskikh Zhidkofaznykh Reaktsii* (Rate Constants for Homolytic Liquid-Phase Reactions), Nauka, Moscow, 1971, 711 pp
10. W L Jorgensen *Acc. Chem. Res.*, 1989, **22** 184
11. I P Bazarov, E V Gevorkyan, P N Nikolaev *Neravnovesnaya Termodinamika i Fizicheskaya Kinetika* (Non-Equilibrium Thermodynamics and Physical Kinetics), Izd. Moskov. Gos. Univ., Moscow, 1989, 240 pp
12. D Chandler *Introduction to Modern Statistical Mechanics,* Oxford University Press, Oxford, 1987, 274 pp
13. H Gould, J Tobochnik *Computer Modelling in Physics* (Translated into Russian), Mir, Moscow, 1990, Part 2
14. D V Kheerman *Metody Komp'yuternogo Eksperimenta v Teoreticheskoi Fizike* (Methods for Computer Experiments in Theoretical Physics), Nauka, Moscow, 1990, 125 pp
15. R W Zwanzig *J. Chem. Phys.*, 1954, **22** 1420
16. J Chandrasekhar, S F Smith, W L Jorgensen *J. Am. Chem. Soc.*, 1985, **107** 154
17. J D Madura, W L Jorgensen *J. Am. Chem. Soc.*, 1986, **108** 2517
18. P A Bash, M J Field, M Karplus *J. Am. Chem. Soc.*, 1987, **103** 8092
19. J-K Kwang, G King, S Creighton, A Warshel *J. Am. Chem. Soc.*, 1988, **110** 5297
20. V A Valuev, G E Norman, V I Podlipchuk *Matematicheskoe Modelirovanie. Fiziko-Khimicheskie Svoistva Veshchestva* (Mathematical Modelling. Physicochemical Properties of Matter) (Edited by A A Samarskii, N N Kalitkin), Nauka, Moscow, 1989, p. 5
21. D Chandler *J. Chem. Phys.*, 1978, **68** 2959
22. J C Keck *Adv. Chem. Phys.*, 1967, **13** 85
23. J C Keck *Adv. Atom. Mol. Phys.*, 1972, **8** 39
24. J B Anderson *J. Chem. Phys.*, 1973, **58** 4684
25. J B Anderson *J. Chem. Phys.*, 1975, **62** 2446
26. R O Rosenberg, B Berne, D Chandler *Chem. Phys. Lett.*, 1980, **75**(1) 162
27. J A Montgomery, Jr, S Holmgren, D Chandler *J. Chem. Phys.*, 1980, **73** 3388
28. J Jonas *Acc. Chem. Res.*, 1984, **17** 74
29. J Ashcroft, C-L Xie, J Jonas *J. Chem. Phys.*, 1989, **90** 5386
30. R A Kuharsky, D Chandler, J A Montgomery, et al. *J. Phys. Chem.*, 1988, **92** 3261
31. M A Wilson, D Chandler *Chem. Phys.*, 1990, **149** 11
32. J P Bergsma, J R Reimers, K R Wilson, J T Hynes *J. Chem. Phys.*, 1986, **85** 5625
33. J P Bergsma, B J Gertner, K R Wilson, J T Hynes *J. Chem. Phys.*, 1987, **86** 1356
34. B J Gertner, K R Wilson, J T Hynes *J. Chem. Phys.*, 1989, **90** 3537
35. J E Straub, M Borcovec, B J Berne *J. Chem. Phys.*, 1986, **84** 1788
36. B J Berne *Multiple Time Scales* (Edited by J E Brackbill, B I Cohen), Academic Press, New York, 1985, p. 419
37. J E Straub, B J Berne *J. Chem. Phys.*, 1985, **83** 1138

38. J E Straub, D A Hsu, B J Berne *J. Phys. Chem.*, 1985, **89** 5188
39. M Borcovec, P Talkner *J. Chem. Phys.*, 1990, **92** 5307
40. J A Montgomery, Jr, D Chandler, B Berne *J. Phys. Chem.*, 1979, **70** 4056
41. D Bohm, E P Gross *Phys. Rev.*, 1979, **75** 1864
42. C W Gardiner *Handbook of Stochastic Methods for Physics, Chemistry, and the Natural Sciences* (Translated into Russian), Mir, Moscow, 1986, 528 pp
43. J T Hynes *Chem. Phys. Lett.*, 1981, **79** 344
44. S Adelman *Adv. Chem. Phys.*, 1980, **44** 143
45. R Kubo, M Toda, N Hatshisume *Statistical Physics*, Springer Verlag, Berlin, 1985, Part II, 279 pp
46. M V Basilevsky, G E Chudinov *Mol. Phys.*, 1988, **65** 1221
47. L D Landau, E M Lifshits *Statisticheskaya Fizika* (Statistical Physics), Nauka, Moscow, 1976, Part I, 584 pp
48. H A Kramers *Physica*, 1940, **77** 284
49. J Schroeder, J Troe *Annu. Rev. Phys. Chem.*, 1987, **38** 163
50. G R Fleming, S H Courtney, M V Balk *J.Stat. Phys.*, 1986, **42** 83
51. R F Grote, J T Hynes *J. Chem. Phys.*, 1980, **73** 2715
52. M V Basilevsky, G E Chudinov *Chem. Phys.*, 1990, **144** 155
53. H Mori *Prog. Theor. Phys.*, 1965, **33** 424
54. E Cortes, B J West, K Lindenberg *J. Chem. Phys.*, 1985, **82** 2708
55. A O Caldeira, A J Leggett *Ann. Phys. (N.Y.)*, 1983, **149** 374
56. H Grabert, U Weiss *Phys. Rev. Lett.*, 1984, **53** 1787
57. E Pollak *J. Chem. Phys.*, 1986, **86** 865
58. Yu I Dakhnovskii, A A Ovchinnikov *Mol. Phys.*, 1986, **58** 237
59. H Grubert, P Olschovskii, U Weiss *Phys. Rev., B*, 1987, **36** 1931
60. B J Gertner, J P Bergsma, K R Wilson, et al. *J. Chem. Phys.*, 1987, **86** 1377
61. J S Langer *Ann. Phys. (N. Y.)*, 1967, **41** 108
62. H A Weidenmüller, Jing-Shang Zhang *J. Stat. Phys.*, 1984, **34** 191
63. R Grote, J T Hynes *J. Chem. Phys.*, 1981, **74** 4465
64. R Grote, J T Hynes *J. Chem. Phys.*, 1981, **75** 2191
65. A Nitzan *J. Chem. Phys.*, 1987, **86** 2734
66. A Nitzan *Adv. Chem. Phys.*, 1988, **70** 489
67. R A Marcus *J. Chem. Phys.*, 1956, **24** 966
68. A M Kuznetsov, J Ulstrup, M A Vorotyntsev *The Chemical Physics of Solvation* (Edited by R R Dogonadze, et al.), Elsevier, Amsterdam, 1988, Part C, 1988, p. 163
69. S I Pekar *Issledovanie po Elektronnoi Teorii Kristallov* (Studies on the Electronic Theory of Crystals), Fizmatgiz, Moscow–Leningrad, 1951, 265 pp
70. W Brown *Dielectrics* (Translated into Russian), Inostr. Lit., Moscow, 1961, 321 pp
71. H Frohlich *Theory of Dielectrics* (Translated into Russian), Inostr. Lit., Moscow, 1960, 321 pp
72. M Ya Ovchinnikova *Khim. Fiz.*, 1985, **4** 3
73. I V Alexandrov *Chem. Phys.*, 1980, **51** 449
74. D Zusman *Chem. Phys.*, 1980, **49** 295
75. V G Levich, R R Dogonadze *Dokl. Akad. Nauk SSSR*, 1959, **124** 123
76. M Sparpaglione, S Mukamel *J. Phys. Chem.*, 1987, **91** 3938
77. M Sparpaglione, S Mukamel *J. Chem. Phys.*, 1987, **88** 3623, 4300
78. A Garg, J N Onuchic, V Ambegaocar *J. Chem. Phys.*, 1985, **83** 4491
79. I Rips, J Jortner *J. Chem. Phys.*, 1987, **87** 2090
80. A I Burshtein, A A Zharikov *Chem. Phys.*, 1991, **152** 23
81. A I Burshtein, B I Yakobson *Khim. Vys. Energ.*, 1980, **14** 291
82. E D German, A M Kuznetsov *Kinetika Zhidkofaznykh Reaktsii Perenosa Zaryada* (Kinetics of Liquid-Phase Charge-Transfer Reactions), Izd. VINITI, Moscow, 1990, 150 pp
83. M D Newton *Chem. Rev.*, 1991, **91** 767
84. M V Basilevsky, G E Chudinov *Chem. Phys.*, 1991, **157** 327, 345
85. M D Newton, N Sutin *Ann. Rev. Phys. Chem.*, 1984, **35** 437
86. L D Zusman *Chem. Phys.*, 1988, **119** 51
87. R A Marcus *Chem. Phys. Lett.*, 1987, **133** 471
88. R A Marcus, R Almeida *J. Phys. Chem.*, 1990, **94** 2973, 2978
89. G Grampp, W Harrer, W Jaenicke *J. Chem. Soc., Faraday Trans., Part 1*, 1987, **83** 161
90. A Kapturkiewicz, W Jaenicke *Z. Phys. Chem.*, 1988, **160** 169
91. M McGuir, G McLendon *J. Phys. Chem.*, 1986, **90** 2549
92. I Rips, J Klafter, J Jortner *J. Phys. Chem.*, 1990, **94** 8557
93. M M Dygas, B J Matkovsky, Z Shuss *J. Chem. Phys.*, 1986, **84** 3731
94. M V Basilevsky, G E Chudinov *Mol. Phys.*, 1990, **71** 461
95. A Masad, D Huppert, E M Kosower *Chem. Phys.*, 1990, **144** 391
96. P F Barbara, W Jarzeba *Acc. Chem. Res.*, 1988, **21** 195
97. N Agmon, R Kosloff *J. Phys. Chem.*, 1987, **91** 1988
98. N Agmon, S Rabinovich *Ber. Bunsenges. Phys. Chem.*, 1991, **95** 278
99. J M Hicks, M T Vandersall, E V Sitzmann, K B Eisenthal *Chem. Phys. Lett.*, 1987, **135** 413
100. D P Milar, K B Eisenthal *J. Chem. Phys.*, 1985, **83** 5076
101. A M Berezhkovskii *Dokl. Akad. Nauk SSSR*, 1988, **298** 880
102. S Lee, J T Hynes *J. Chem. Phys.*, 1988, **88** 6853, 6863
103. A M Berezhkovskii, V Y Zitserman *Chem. Phys. Lett.*, 1989, **158** 369
104. A M Berezhkovskii, V Y Zitserman *Physica, A*, 1990, **166** 585
105. A M Berezhkovskii, V Y Zitserman *Chem. Phys.*, 1991, **157** 141
106. N Agmon, J J Hopfield *J. Chem. Phys.*, 1983, **78** 6947
107. H Sumi, R A Marcus *J. Chem. Phys.*, 1986, **84** 4894
108. W Nadler, R A Marcus *J. Chem. Phys.*, 1987, **86** 3906
109. M V Basilevsky, V M Ryaboy, N N Weinberg *J. Phys. Chem.*, 1990, **94** 8734
110. V A Tolkatchev *Chem. Phys.*, 1987, **116** 283
111. G van der Zwan, J T Hynes *J. Chem. Phys.*, 1982, **76** 2993
112. V N Kondrat'ev, E E Nikitin *Kinetika i Mekhanizm Gazofaznykh Reaktsii* (Kinetics and Mechanisms of Gas-Phase Reactions), Nauka, Moscow, 1974, 558 pp
113. E E Nikitin *Teoriya Elementarnykh Atomno-Molekulyarnykh Protsessov v Gazakh* (Theory of Elementary Atom–Molecule Processes in Gases), Khimiya, Moscow, 1970, 455 pp
114. M V Basilevsky, S I Petrochenko *Chem. Phys.*, 1989, **130** 103

Received 20th February 1992

Translated from *Uspekhi Khimii* **61** 1224–1242 (1992) U.D.C. 541.17+548.5

Solvent effect on the kinetics of crystal growth

E B Treivus
St. Petersburg University

ABSTRACT. Experimental data for the solvent effect on the kinetics of crystal growth are summarised. The common analytical method based on the concept that crystallisation in solutions occurs essentially through random addition of particles to the crystal surface (normal growth mechanism) and the means for estimating the contribution of this mechanism are critically examined. The conclusion is made that the role of such a mechanism is overstated. A theory is formulated that enables the solvent effects pertaining to layered facial crystal growth to be estimated.

The bibliography contains 52 references.

Contents

I. Introduction 673
II. Treatment of experimental data within the framework of the normal growth mechanism 673
III. Experimental data analysed within the framework of the layered growth mechanism 678

I. Introduction

Solvent effects on crystallisation are interesting for a number of reasons. Solvent exchange is a useful method of studying mechanisms of chemical reactions in solutions, in particular, the growth of crystals. Finding the principles underlying this area is also worthwhile for applications since the current trend is toward expanding the number of solvents (organic liquids, metal melts, inorganic salts and oxides) used to grow crystals from solutions. The choice of solvent is important to various sectors of the chemical industry (processing crude petroleum, production of mineral fertilisers, reagents, pharmaceuticals, etc.) owing to the need to promote crystallisation and the desire to gain a greater yield and to change the shape of the crystallites in the required direction. In particular, the caking of a substance, the effectiveness of its separation from the mother liquor, its pharmaceutical efficacy, etc., depend on this shape. A review of studies in this area was published abroad more than 10 years ago.[1] Analogous publications have not appeared in the domestic literature.

II. Treatment of experimental data within the framework of the normal growth mechanism

The solvent was known to affect crystal shapes, i.e., the ratio of growth rates of their various faces, even at the start of the present century. Thus, the solvent affected the habit of crystals of urea, sulphur, etc.[2] According to Orlov,[3] these facts were related to the change of surface tension of the various faces since shortly before this the well-known Gibbs–Curie principle about the minimum surface energy of an equilibrium crystal had been formulated. It is now evident that this principle is inapplicable to nonequilibrium crystal shapes. How the concept of the role of surface energy in the kinetics of crystal growth has up to now been transformed will be clear from the following exposition.

Orlov[3] discovered that the facetting of NaOH crystals becomes complicated on going from aqueous solution to formamide and also on going to a mixture of water with certain hydroxy-acids. According to his viewpoint, the shape of crystals changes if the dissolved substance reacts chemically with the solvent. He saw signs of this in the high dielectric constant of formamide and in the structural features of the solvents used. A specific interaction with different crystal faces of complexes of the crystallising species and solvent species that have a variable structure in different solutions can change the crystal habit.[3] Apparently, this study was the first in which the possible role during crystallisation of a change in solution structure owing to a solvent change was pointed out.

Wells[4] pointed out the significance of a specific solvent interaction with different crystal faces. He illustrated this using resorcinol as an example. Certain opposing faces of resorcinol crystals have different structures. According to Wells, the faces terminating in hydroxyl groups are blocked by water molecules. This leads to preferential development of these faces during formation of resorcinol crystals. The nonpolar solvent benzene does not affect this selective adsorption. The crystal grows symmetrically in opposite directions.

Both these ideas are expanded upon or confirmed in subsequent studies. Kleber and Raidt[5] discovered that salol crystals in nonpolar solvents (CCl_4, C_6H_6) and in acetone have a shape corresponding to their symmetry type $2/mm$. The external symmetry is reduced to 22 if polar solvents (CH_3OH, C_2H_5OH, C_3H_7OH) are used. This phenomenon was related[5] to the solution structures. In nonpolar solvents, salol molecules are associated; in polar, they are not associated. However, it is not clear how this is related to the external crystal facetting. The concept of specific solvent adsorption has been developed.[6] The formation of a new face on $Hg(CN)_2$ crystals in CH_3OH solution was explained by epitaxy on this face of the complex $Hg(CN)_2.CH_3OH$. The similarity of the atomic distributions in planes of the growing faces of $Hg(CN)_2$ and $Hg(CN)_2.CH_3OH$ crystals confirms that epitaxy occurs.

Thus, the position was in essence taken[6] that solvent is specifically adsorbed if there are epitaxial relationships between faces of the crystallising substance and the solvent (a compound with it is a particular instance). The scale of the dimensional fit is an important condition and significant sign of the extent of specific solvent adsorption. It is noteworthy that, apparently, Petrov[7] first expounded the idea of selective epitaxial solvent adsorption on different faces of a single crystal and its role in their growth features.

Then, this idea was directly confirmed[8] by results of ice crystal formation on different faces of sodium bromate crystals.

This short synopsis is necessary, in particular, because the domestic studies are not mentioned in the previous review.[1]

According to Berkovitch-Yellin,[9] polar faces preferentially adsorb polar solvent molecules. Nonpolar ones are solvated by nonpolar solvents. The solvent effect should be especially distinctly evident for crystals of those substances for which the different faces have considerably different polarities. By the polarity of a face is meant the degree of contrast in its electrostatic relief that is quantitatively characterised by the difference of the positive and negative peaks in the map of the electrostatic potential of this face. Such maps have been presented[9] for different crystal faces of benzamide, benzoic acid, α-glycine, E-cinnamide and succinic acid. The maxima of the positive and negative potentials are given. Within the framework of his hypothesis, Berkovitch-Yellin qualitatively explains the crystal shape of these compounds obtained from different solutions. Certainly this hypothesis helps the problem to be understood and possesses a certain predictive capability. However, the importance of dimensional fits is ignored in it.

According to Chan et al.,[10] hexamethylmelamine (an anti-tumour drug) crystals become most anisometric with increasing supersaturation on crystallisation from polar media. Crystals formed in polar media are less sensitive to a change of supersaturation. The spectroscopic features of solutions of this compound in both types of solvents are the same. The crystallisation of two organic compounds was used[10] to demonstrate that relatively well formed isometric crystals are formed from solutions that differ in ideal solubility. Needle-like crystals grow in other solutions. These studies are attempts to find common features of the solvent effect on crystal growth.

The solvation of different faces was quantitatively estimated for saccharose crystals in aqueous solution from the change of surface tension.[12]

For all studies up to the middle of the 1960s, and for many earlier ones including those mentioned above, a qualitative approach and the lack of control of the supersaturation and temperature was characteristic. It was noted in the best instances at what supersaturation, high or low, the experiments were conducted. The temperature was approximately indicated. The results of similar studies are dubious since they may be due not to a solvent effect but to the factors mentioned above. Furthermore, these data are not always reproducible. The first quantitative measurements of the growth rates in different solutions with accurately controlled conditions were described in 1967.[13] It was found that the growth rate of glyceryltripalmitate and glyceryltristearate (measured for one crystal direction) crystals is much higher in CCl_4 solution than in glyceryltrioleate solution. This is consistent with the noticeably higher solubility of these tristearides in the first solvent than in the second. This feature was not noted.[13] However, it then turned out that it is fundamental.

It has been discovered[14] that the growth rate of urotropine crystals from aqueous, ethanol and aqueous-acetone solutions directly depends on its solubility in these media. The solubility of biphenyl in toluene is almost 20 times greater than in CH_3OH (in mole fractions). The growth rate of biphenyl crystals from toluene solution is also almost 20 times greater than from CH_3OH.[15] The kinetics of KNO_3 crystal growth from a series of five solvents and four of their binary mixtures obey the same rules.[16] The growth rate of succinic acid crystals[17] with solubility expressed in molality or molarity also directly depends on its solubility in water and isopropanol although an inverse dependence is obtained if the solubility is expressed in mole fractions. The growth rates of separate faces of hexatriacontane crystals are directly proportional to the solubility of this paraffin in heptane, decane, pentane and petroleum ether.[18]

Table 1. Growth rate of *para*-xylene crystals V at various relative supersaturations σ (0 °C, 30 mass% solvent).[20]

Solvent	m_0	σ	10^4V, cm sec^{-1}	$10^2\beta$, cm sec^{-1}
Ortho-xylene	21,7	0,014	1,0	0,71
Toluene	21,7	0,012	0,7	0,58
Meta-xylene	21,8	0,009	0,6	0,67
Benzene	21,8	0,006	0,8	1,3
Ethylbenzene	21,9	0,002	2,2	11,0

Note. The concentration of the saturated solution m_0 in molality was calculated by us.

Table 2. Thermodynamic and kinetic parameters for growth of urea crystals (25 °C).[21]

Solvent	m_0	ΔH_{cr}, kJ mol^{-1}	α_2	α_3		$10^6\beta_2$, mol cm^{-2} sec^{-1}	
				(100)	(011)	[100]	[001]
Propanol	0,52	27	7,9	3,3	5,0	0,43	1,3
Ethanol	1,04	20	5,9	3,2	4,7	0,26	3,6
Ethyleneglycol	7,45	12	3,6	2,4	3,5	0,38	0,89
N-Methylformamide	7,45	11	2,9	2,4	3,6	1,5	3,5
Formamide	8,79	10	3,2	2,4	3,6	0,70	8,2
Water	20,0	12	3,2	2,4	3,7	43	140

The same was observed for growth rates of individual faces of stearic acid crystals in hexane, decane, dodecane and octane.[18,19] The crystallisation of *para*-xylene (Table 1), which was studied in connection with the problem of separating the precipitate from the mother liquor, and urea (Table 2) can also be used as examples. The kinetic coefficient β appears in both tables as a parameter characterising the growth rate. In the first instance, it is calculated by us from original data presented in Table 1 using the equation $\beta = V/\sigma$. In other words, it is assumed that the growth rate is linearly dependent on the supersaturation. In fact, this function is nonlinear and β is therefore somewhat high. In the second instance, β was determined using the equation $\beta = V/(\sigma - \sigma_{cr})$, where σ is the total supersaturation of the solution and σ_{cr} is the critical supersaturation within which the face does not grow. The quantity σ_{cr} is unique for different solutions. It is zero for aqueous and formamide solutions of urea. The quantity α (Table 2) is discussed below.

In general, the correlation between the crystal growth rate and the solubility is considered to be firmly established although there are exceptions. For example, an inverse dependence is observed for the growth rate of stearic acid crystals from butanone and octane-2-one solutions (Table 3). It is noteworthy that the described feature contradicts the old Van't Hoff rule,[25,26] according to which the rate constant is inversely proportional to the solubility of the reagents.

Table 3. Data for growth of *B*- and *C*-modifications of stearic acid crystals.[22–24]

Solvent	m_0 (25 °C)	ΔH_{cy}, kJ mol^{-1} (25 °C)		V, rel. units		$E^{\neq}$, kJ mol^{-1}	
		B	*C*	*B*	*C*	*B*	*C*
Butanone	0.16	78	74	2.4	2.9	180	105
Octane-2-one	0.37	72	67	1	1	110	73

Note. The activation energy $E^{\neq}$ for growth in butanone solution is found for the (110) face at 13–25 °C; from octane-2-one solution, 16–29 °C. The solubility in molality is calculated by us using previous data.[22,24]

The features of crystal growth from various solvents were analysed using the so-called "entropy factor" (α-factor, Jackson–Temkin factor, roughness factor or parameter),[1,27–30] which was first introduced to analyse growth of crystals from the melt. Small α-factors indicate small differences between the bond energy of species in the crystal and that of the same species with solvent or similar entropies for the crystal and dissolved substance. In other words, these α-factors reflect the strong solvation of the crystal faces, characterised by a low interfacial surface tension. Hence, atomic species should add randomly at small α to the crystal surface at any point (so-called "normal" or "continuous" crystal growth). As a result, the face should be "atomically rough". It is noteworthy that the term "atomically rough" has two meanings. These are the morphological one, as here, and the energetic one. In the second instance, the atomic roughness is the source of normal growth and not its consequence.

For certain intermediate α values, where the surface tension of a face and, consequently, the end of an atomic layer on it, is comparatively small, layered growth of an ideal (defect-free) face is possible owing to formation on it of two-dimensional nuclei even at low supersaturations. Further increasing α should indicate the necessity of large supersaturations for two-dimensional nucleation. At low supersaturations at these α values, the ideal face should not grow at all. At relatively high α values (large surface tension), layered growth is possible that is caused only by dislocations in the crystals. Dislocational growth becomes more significant as α increases. In other words, higher α values indicate that the face is atomically smooth.

The difference between an atomically rough surface and an atomically smooth (singular) one is illustrated in Fig. 1, in which free-energy activation barriers to transfer of an atomic species from solution onto the crystal and its migration along the face are presented for both instances. The barrier (solid line) to direct transfer into the crystal, characterised by the quantity of $\Delta\overleftarrow{G}_0^{\neq}$, is also shown in Fig. 1. This barrier is higher than the previous one since it is accompanied by more extensive desolvation. All points on an atomically rough surface are equivalent for adding atoms to it. They have identical energies for adding atoms to kinks in a step on the crystal surface. The dashed line in Fig. 1*b* outlines the barrier to diffusion along an atomically rough surface, which is also rather high compared with an atomically smooth surface. There should be intermediate instances since it is assumed that the contribution from the normal growth mechanism can vary.

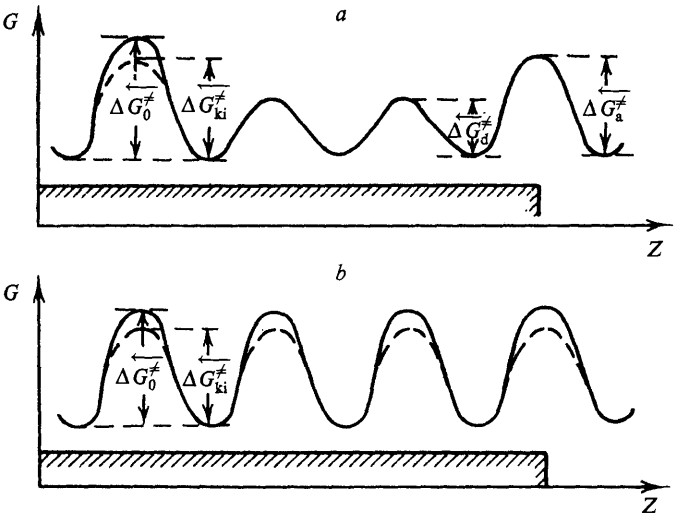


Figure 1. Free energy as a function of position of an atomic particle on a crystal surface (the crystal surface is hatched): an atomically smooth face ($\alpha \gtrsim 3$) (*a*) and an atomically rough face ($\alpha \lesssim 3$) (*b*). The quantity z is the reaction coordinate, $\Delta\overleftarrow{G}_a^{\neq}$ is the free energy of activation for transferring particles from solution into the adsorbed layer on the face (this transfer is accompanied by incomplete desolvation of the crystallising particles), $\Delta\overleftarrow{G}_d^{\neq}$ is the activation energy for surface diffusion of adatoms, $\Delta\overleftarrow{G}_{ki}^{\neq}$ is the activation energy for transfer from the adsorbed layer on a face into a kink on a step accompanied by further partial desolvation (the corresponding barrier is shown as a dashed line).

Thus, a phase transition characterised by low α values should have a high growth rate with a linear dependence on supersaturation and poorly facetted, more or less isometric crystals. Increased growth rates for the normal mechanism are the result of a high density of growth sites on the crystal surface. Crystallisation at high α values should be accompanied by the nonlinear dependences of the growth rate on supersaturation that are typical of layered growth and formation of well formed crystals with a more distinct anisometry than for normal growth, according to the structure of a given crystal. The correlation between α and the crystal-growth features are well observed for melts.

Computer modelling demonstrated (see also previous theoretical estimates[31]) that surface roughness, normal growth and a linear dependence of rate on supersaturation occur for α less than a critical $\alpha_{cr} \approx 2.5$ (Ref. 1) or 3 (Ref. 28). For the range $2.5 \lesssim \alpha \simeq 4$ (Ref. 1) [according to other estimates from 3 to 5 (Ref. 28)], two-dimensional nuclei form comparatively easily and the dependence of growth rate on supersaturation begins to acquire a nonlinear nature. At larger α in a relatively broad range of supersaturations, growth is possible only if dislocations are present and the faces are atomically smooth. These results were obtained by modelling a Kossel crystal (a crystal consisting of closest packed cubes) and considering interactions only between nearest neighbours. For actual crystals differing in structure, types of chemical bonds and shapes of the species comprising them, α values indicating one crystallisation mechanism or another possibly will greatly vary.

The following equations are proposed for calculating α for solutions

$$\alpha_1 = \zeta \frac{\Delta H_{cy}}{RT_{cy}} = \zeta \frac{\Delta S_{cy}}{R}, \quad (1)$$

$$\alpha_2 = \frac{4\gamma_{1a}}{RT_{cy}}, \quad (2)$$

$$\alpha_3 = \zeta \left(\frac{\Delta H_f}{RT_f} - \ln x \right). \quad (3)$$

Here ζ is the crystallographic anisotropy factor that depends on the actual face (ratio of bond energy of the crystal building block within an atomic layer parallel to the given face to the total bond energy or, to a first approximation, the ratio of the number of nearest neighbours in an atomic layer to the coordination number), ΔH_{cy} is the heat of crystallisation, ΔS_{cy} is the entropy of crystallisation, γ_{1a} is the surface tension of an end of an atomic layer on the given crystal face, ΔH_f is the heat of fusion, T_{cy} is the crystallisation temperature, and T_f is the melting point (m.p.). The quantity x has been given different meanings in various studies.[15,17,28] At present, solubilities of substances in mole fractions are preferred for x.

Calculations of α using Eqn. (1) have been shown to be unreliable[1] although this expression is used with ΔH_f and ΔS_f for melts. It is well known that the heat and, therefore, the entropy of crystallisation sometimes have negative values. This makes calculation of α using Eqn. (1) meaningless. Unjustifiably small α are obtained for athermal solutions that have low ΔH_{cy} although they are far from ideal. Furthermore, Eqn. (1) does not consider the individual solvation of different faces. A calculation using Eqn. (1) and ΔS_{cr} for growth of urotropine crystals from aqueous solution (apparently ignoring the sign of ΔS_{cy} since the heat of crystallisation of urotropine from aqueous solution is negative) gave $\alpha = 0.9$.[27] This should indicate that poorly facetted crystals grow. However, urotropine crystals from aqueous solution form typical regular rhombododecahedra and usually capture inclusions of solution. This is characteristic of growth under conditions of "diffusional depletion" (but not of normal growth). Eqn. (1) is not used much anymore. However, the correlation between the growth rate and heat of crystallisation cannot be invalidated (see Table 2), although there may be extenuating circumstances.

Eqn. (2) has previously been applied.[21,27,32,33] Calculations for urotropine using Eqn. (2) and surface tension values of the surface γ_s obtained from the kinetic data for crystal nucleation with subsequent conversion to γ_{1a} gives $\alpha = 0.1$.[27]

Thus, urotropine crystals from aqueous solution should be poorly facetted and rounded according to these calculations. This contrasts with their actual shape. The quantity γ_{1a} for Rochelle salt ($\alpha = 5.2$, well facetted crystal) was calculated[32] on the basis of the empirical correlation between γ_s and ΔH_{cy} known from the literature. The quantity γ_{1a} was analogously determined for urea crystals.[21] The α values (see Table 2) agree with the regular shape of these crystals. This correlation is not accurate enough to calculate α. It loses meaning for solutions with $\Delta H_{cy} < 0$ and for athermal solutions. The quantity γ_{1a} for octogen crystals was calculated[33] on the basis of experimental stability data for supersaturated solutions. Such determinations give γ_s close to the true values. However, these are evidently not accurate enough to calculate γ_{1a}. Furthermore, if the crystal has complicated facetting and this method is used, averaged γ_s are obtained for the crystal as a whole and not for an actual face. For octogen crystals formed from dimethylsulphoxide solution, $\alpha = 0.26$. For such an α value, the crystals of this compound should grow by the normal mechanism, be poorly facetted, and have a linear dependence of rate on supersaturation. However, they were regularly shaped and the dependence of growth rate on supersaturation was distinctly nonlinear.[33]

For octogen in cyclohexane, the agreement of theory and experiment was satisfactory. Thus, $\alpha = 0.6$, the crystals are poorly facetted, and the growth rate depends linearly on supersaturation. According to the literature,[33] the process is diffusion limited, evidently, owing to the fast growth rates. The diffusion limit should be the reason for this linear dependence. However, the fact that the growth rates are fast should argue in favour of a normal mechanism.

The quantity γ_s was converted to γ_{1a} by assuming that the surface tensions of a face and an end of an atomic layer are identical.[27,33,1] This can be disputed by considering the differences in the number of dangling chemical bonds for the species located on the smooth face and on the end of an atomic layer. Furthermore, the symbol of a step end may not coincide with that of the given face if the crystal has complicated facetting. Even for the instance where the crystal has simple facetting, the symbol of the layer end may not correspond to the symbol of this shape (for example, the crystal is cubic and the layer is oriented along [110]). However, it is well known that the surface tension of a layer end depends on its orientation.

Eqn. (3) is used most. This apparently is due to the fact that calculations using it are the easiest. The calculations are contradictory. Obviously, this equation gives small α values for a given substance the greater its solubility. Since the solubility and growth rate are correlated, a systematic inverse correlation between α calculated using Eqn. (3) and the crystal growth rate is observed (an example can be found in Table 2). The two following examples concerning the relationship between α and the crystal shape are interesting.

The entropy factor for biphenyl crystals growing from CH_3OH and toluene solution were calculated using Eqn. (3) (Table 4). The α_{cr} values for different faces were also determined. As it turned out, the faces (001) and (110), for which $\alpha > \alpha_{cr}$, are planar. The face $(20\bar{1})$, for which $\alpha \lesssim \alpha_{cr}$, is rounded. The other two faces, which have comparatively high α_{cr}, are practically unobserved in the facetting. This is quite natural in view of their fast growth rates characteristic of a normal mechanism.

The second example involves crystallisation of naphthalene[34] from solutions in biphenyl and phenanthrene at the eutectic temperatures. It can be seen from Table 5 that the face (001) has the highest σ values. Thus, this face is planar and dominates in crystals at all studied supersaturations. The crystal is platelike along this face.

The smallest α are seen on $(20\bar{1})$. This face has the fastest growth rates and becomes rounded at $\Delta T > \Delta T_{cy}$. The face (110) has an intermediate α value. In biphenyl solution, the eutectic temperature of which is comparatively far from the m.p. of naphthalene, ΔT_{cy} for (110) is much greater than for $(20\bar{1})$. For crystallisation from the eutectic with phenanthrene, the temperature of which is close to the m.p. of naphthalene, ΔT_{cy} for both faces are similar (the approach of the crystallisation temperature to the m.p. neutralises the individual features of the different faces).

Table 4. The α-factor for biphenyl crystals at 30 °C.[15]

Face	CH_3OH	Toluene	α_{kp}
(001)	7.8	6.4	2.6
(110)	4.3	3.5	2.8
$(20\bar{1})$	3.1	2.5	2.7
$(11\bar{1})$	3.5	2.9	3.4
(110)	2.7	2.2	3.0

Table 5. Parameters for growth of naphthalene crystals from biphenyl (x = 0.44, 39.4 °C) and phenanthrene solutions (x = 0.98, 78.9 °C).[34]

Face	ζ	Biphenyl		Phenanthrene	
		α	ΔT_{cy}	α	ΔT_{cy}
(001)	0.820	5.78	–	5.13	–
(110)	0.409	2.94	1.1	2.62	0.3
$(20\bar{1})$	0.380	2.74	0.3	2.43	0.2

The growth of naphthalene crystals has been studied in detail.[35] It was found that rounded surfaces growing by a normal mechanism are formed in solutions of those solvents that have benzene or similar rings in their structure (benzene, toluene, pyridine, etc.). Fully facetted crystals are formed in solutions of solvents that do not have aromatic rings or are elongated or spherical (hexane, CH_3OH, $CHCl_3$, etc.). Elwenspoek et al.[35] suggest that the solvent in the first instance forms an oriented ordered adsorption layer on the naphthalene crystal surface and that the surface tension of the crystals in these solvents is relatively low. In the second instance, there is no such ordered layer and the surface tension is relatively high.

Let us illustrate examples where the observations and calculations using Eqn. (3) do not agree. The dependence of growth rate on supersaturation for the triglycerides mentioned above that is found for CCl_4 solution is much more nonlinear than for glyceryltrioleate solution although α = 2.8 in CCl_4 and α = 4.5 in trioleate.[13] For succinic acid in water and in isopropanol (Table 6), $\alpha_{(010)} > \alpha_{(001)}$; however, $V_{(010)} > V_{(001)}$. The habit changes from platelike along (001) in water to prismatic along [100] in isopropanol. This is in no way predicted on the basis of the α values. These discrepancies between theory and experiment were explained for succinic acid[17,28] as the result of solvation by isopropanol of the ends of atomic steps on the crystal faces. However, this only means that Eqn. (3) is unsatisfactory for calculating α. All varieties of interactions of the compound with the solvent are taken into consideration in Eqn. (3) only through the solubility. The individual features of the solvation of the different faces are ignored. The correction coefficient in Eqn. (3) that reflects the individual interaction of actual solution species and has previously been given[36] is difficult to calculate in practice.

Table 6. Parameters of succinic acid crystallisation.[17]

Face	ζ	Water		Isopropanol	
		α	10^6V	α	10^6V
(010)	0.67	7.8	15	8.0	1.0
(001)	0.5	5.8	4.0	6.0	0.1

Note. The growth rate is in cm sec^{-1} at σ = 0.015.

The data described suggest that in general application of α to solutions is problematical. Eqn. (3) is interesting for calculating an approximate α. Eqn. (2) is most general although it is difficult to use in practice owing to the complexity of determining the surface tension of the end of an atomic layer. The conversion to a rough surface at certain small but finite γ_{st} has been confirmed.[36,37] This contradicts the common viewpoint[31] according to which a condition for the conversion to a rough surface is the reversion of γ_{st} to zero. Regardless of the end construction (degree of roughness), the atomic step is an interface. Therefore, γ_{st} cannot revert to zero.

The method for analysing crystallisation from solutions that depends on use of α is counterposed to the method[28] based on direct analysis of solvation of a face and that[9] based on an analysis of solvation and its relation to the activational barriers. Such contrast is unfounded in view of the auxiliary nature of α. Its significance is to indicate the features of a phase transition on a crystal surface. If both methods contradict each other, α is calculated using an inaccurate formula.

Direct determinations of the activation energy during crystallisation from various media are rare. It has been established that the increase of solubility and growth rate of hexatriacontane in the series decane–heptane–pentane is accompanied by a decrease of activation energy, which equals to 205, 146 and 121 kJ mol^{-1}, respectively.[28] The increased solubility of stearic acid crystals (see Table 3) is also accompanied by a decrease of activation energy and heat of crystallisation.

In general, the examples of normal growth of crystals from solutions are selective and include organic compounds at formation temperatures that differ little from the m.p. Facetted growth is characteristic for crystals in solution. Faces develop owing to expansion of layers on them. Therefore, features of crystallisation from solutions should be theoretically explained by first examining layered facetted growth.

III. Experimental data analysed within the framework of the layered growth mechanism

1. Kinetic equation for the phase transition of an individual atomic species.

The known equation from the activated-complex theory[25,26,38] is usually used to describe the elementary step of crystallisation:

$$V = 0.5\nu\kappa \exp\left(-\Delta G^{\neq}/RT\right)\Pi\alpha_i^{\nu_i}. \quad (4)$$

Here ν is a frequency factor, κ is a transition coefficient, $\Pi a_i^{\nu_i}$ is the product of the activities of the starting reagents taken to powers equal to the stoichiometry coefficients ν_i of the reactants, and $\Delta G^{\neq}$ is the free energy of activation. The factor 0.5 reflects the possibility that the activated complex can decompose in the forward and reverse directions. The quantity $\Delta G^{\neq}$ consists of two terms:

$$\Delta G^{\neq} = \Delta G_{st}^{\neq} + \Delta G_{solv.}^{\neq}. \quad (5)$$

Here $\Delta G_{st}^{\neq}$ is the standard free energy of activation, $\Delta G_{solv}^{\neq}$ is the solvation energy of the activated complex determined from the expression $\Delta G_{solv}^{\neq} = RT\ln\gamma^{\neq}$, and $\gamma^{\neq}$ is the activity coefficient of the activated complex.

The coefficient κ is invariably omitted in studies on crystal growth as is the factor 0.5. Concentrations are used instead of activities. The quantity $\gamma_{st}^{\neq}$ is also ignored. Thus, $\Delta G_{st}^{\neq}$ are used although this is not always noted. In other words, an ideal systems are examined. Such simplifications are inadmissable in analysing crystallisation from solutions. Evidently, $\Delta G_{st}^{\neq}$ at these temperatures and pressures is independent of solvent, supersaturation, and the presence of impurities. Therefore, there is no basis with such an approach to make any assumptions about a change of activation barrier under the influence of these factors.

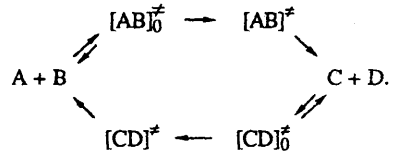
Activated-complex theory has often been criticised[39–43] (see also references in Ref. 26) mainly because the complex is postulated to be in thermodynamic equilibrium with the starting species. However, provisions are made for the further development even in the basic theory. It was noted that κ can substantially differ from unity for reactions in both gases (Ref. 25, p. 280) and in solutions (Ref. 25, p. 415). The necessity to differentiate the activated complex itself and the transition state has been pointed out (Ref. 25, pp 274–278). According to Glasstone et al.,[25] this is the reason that the transmission coefficient characterising the probability of a transfer through the activation barrier differs from unity. This idea was then further developed. According to Shakhparonov,[38] the formation of an activated complex does not imply its immediate decomposition. After it forms, there follows a fluctuating energy redistribution within it and formation of the transition state itself that ensures decomposition in the forward direction.

A detailed kinetic theory of chemical reactions in solutions that supplements the classical approach by taking into account the theory of fluctuations has been published.[38,44] The first question that arises is that of the correctness of using the Boltzmann equation, which is known to be valid only for systems with a rather large number of particles. The following considerations are relevant to this.

The activated complex during crystallisation from solutions includes the solvation sphere since the elementary step in solutions involves desolvation. The theory of fluctuations "often leads to good quantitative agreement with experiment" up to sizes of 10 nm. For smaller dimensions, it agrees qualitatively with experiment (Ref. 45, p. 129). The size of the activated complex including the solvation sphere apparently is of this order. Methods for estimating the sizes of such regions have been discussed.[40]

The refined kinetic equation for a phase transition of a separate atomic species during crystallisation from solutions is similar to that given before[38,44] for homogeneous chemical reactions in liquids. It is obtained as follows.

The chemical reaction is written in the form



Here $[AB]_0^{\neq}$ are the activated complexes in equilibrium with the starting compounds A and B, $[CD]_0^{\neq}$ are activated complexes in equilibrium with the reaction products C and D, and $[AB]^{\neq}$ and $[CD]^{\neq}$ are their respective transition states. The activated complexes in the transition state are not in thermodynamic equilibrium with other species. However, the transition states $[AB]^{\neq}$ and $[CD]^{\neq}$ are indistinguishable whereas $[AB]_0^{\neq}$ and $[CD]_0^{\neq}$ are distinguishable since they are not in thermodynamic equilibrium with each other.

The activated complex in the transition state, which includes the solvation sphere, is considered as a subsystem and the solution surrounding it, the system. According to the Boltzmann equation, the concentration of these subsystems is

$$m^{\neq} = m_0^{\neq}\exp\left(-\frac{\Delta G_{fl}^{\neq}}{RT}\right), \quad (6)$$

where $\Delta G_{fl}^{\neq}$ is the difference between the free energy of the system containing one mole of activated complexes in the transition state and its free energy in the absence of these complexes. Let us recall that this equation also forms the basis for the more expanded kinetic theory of nucleation.

The pre-exponential factor $m_0^{\neq}$ is equal to the concentration of the subsystems consisting of activated complexes for which $\Delta G_{fl}^{\neq} = 0$, i.e., in thermodynamic equilibrium with the starting compounds. The chemical potential of such complexes is

$$\mu^{\neq} = \mu_{st}^{\neq} + RT\ln\left(\gamma^{\neq}m^{\neq}\right), \quad (7)$$

where $\mu_{st}^{\neq}$ is the standard potential of the activated complexes.

Using Eqn. (7), $m_0^{\neq}$ can be expressed in terms of the activity of the starting components

$$m_0^{\neq} = K^{\neq}\frac{\Pi a_i^{\nu_i}}{\gamma^{\neq}};\ K^{\neq} = \exp\left(-\frac{\Delta G_{st}^{\neq}}{RT}\right), \quad (8)$$

where $K^{\neq}$ is the equilibrium constant of the activated complexes.

The rate of the elementary step of the reaction is determined by $V = 0.5\nu m^{\neq}$.

Substituting Eqn. (6) and taking into account Eqn. (8) we obtain

$$V = 0.5\nu\exp\left(-\frac{\Delta G_{fl}^{\neq}}{RT}\right)\exp\left(-\frac{\Delta G_{st}^{\neq}}{RT}\right)\frac{\Pi a_i^{\nu_i}}{\gamma_0^{\neq}}. \quad (9)$$

The quantity $0.5\exp(-\Delta G_{fl}^{\neq}/RT)$ can be treated as the coefficient κ. Methods for estimating it have been examined.[38] Possible methods for estimating $\gamma_0^{\neq}$, i.e. $\Delta G_{solv}^{\neq}$, have also been discussed.[46]

For this approach, the free energy of activation is

$$\Delta G^{\neq} = \Delta G_{st}^{\neq} + \Delta G_{solv}^{\neq} + \Delta G_{fl}^{\neq}. \quad (10)$$

Taking into account Eqn. (10), Eqn. (9) acquires the form

$$V = 0.5\nu\exp\left(-\frac{\Delta G^{*}}{RT}\right)\Pi a_i^{\nu_i}. \qquad (11)$$

This expression is of interest to us. It provides broad possibilities for analysing the effect on the rate of the solution composition (solution concentration, supersaturation, solvent). In a non-equilibrium process, the free energies of activation of the forward and reverse reactions are not equal: $\overrightarrow{\Delta G^{\neq}} \neq \overleftarrow{\Delta G^{\neq}}$. At equilibrium, $\overrightarrow{\Delta G_0^{\neq}} = \overleftarrow{\Delta G_0^{\neq}}$.

2. Rate equation for advance of an individual atomic step.

The rate of addition of atomic species to a step of monatomic height [mol (unit length)$^{-1}$ sec^{-1}] is defined on the basis of Eqn. (11) by

$$\vec{V}_{st} = 0.5\nu \sum_{i=1}^{3} \exp\left(-\frac{\overrightarrow{\Delta G_i^{\neq}}}{RT}\right) a_i a[M], \qquad (12)$$

where $\Delta G_i^{\neq}$ is the free energy of activation of the forward reaction for an atomic growth site i on the step and a_i is the activity of the corresponding site (mole fractions per unit length). The index of a site is 1,2,3 (isolated atom at the end of a step, an atom in a kink and at a smooth site). The index is simultaneously equal to the number of chemical bonds to nearest neighbours in the plane of the (100) face for a Kossel crystal. The variable a is the activity of the crystallising substance in solution (for simplicity, the formation of an unhydrated crystal in the absence of a chemical reaction was used). The quantity [M] is a coefficient introduced so that the dimensions of both parts of the equation are equal (omitted from here on).

It is assumed that the heights of the activation barriers $\overrightarrow{\Delta G_i^{\neq}}$ and the concentrations of different types of sites, i.e., a_i, do not change with a departure from equilibrium. Generally speaking, this is incorrect. However, this is not significant for finding the principal relations between the rate of advance of a step and the most important macroscopic parameters characterising it. Combining all quantities in Eqn. (12) except for a into a single rate coefficient for the forward reaction $\vec{k}_{st}$, we obtain

$$\vec{V}_{st} = \vec{k}_{st} a. \qquad (13)$$

It is also assumed that the removal rate of atoms from a step $\overleftarrow{V}_{st}$ is constant and equal at all supersaturations to the rate of the forward reaction at equilibrium:

$$\overleftarrow{V}_{st} = \vec{V}_{st} = \vec{k}_{st} a_0, \qquad (14)$$

where a_0 is the activity of a compound in the saturated solution.

For the step propagation rate V_{st} taking into account that $a/a_0 = \exp(\Delta\mu/RT)$, where $\Delta\mu$ is the difference of chemical potentials of the crystallising substance in the supersaturated and saturated solutions, we obtain

$$V_{st} = \vec{V}_{st} - \overleftarrow{V}_{st} = \overleftarrow{V}_{st}\left(\exp\frac{\Delta\mu}{RT} - 1\right). \qquad (15)$$

The rate of the reverse reaction $\overleftarrow{V}_{st}$ on the basis of Eqn. (11) is written

$$\overleftarrow{V}_{st} = 0.5\nu \sum_{i=1}^{3} \exp\left(-\frac{\overleftarrow{G_i^{\neq}}}{RT}\right) a_i, \qquad (16)$$

where $\overleftarrow{\Delta G_i^{\neq}}$ is the free energy of activation for removal of particles from i sites at equilibrium.

It follows from Eqn. (16) that the rate of the reverse reaction is determined by $\overleftarrow{\Delta G_i^{\neq}}$ and a_i. It is noteworthy that we are interested in crystal growth in a narrow range of supersaturation near equilibrium that corresponds to supersaturations greater than the saturation temperature by 1–3 °C. Such supersaturations are typical of bulk crystallisation and single-crystal growth. The change of thermodynamic driving force in this range of supersaturations does not exceed fractions of a kilojoule. Therefore, it is assumed to be insignificant compared with the expected activation barriers. The change of position of the upper point of the barriers should be close to that for the change of driving force. Thus, the activation barriers in the range of supersaturations usually used should be practically constant. The concentrations of various types of sites on a step and, consequently, a_i, change at the same supersaturations within narrow limits.[48] The assumption made above that the rate of the reverse reaction is constant are based on these considerations.

Let us express a_i and $\overleftarrow{\Delta G_i^{\neq}}$ for atoms at different positions on the step in terms of the corresponding value for atoms in a kink according to the scheme in Fig. 2.

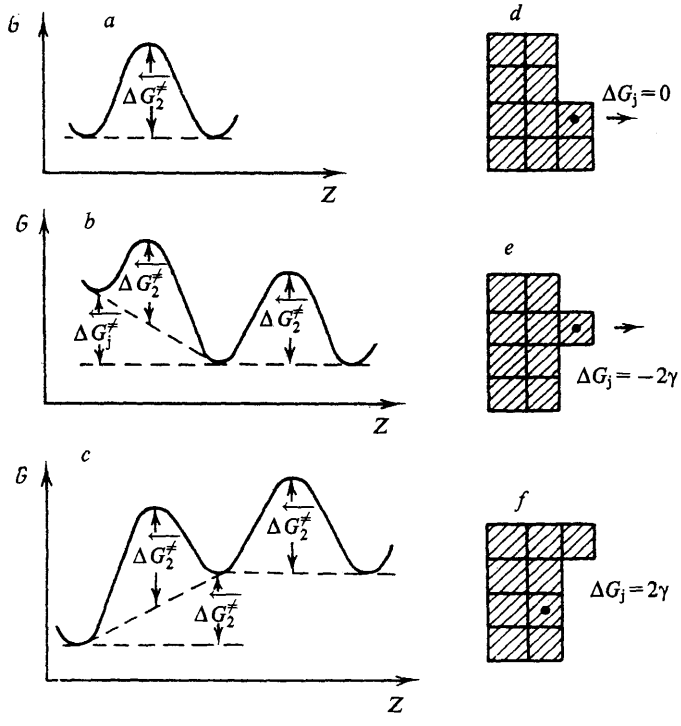


Figure 2. Free-energy activation barrier G (a–c) for transfer of atomic particles at different positions (d–f) from sites on a step into solution (from left to right).[47] The particles being removed are shown by dots.

The chemical potential of particles in solution at equilibrium μ_0 is equal to the chemical potential of particles located in a kink at the end of the step.[31] The chemical potential of an isolated particle on a step is 2γ greater than that of a particle in a kink (see Fig. 2) (γ is the specific free surface energy calculated per area of one atom at the end of a step). On the other hand, the chemical potential of a

particle at a smooth site is 2γ less than that of a particle in a kink since its removal will increase the surface energy of the step (i.e., the whole system) by 2γ. Thus,

$$\mu_{ki}(\mu_2)=\mu_0;\ \ \mu_1=\mu_{ki}+2\gamma;\ \ \mu_3=\mu_{ki}-2\gamma. \tag{17}$$

Setting the standard chemical potential of particles at all points of the step equal to the standard chemical potential of the compound in solution, we obtain from Eqn. (17)

$$a_2(a_{ki})=a_0;\ \ a_1=e^{2\gamma}a_2=e^{2\gamma}a_0;\ \ a_3=e^{-2\gamma}a_2=e^{-2\gamma}a_0. \tag{18}$$

It is noteworthy that a_i are related by the Gibbs–Duhem equation:

$$\sum_{i=1}^{3}x_i d\ln a_i=0.$$

Here x_i are the concentrations of particles at different positions on the end of a step in fractions of the total number of sites:

$$\sum_{i=1}^{3}x_i=1.$$

The quantities $\overleftarrow{\Delta G_i^{\neq}}$ are related as follows (see Fig. 2):

$$\overleftarrow{\Delta G_1^{\neq}}=\overleftarrow{\Delta G_2^{\neq}}-\gamma;\ \ \overleftarrow{\Delta G_3^{\neq}}=\overleftarrow{\Delta G_2^{\neq}}+\gamma. \tag{19}$$

Substituting Eqn. (16) into Eqn. (15), we obtain taking into account Eqns.(18) and (19):

$$V_{st}=0.5\exp\left(-\frac{\overleftarrow{\Delta G_2^{\neq}}}{RT}\right)a_0\left(2\cosh\frac{3\gamma_{st}}{RT}-1\right)\left(\exp\frac{\Delta\mu}{RT}-1\right). \tag{20}$$

The following points are noteworthy. According to Eqn. (20), the growth rate of a step should increase with increasing surface energy. At first glance, this seems paradoxical. However, it is just as paradoxical that the rate of advance of a step is greater the greater the rate of removal of particles from it according to Eqn. (15).

On going to nonequilibrium and increasing the supersaturation, the number of kinks and single atoms on the step increase.[48] Thus, the number of atomic particles belonging to the smooth parts of the step decreases. This means that the activities of the kinks a_2 and single particles a_1 increase whereas the activity of atomic particles at the smooth sites a_3 decreases. Thus, besides increasing the position of the free-energy minimum for particles in solution, the position of the minimum for various types of particles on the step increases or decreases (see Fig. 2). It can be assumed that the position of the minima for the latter changes to a lower value than for particles in solution. The position of the free-energy maxima (tops of the activation barriers) also changes with a change of supersaturation. However, it is not clear to what value it changes. There is no basis to think that they decrease by $\Delta\mu/2$ for the forward and increase by $\Delta\mu/2$ for the reverse reaction, as previously assumed.[47,49] These effects, as already noted above, are ignored here.

3. Rate equation for growth of a crystal face.

Dislocations, as a rule, are the source of growth layers on faces during formation of crystals from solutions. A two-dimensional nucleus can predominate only during growth of perfect crystals from carefully purified solutions. During crystallisation under ordinary conditions, it begins to contribute to growth of faces only at rather large supersaturations. The presence of dislocations ensures that steps are always present on a face, even where the crystal is in equilibrium with the medium. Therefore, the face growth rate is

$$V=V_{st}B, \tag{21}$$

where B is the total length of dislocation steps of atomic height per unit area of face at a given supersaturation.† Let us substitute Eqn. (20) into Eqn. (21) and find a linear approximation to Eqn. (21) near equilibrium (i.e. the first term in the expansion of the latter equation in a Maclaurin series):

$$V=0.5v\exp\left(-\frac{\overleftarrow{\Delta G_{ki}^{\neq}}}{RT}\right)B_0\left(2\cosh\frac{3\gamma_{st}}{RT}-1\right)a_0\sigma. \tag{22}$$

Here B_0 is the density of dislocation steps at equilibrium. The supersaturation is $\sigma\approx\Delta\mu/RT$. Introducing for simplification the parameter B_0, we obtain, according to Eqn. (22), an expression for the kinetic coefficient β, which determines the slope of the curve for the growth rate at zero coordinates:

$$\beta=\beta_0B_0\exp\left(-\frac{\overleftarrow{\Delta G_{ki}^{\neq}}}{RT}\right)\left(2\cosh\frac{3\gamma_{st}}{RT}+1\right). \tag{23}$$

The parameter β is calculated in practice (see Section II). According to the resulting equation, the solution composition affects the growth rate through B_0, the free energy of activation $\overleftarrow{\Delta G_{ki}^{\neq}}$ and the specific free surface energy of a step γ_{st}. The density of steps depends on the crystal imperfection, which in turn is determined by the impurities in solution. Two other quantities reflect the degree of solvation of crystallising particles and the solvation of the actual crystal face.

Thus, at large departures from equilibrium we have:

$$V=\beta\frac{\Delta\mu}{RT}\cong\beta\frac{\Delta a}{a}\cong\beta\sigma. \tag{24}$$

This means that if the driving force is represented as $\Delta\mu/RT$ (i.e., $\Delta a_0/a_0$ or σ), then the kinetic coefficient is equal to the rate of reverse reaction $\overleftarrow{V}$ at equilibrium [mol (unit area)$^{-1}$)]. If the driving force is represented as the difference of the activities, then

$$V=\overleftarrow{k}_0\Delta a, \tag{25}$$

where $\overleftarrow{k}_0$ is the rate constant of the forward reaction at equilibrium. Thus, $\beta=\overleftarrow{k}_0a_0$. Since a_0 = const regardless of the solvent, then β and $\overrightarrow{k}_0$ in all solutions for a single substance at a given temperature differ only by a constant factor.

The apparent Arrhenius activation energy of the reverse reaction is found as usual from the temperature dependence of β

$$\partial\ln\beta/\partial(1/T)=-\overleftarrow{E}^{*}/R. \tag{26}$$

The Arrhenius activation energy of the forward reaction is found from the temperature dependence of $\overrightarrow{k}_0$:

$$\partial\ln\overrightarrow{k}_0/\partial\ (1/T)=-\overrightarrow{E}^{*}/R. \tag{27}$$

The free energy of activation in Eqn. (23) is determined using the known equations

$$\overleftarrow{\Delta G_{ki}^{\neq}}=\Delta\overrightarrow{G}_{ki}^{\neq}=\overleftarrow{\Delta H_0^{\neq}}-T\Delta\overleftarrow{S}_0^{\neq}=\Delta\overrightarrow{H}_0^{\neq}-T\Delta\overrightarrow{S}_0^{\neq}, \tag{28}$$

where $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are the enthalpy and entropy of activation for the forward and reverse reactions. The subscript

† The possibility that atomic and larger steps may be present on the crystal faces is ignored. They form through consolidation of atomic steps, like other cooperative effects arising between steps, owing to impurities and solvent diffusion. These factors are peripheral to our examination. Furthermore, these factors at small supersaturations have a comparatively weak effect on the growth of steps.

zero indicates that these quantities refer to equilibrium conditions. The activation energy $\vec{E}^{\neq}$ is evidently related to $\Delta H^{\neq}$; $\overleftarrow{E}^{\neq}$, to $\Delta H^{\neq}$.

The quantity B_0 should be practically constant if crystals of a given compound obtained under identical conditions are used as seeds to grow crystals from various solvents. This occurs because the dislocation density in them in all instances will be about the same. It is even better if the same crystals are used as seeds in the experiments, as was previously done.[21] Thus, the solvent effect can change only the parameters of $\Delta G^{\neq}$ and γ_{st}. These quantities are related to the enthalpy of crystallisation. Let us examine first the relation of $\Delta H^{\neq}$ to ΔH_{cy}.

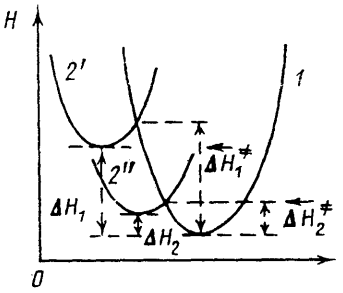


Figure 3. Enthalpy of a crystal–solution system as a function of coordinates of crystallising particles.

Suppose, in analogy with the previous potential curves,[46] that line *1* in Fig. 3 is the curve for the enthalpy change of the system after a position change of an atomic particle belonging to the crystal along the reaction coordinate z (calculated per mole of substance). Obviously, the minimum on this curve does not depend on solvent. Intermediate steps (position of the particle on a step on the face, adsorbed on the surface) are not considered. The line *2'* is the curve for the enthalpy change of the system after a position change of a dissolved particle in solvent 1; line *2''*, the same after a position change of a particle in solvent 2. The quantities ΔH_1 and ΔH_2 are the enthalpies of the phase transition in the first and second instances. The quantity $\Delta H_1 > \Delta H_2$. Therefore, the activation enthalpy of the reverse reaction is greater in the first instance than in the second. Thus, the heat of crystallisation and the enthalpy of activation of the forward reaction are directly correlated. In exactly the same way, the heat of the process and the enthalpy of activation of the forward reaction should be directly correlated since β and $\vec{k}_0$ are related by a constant factor. This means that the minimum on curve *2* in Fig. 3 must shift along the z axis on going from one solvent to another (the reaction radius changes). If the curve does not shift, then the activation energy of the forward and reverse reactions should change in opposite directions on going from one medium to another, which is impossible.

This theory was previously used[21] to explain the features described in Section II.

It is well known that an increase of the free energy of activation owing to an increase of the enthalpy of activation is usually accompanied by a decrease due to an increase of the entropy of activation (the so-called "compensation effect") since the change of the enthalpy and entropy of activation, as a rule, have the same sign. This was also confirmed for crystallisation.[50] However, the enthalpy of activation still plays the dominant role. Thus, there should be an inverse correlation between the heat of crystallisation and the growth rate. This is observed for urea (see Table 2). Furthermore, it is also possible that the entropy of activation (more accurately, the term $T\Delta S^{\neq}$) in Eqn. (28) changes more than the enthalpy of activation $\Delta H^{\neq}$. As a result, despite the decrease of activation energy, the crystal growth rate will decrease. It has been pointed out[26] that situations are also possible where the enthalpy and entropy of activation change differently.

The heat of crystallisation in solutions is determined using the known equation,[51] according to which, to a first approximation, $\Delta H_{cy} \sim m_0^{-1}$. This explains the direct correlation between the growth rate and the solubility of a given substance in the series of solvents described in Section II.

The specific surface free energy of crystals and their solubility are inversely correlated.[52] Thus, if the role of surface energy were to dominate over the effect of growth, then the increase of solubility would lead, in agreement with Eqn. (22), to a reduction of growth rate. However, as a rule, the opposite is experimentally observed. This means that the role of surface energy in the solvent effect on facetted growth of crystals is second-order compared with the role of activation barriers. Special instances ($\Delta H_{cy} < 0$) and isolated examples of a rate reduction with an increase of solubility require special investigations.

We emphasise that the described examination of the crystallisation is limited to layered dislocation growth. Its signature is the formation of well formed crystals with stable growth layers centered on the faces. The skeletal nature of the growth faces is not consistent with the normal mechanism and is only an indication of unequal diffusion of a substance to the faces (diffusional depletion due to a rate that is too fast). Rounding of the faces (antiskeletal growth) is not an unambiguous indication of the normal growth mechanism since it can be the result, like in the known example of KH_2PO_4 crystallisation, of layered growth that is hindered by trace impurities adsorbed on the faces.

References

1. R J Davey *Current Topics in Material Science*, 1982, **2** 429
2. P Groth *Chemische Krystallographie* (Chemical Crystallography), Verlag von Wilhelm Engelman, Leipzig, 1906–1919, Vols. 1–5
3. P P Orlov *Izv. Akad. Nauk SSSR, Otd. Fiz.-Mat. Nauk*, 1928, (6/7) 529
4. A F Wells *New Investigations in Crystallography and Crystal Chemistry* (Translated into Russian), Izdatinlit, Moscow, 1950, No. 2, p. 5
5. W Kleber, H Raidt *Z. Phys. Chem. (Leipzig)*, 1963, **222** 1
6. M Ledesert, J C Monier *Adsorption et Croissance Cristalline*, Coll. Intern. N 152, Paris, 1965, p. 537
7. T G Petrov *Kristallografiya*, 1964, **9** 541
8. T G Petrov, A P Kasatkin *Kristallografiya*, 1967, **12** 735
9. Z Berkovitch-Yellin *J. Am. Chem. Soc.*, 1985, **107** 8239
10. H K Chan, I Gonda, A J McLachlan *J. Cryst. Growth*, 1990, **104** 355
11. Y Tanaka, M Matsuoka *J. Cryst. Growth*, 1990, **99** 1130
12. M Saska, A S Myerson, *J. Cryst. Growth*, 1983, **61** 546

13. W Skoda, M Van den Tempel *J. Cryst. Growth*, 1967, **1** 207
14. J R Bourne *Chimia*, 1978, **32** 47
15. H J Human, J P Van der Eerden, L A M J Jetten, J G M Oderkerken *J. Cryst. Growth*, 1981, **51** 589
16. E B Treivus *Kristallografiya*, 1982, **27** 165
17. R J Davey, J W Mullin, M J L Whiting *J. Cryst. Growth*, 1982, **58** 304
18. W Beckmann, R Lacmann *Chem. Ing. Tech.*, 1987, **59** 82
19. W Beckmann *Industrial Crystallization-87*, Praga, 1989, p. 481
20. R De Goede, G M Van Rosmalen *J. Cryst. Growth*, 1990, **104** 399
21. E B Treivus, S C Kim *Tezisy Dokladov 8-oi Vsesoyuznoi Konferentsii po Rostu Kristallov* (Abstracts of Papers of the Eighth All-Union Conference on Crystal Growth), Khar'kov, 1992, Vol. 2, Part 1, pp 13–14
22. W Beckmann, R Boistelle, K Sato *J. Chem. Eng. Data*, 1984, **29** 211
23. W Beckmann, R Boistelle *J. Cryst. Growth*, 1985, **72** 621
24. W Beckmann, S Kämmer, J Meier, R Boistelle *J. Cryst. Growth*, 1986, **74** 326
25. S Glasstone, K J Laidler, H Eyring *The Theory of Rate Processes. The Kinetics of Chemical Reactions, Viscosity Diffusion and Electrochemical Phenomena* (Translated into Russian), Gosizdatinlit, Moscow, 1948, 584 pp
26. C Reichardt *Solvents and Solvent Effects in Organic Chemistry* (Translated into Russian), Mir, Moscow, 1991, 763 pp
27. J R Bourne, R J Davey *J. Cryst. Growth*, 1976, **36** 278, 287
28. R J Davey *J. Cryst. Growth*, 1986, **76** 637
29. M Elvenspoek *J. Cryst. Growth*, 1986, **78** 353
30. K Sangwall *J. Cryst. Growth*, 1989, **97** 393
31. A A Chernov *Sovremennaya Kristallografiya* (Modern Crystallography), Nauka, Moscow, 1980, Vol. 3, p. 7
32. E Kirkova, S Teodosieva, N Teodosiev *Gos. Sof. Univ., Khim. Fak.*, 1982(1986), **76** 178
33. P Duverneuil, N Hiquily, C Laquerie, R Ousset *Industrial Crystallization-87*, Praga, 1989, p. 525
34. V V Podolinskii, V G Drykin *Kristallografiya*, 1988, **33** 793
35. M Elwenspoek, P Bennema, J P Van der Eerden *J. Cryst. Growth*, 1987, **83** 297
36. M Elwenspoek *Mol. Phys.*, 1988, **64** 229
37. M Elwenspoek, J P Van der Eerden *J. Phys. A: Math., Gen.*, 1987, **20** 669
38. M I Shakhparonov *Mekhanizmy Bystrykh Protsessov v Zhidkostyakh* (Mechanisms of Fast Processes in Liquids), Vysshaya Shkola, Moscow, 1980, 352 pp
39. V A Pal'm *Voprosy Khimicheskoi Kinetiki, Kataliza i Reaktsionnoi Sposobnosti* (Problems of Chemical Kinetics, Catalysis and Reactivities), Izd. Akad. Nauk SSSR, Moscow, 1955, p. 75
40. S Z Roginskii, Yu L Khait *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1961, 771, 1198
41. M Simonyi, I Mayer *Acta Chim. Acad. Sci. Hung.*, 1975, **87** 15
42. Deng Gonghao *Sci. Sin.*, 1980, **23** 969
43. J L Skinner, P G Wolynes *J. Chem. Phys.*, 1980, **72** 4913
44. M I Shakhparonov *Zh. Fiz. Khim.*, 1984, **58**(3) 529 [English translation in *Russ. J. Phys. Chem.*, 1984(3)]
45. M I Shakhparonov *Vvedenie v Sovremenuyu Teoriyu Rastvorov* (Introduction to Modern Theory of Solutions), Vysshaya Shkola, Moscow, 1976, 296 pp
46. L I Krishtalik *Elektrodnye Reaktsii. Mekhanizmy Elementarnogo Akta* (Electrode Reactions. Mechanisms of the Elementary Event), Nauka, Moscow, 1979, 224 pp
47. F L Binsbergen *Kolloid Z. Z. Polym.*, 1970, **237** 289
48. A A Knizel, E B Treivus *Fizika Kristallizatsii* (Physics of Crystallisation), Kalinin, 1989, p. 27
49. G H Gilmer, P Bennema *J. Appl. Phys.*, 1972, **43** 1347
50. E B Treivus *Zh. Fiz. Khim.*, 1979, **53**(5) 1088 [English translation in *Russ. J. Phys. Chem.*, 1979(5)]
51. A N Kirgintsev *Ocherki o Termodinamike Vodno-Solevykh Sistem* (Outlines of the Thermodynamics of Water–Salt Systems), Nauka, Novosibirsk, 1976, 200 pp
52. P Bennema, O Söhnel *J. Cryst. Growth*, 1990, **102** 547

Received 6th February 1992

Translated from *Uspehki Khimii*, **61** 1243–1267 (1992) U.D.C. 541.14

The photochemistry of coumarins

N A Kuznetsova, O L Kaliya
Institute of Organic Intermediates and Dyes, Moscow

ABSTRACT. **The luminescence-spectroscopic properties, photophysical characteristics, and the most important photochemical reactions of phosphors of the coumarin series and natural furocoumarins are examined.**

The bibliography includes 130 references

Contents

I. Introduction 683
II. Spectra and excited states 683
III. Photochemical properties 687

I. Introduction

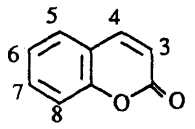
Superb luminescence in the blue-green part of the spectrum is characteristic of the majority of coumarin derivatives. By virtue of this property, coumarins have found extensive applications as optical bleaching agents,[1] in the creation of active media for tunable lasers,[2] and as luminescence labels.[3] Furocoumarins or psoralens are epidermal photosensitisers and are used in the phototherapy of skin diseases.[4] Coumarin derivatives are also of interest for the creation of photochromic materials.[5] Numerous studies devoted to the synthesis, properties, and applications of compounds of this class have been published recently. The principal methods of synthesis, reactivities, and lasing characteristics of 7-aminocoumarins have been recently reviewed.[6] Since the main applications of coumarins involve the transformation of radiation, photochemical studies are of decisive importance in the search for their new more effective and photostable derivatives. The luminescence-spectroscopic properties of coumarins are briefly analysed in the present review and a systematic account is given of data on their photochemistry, mainly those published in the literature during the last ten years.

II. Spectra and excited states

1. Absorption and fluorescence spectra

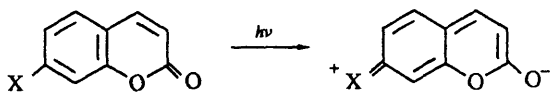
Our aim was not to carry out an exhaustive survey of the luminescence-spectroscopic properties of all the known coumarin derivatives.[7–11] We shall confine ourselves to the most general features of their dependence on the structure of the dye.

The luminescence-spectroscopic properties of coumarins are determined by the relative positions of the lowest electronically excited states of the $n\pi^*$ and $\pi\pi^*$ type. The unsubstituted coumarin does not fluoresce—it has a singlet lowest excited state of the $n\pi^*$ type with an energy of 3.4 eV.[12]



Coumarin

The most common phosphors among the compounds considered are 7-amino- and 7-hydroxy-derivatives. The introduction of an electron-donating substituent in the 7-position in coumarin has only a slight effect on the energies of the $S_{n\pi^*}$ and $T_{n\pi^*}$ states, while the energies of the $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ states diminish appreciably under these conditions as a consequence of the conjugation of the electron-donating substituent with the aromatic system and they become the lowest states[12] with a considerable contribution by the state with intramolecular charge transfer owing to the promotion of an electron from the electron-donating substituent to the carbonyl group:



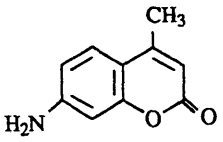
X = NR_2, OR.

The polarisation of the molecule on excitation is also indicated by the greater bathochromic shift of the fluorescence bands of 7-aminocoumarins relative to the absorption bands with increase in solvent polarity.[7] The estimated change in the dipole moment on excitation to the S_1 state is $\Delta\mu$ = 6.84 and 8.02 D for 7-amino and 7-diethylamino-4-methylcoumarins respectively.[13]

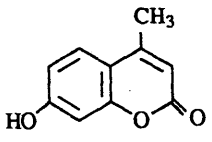
The data presented in Table 1 for certain coumarins illustrate the following characteristics of the influence of structural factors on the electronic absorption and fluorescence spectra. In comparing the spectroscopic parameters, account must be taken of the fact that the methyl group in the 4-position of the 4-pyrone ring does not affect the positions of the long-wavelength bands.

1. It has been demonstrated in relation to aminocoumarins with different positions of the amino-group in the molecule (Table 1) that the maximum bathochromic shift of the absorption spectra is observed when an electron-donating substituent is introduced in the 6 and 7-positions (the effect of substitution in the 6-position is

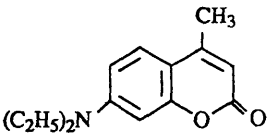
greater[20]) as a consequence of the greater stabilisation of charge transfer on excitation.



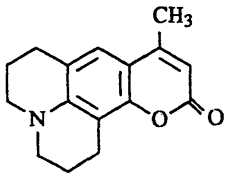
Coumarin 120



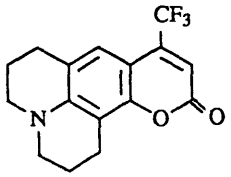
4-Methylumbelliferone



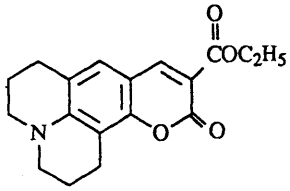
Coumarin 1



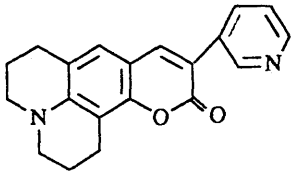
Coumarin 102



Coumarin 153



Coumarin 504



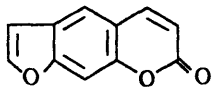
Coumarin 510

2. The bathochromic shifts of the absorption and fluorescence spectra depend on the electron-donating properties of the substituent. Thus the amino-group is a stronger electron donor than the hydroxy-group and has a greater effect than the latter on the energy of the S_1 state of coumarin. Alkylated amino-groups intensify the electron-donating properties of the substituent and lead to a further successive shift of the absorption and fluorescence bands of coumarins 120, 1, and 102 to the long-wavelength region.

3. The introduction of an electron-accepting substituent, for example, the trifluoromethyl, ethoxycarbonyl, aryl, heteroaryl, and other groups, into the pyrone fragment of the molecule induces an even greater shift of the absorption and fluorescence maxima into the red region as a consequence of the further enhancement of the degree of charge transfer. This conclusion is confirmed by the spectroscopic data presented in Table 1 for coumarin 102, on the one hand, and for coumarins 153, 504, and 510, on the other. The introduction of electron-donating substituents into the pyrone fragment of 7-aminocoumarins results in the opposite effect.[21]

The above features refer to the influence of structural factors on the absorption and fluorescence of neutral forms of coumarin derivatives, the acid–base reactions of which make it possible to expand considerably the spectral range of luminescence.[22–25]

Furocoumarins (derivatives of psoralen), exhibiting a photo-therapeutic effect, are of considerable interest.



Psoralen

The absorption spectra of the majority of furocoumarins are similar to that of psoralen, the lowest excited $S_{\pi\pi^*}$ state of which lies somewhat below the $S_{n\pi^*}$ state.[4]

Table 1. The luminescence spectroscopic parameters of coumarins in ethanol.

Coumarin	Wavelength, nm		Fluorescence quantum yield	Refs.
	in absorption	in fluorescence		
3-Aminocoumarin*	324	–	–	[14]
6-Aminocoumarin	370	–	–	[15]
Coumarin 120	354	435	–	[16]
8-Aminocoumarin	300	–	–	[15]
6-Hydroxy-4-methylcoumarin	340	427	–	[17]
4-Methylumbelliferone	320	385	0,208	[18]
Coumarin 1	353	450	0,73	[16, 19]
Coumarin 102	387	473	0,95	[19]
Coumarin 153	421	531	0,38	[19]
Coumarin 504	436	480	–	[16]
Coumarin 510	452	–	–	[16]

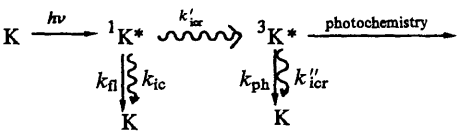
*Solvent — methanol.

2. The fluorescence efficiency

The fluorescence quantum yields of compounds of the coumarin series are determined both by internal factors (non-radiative internal conversion to the ground state and the intersystem crossing to the triplet state) and by external factors (interaction of the excited molecules with other molecules).

We shall consider the role of internal factors, which include the processes leading to the deactivation of excited states presented in Scheme 1.

Scheme 1



where K, $^1K^*$, and $^3K^*$ are coumarin derivatives in the ground, first excited singlet, and triplet states, k_l, k_{ph}, k_{ic}, and k_{icr} are the rate constants for fluorescence, phosphorescence, internal conversion, and intersystem crossing respectively.

It follows from Scheme 1 that a low fluorescence yield is observed in the case of predominant deactivation of the excited singlet state in non-radiative processes involving internal conversion to the ground state (k_{ic}) or intersystem crossing to the triplet state (k_{icr}^{i}).

Theoretical calculations for 7-aminocoumarin derivatives showed that they belong to the fifth luminescence type of molecules with heteroatoms having higher energies of the $S_{\pi\pi^*}$ states relative to the triplet states of the $\pi\pi^*$ type.[12] Since the intersystem transition between these states is forbidden,[26] the population of the triplet levels (the main pathway leading to the loss of the energy of the fluorescent state of heteroaromatic compounds) is small in the case of 7-aminocoumarins (the quantum yield of the excited triplet states is $\varphi_T < 0.05$).[19]

The probability of intersystem crossing is determined, apart from the nature of the excited singlet and triplet states, also by the energy gap between them, increasing with decrease in the $S-T$ splitting. The energy gaps between the S_1 state and the triplet state closest to it have been calculated[12] for a series of 7-aminocoumarin derivatives. It was shown that, for compounds of the coumarin series, a relation is observed between the fluorescence quantum yields and the relative positions of the singlet and triplet states, in agreement with the ideas described.

The non-radiative deactivation via internal conversion is the second important pathway leading to the loss of the energy of the fluorescence states — it takes place mainly as a result of transitions between the vibronic levels of the S_1 and S_0 states and via hydrogen bonds. Comparison of the fluorescence quantum yields of coumarin 1 and coumarin 102 (Table 1) confirms the conclusion[27–29] that the fixation of the alkyl amino-group as a result of the incorporation of the alkyl substituent in a ring makes it possible to diminish the non-radiative excitation energy losses on rotation of the amino-groups in the excited state and permits a significant increase in the fluorescence quantum yield.

The deactivation of the fluorescent state via the hydrogen bond between 7-aminocoumarin and the solvent has been postulated to account for certain experimental data,[7,29] but it is apparently less effective than other pathways leading to the dissipation of excitation energy. Thus detailed studies have been made[13,19,27,30] of the dependences of the positions of the fluorescence bands, quantum yields, and lifetimes on the solvent polarity. It was found that in the case of 7-alkyl-aminocoumarins with a free amino-group, anomalously weak fluorescence, displaced to the red region, is observed in polar solvents. This phenomenon also occurs in solvents which do not form hydrogen bonds.[30] On the basis of these observations for 7-alkylaminocoumarins with a free amino-group, the following new model of the non-radiative deactivation of the excitation energy has been proposed. Two excited states with intramolecular charge transfer are postulated — a planar state which emits with a high efficiency and a "twisted" state, the degradation of the excitation energy of which is achieved mainly by a non-radiative pathway.[13,19,30,31] The activation barrier to the transition from the emitting planar state to the "twisted" state diminishes with increase in solvent polarity. For 7-aminocoumarins with a bound amino-group (coumarins 102, 153, etc.), only the planar excited state with intramolecular charge transfer can exist. With increase in solvent polarity, the fluorescence of such compounds shifts towards longer wavelengths and the efficiency and lifetime of the fluorescence change little under these conditions. In the case of 7-amino-coumarins with a free amino-group, there is a possibility of the formation of a non-luminescent "twisted" excited state in polar solvents, which is manifested by a significant decrease in the fluorescence efficiency and lifetime and its displacement towards longer wavelengths with increase in solvent polarity. For 7-amino-coumarins with a bound amino-group, the formation of a "twisted" non-luminescent excited state with intramolecular charge transfer is possible when the molecule contains other substituents capable of rotation.[32] It is noteworthy that the concept, developed in a number of studies,[13,19,30,31] that there are two types of excited states in coumarins with a free amino-group has not been confirmed experimentally in studies on the induced absorption and emission spectra of these compounds by picosecond spectroscopy.[33]

For coumarin derivatives with close lowest $\pi\pi^*$ and $n\pi^*$ states, the probability of non-radiative deactivation increases sharply as a consequence of vibrational interactions leading to a displacement of levels (the "proximity effect"). The effective non-radiative degradation of the excitation energy of 4-methylumbelliferone in aprotic media[18] and of furocoumarins[34] has been interpreted in terms of these ideas.

The fluorescent state energy deactivation processes, determined by external factors, including the interaction of the excited molecules with the molecules of quenching agents, are also extremely important. The oxygen present in solution, which induces the intersystem crossing to the triplet state by exchange interaction, is usually the cause of the quenching of the fluorescence of dyes of different classes.[35] Fletcher and co-workers[36] determined the relative fluorescence quantum yields (φ_{fl}) for a series of coumarin dyes in ethanol as a function of oxygen concentration. They established that the fluorescence of all the test compounds diminishes significantly in the presence of oxygen. For example, in the case of coumarin 1 the quantum yields φ_{fl} were 0.57, 0.79 and 0.85 in ethanol saturated with oxygen, air, and argon respectively.[36] Shakhverdov, et al.[35] noted high values of the constants for the quenching of the fluorescence of 7-aminocoumarins by oxygen ($k \geqslant 10^{10}$ litre mol^{-1} s^{-1}) accompanied by low rate constants for their intersystem crossing ($k_{cr} = 0.3 \times 10^7$ and 0.4×10^7 s^{-1} for coumarins 1 and 102), which is inconsistent with the quenching of the fluorescent state via the mechanism involving the oxygen-induced intersystem crossing to the triplet state. On the other hand, the rate constants for the quenching of the fluorescence of coumarin by oxygen agree with the relative positions of the states involving charge transfer from the dyes to oxygen.[35] On the basis of this relation, Shakhverdov, et al.[35] concluded that the mechanism of the quenching of the fluorescence of coumarin dyes by oxygen is based on donor–acceptor interactions.

The quenching of the fluorescence of umbelliferone derivatives by inorganic ions has been investigated.[37–40] Since the results could not be explained by the heavy atom effect,[39] the most probable mechanism in this instance is believed to involve[39] quenching via electron transfer. The methyl group in the 4-position in the pyrone ring provides a partial shield to the quenching of the fluorescence of coumarin by halide ions.[39]

The rate constants for quenching by electron donors and acceptors increase with decrease in the free energy of electron transfer with participation of 7-aminocoumarins in the excited singlet state, and for donors with $E_{1/2}^{ox} < 1.0$ V and acceptors with $E_{1/2}^{red} > -1.5$ V (relative to the saturated calomel electrode) the rate constants for the quenching of 7-aminocoumarins in the S_1 state are close to diffusion rate constants.[41]

3. Excited triplet states

The triplet–triplet absorption spectrum of unsubstituted coumarin in ethanol, measured in several studies,[42–44] revealed the occurrence of an intense long-wavelength transition $T_1 \rightarrow T_3$ with a

maximum λ_{max} = 459 nm and a molecular extinction coefficient ε_T = 13000 litre mol^{-1} cm^{-1}. This transition is polarised in the molecular plane along the long axis of the molecule. A weak $T_1 \rightarrow T_2$ transition occurs at lower frequencies. The intersystem crossing quantum yield in water and the energy of the first triplet state of coumarin are φ_T = 0.054[45] and 262 kJ mol^{-1} [46] respectively. According to a theoretical study,[47] a strong polarisation of the bond between the third and fourth carbon atoms is characteristic of the T_1 state of coumarin. The lifetimes of the excited triplet states of both coumarin and its derivatives, which are in the microsecond range,[19,45,48] depend on the solution concentration. At low concentrations, the excited triplet states are degraded via a first-order process. For example, in the case of unsubstituted coumarin, the rate constant for this process in benzene is 2.6 × 10^5 s^{-1}.[45] With increase in coumarin concentration, τ_T diminishes as a consequence of the quenching of the triplets by interaction with the ground state and the rate constant for quenching via a second-order reaction is 1.5 × 10^8 litre mol^{-1} s^{-1} for coumarin in benzene.[4]

Laser-type 7-aminocoumarin has low yields of intersystem crossing to the excited triplet state (φ_T < 0.05;[19] for coumarin 1 in ethanol, φ_T = 0.006[49]). The phosphorescence lifetimes of these compounds at 77 K are in the range corresponding to several seconds,[42] which is characteristic of excited triplet states of the $\pi\pi^*$ type.

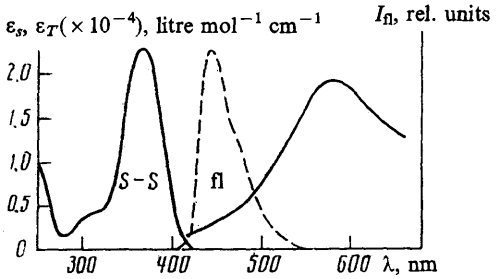


Figure 1. The $S-S$ and $T-T$ absorption and fluorescence spectra of coumarin 1;[42] I_{fl} = fluorescence intensity.

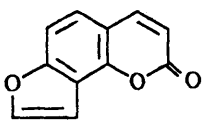
Fig. 1 illustrates the absorption spectrum of coumarin 1 in the excited triplet state obtained by pulsed laser photolysis.[42] Similar spectra have been obtained for a series of other 7-substituted coumarins. It is seen (Fig. 1) that the $T-T$ absorption of these compounds is represented by a broad band whose short-wavelength slope overlaps the luminescence spectrum. In order to estimate the loss of lasing energy in absorption by triplet levels, the molecular extinction coefficients for the $T-T$ absorption have been determined[50] in the region corresponding to the luminescence of the most important lasing coumarin dyes in ethanol.

As in the case of $S_0 \rightarrow S_1$ transitions, the methyl group in the 4-position in the pyrone ring does not alter the position of the maximum in the $T-T$ absorption spectrum, whereas the introduction of electron-donating substituents in the 7-position shifts the spectral maxima to the low-frequency region.[42] The characteristics of the $T-T$ absorption spectra of certain lasing coumarin dyes are[λ_{max}^{T-T}, nm (ε_T, litre mol^{-1} cm^{-1})]: coumarin 1—570 (15050),[51] coumarin 102—580 (14000),[48] coumarin 153 in benzene—580 (10000),[52] and 7-hydroxycoumarin in frozen alcohol—510 (18500).[44] The energies of the triplet levels determined by the energy transfer method using various triplet donors and acceptors are 240, 240, 210, and 217 kJ mol^{-1} for coumarins 1, 102, and 153 and 7-diethylamino-4-trifluoromethylcoumarin respectively.[48,51,52] As in the case of excited singlet states, the energies of the triplet levels of 7-aminocoumarins are lowered when the CH_3 group is replaced by the electron-accepting CF_3 group in the pyrone part of the molecule and T_1 therefore has the character of a state with charge transfer.

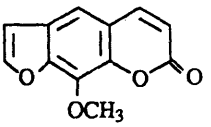
Table 2. Characteristics of the excited triplet states of furocoumarins in benzene.[34,53]

Furocoumarin	$\varphi_T \pm 10\%$	λ_{max}^{T-T}, nm	ε_T, litre mol^{-1} cm^{-1}	E_T, kJ mol^{-1}
Psoralen	0.03	450	8100	278
Angelicin	0.03	430	5500	–
8-Methoxypsoralen	0.01	480	10000	270
4,5',8-Trimethylpsoralen	0.21	450	7750	–
6,4,4'-Trimethylangelicin	0.13	450	6300	–
3-Ethoxycarbonylpsoralen	0.30	410	11500	271
3-Acetoangelicin	0.54	430	13200	–

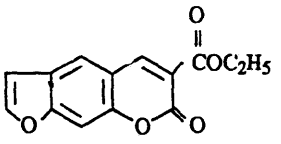
Like many aromatic carbonyl-containing compounds, furocoumarins or psoralens, which is another important group of coumarins, have $n\pi^*$ levels which are close to the lowest excited states of the $\pi\pi^*$ type.[34] This phenomenon, the so called "proximity effect", leads to intense non-radiative degradation of the excitation energy involving its transfer to both the ground and excited triplet states. The dependence of the efficiency of the non-radiative degradation on the relative positions of the levels is used to explain the characteristic features of the influence of the structure of furocoumarin on the quantum yield of the intersystem crossing, which are illustrated by examples in Table 2. The photophysical and spectroscopic parameters of the excited triplet states for a wide range of furocoumarins have been published in the literature.[34,54] The quantum yields of the intersystem crossing of furocoumarins vary within wide limits as a function of their structure—from 0.01 for 8-methoxypsoralen to 0.54 for 3-acetylangelicin (Table 2).



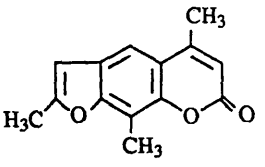
Angelicin



8-Methoxypsoralen



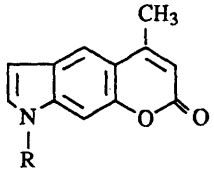
3-Ethoxycarbonylpsoralen



4,5',8-Trimethylpsoralen

The introduction of a methyl group increases φ_T. For example, φ_T = 0.21 for 4,5′,8-trimethylpsoralen, whereas the intersystem crossing yield for unsubstituted psoralen is much lower, amounting to 0.03. Similarly, 6,4,4′-trimethylangelicin has φ_T = 0.13, while angelicin itself has φ_T = 0.03. The yields φ_T increase also when an additional carbonyl group is introduced into the furocoumarin molecule. Thus the intersystem crossing quantum yield increases from φ_T = 0.03 to φ_T = 0.30 and 0.54 when the hydrogen atom in the 3-position in psoralen and angelicin is replaced by the ethoxycarbonyl and acetyl groups respectively. The molar extinction coefficients also increase on passing to furocoumarins containing an additional conjugated carbonyl group. The energies of the triplet levels of furocoumarins decrease when both electron-donating substituents and groups containing a carbonyl moiety conjugated with the aromatic system are introduced into the molecule (Table 2).

The pyrrolocoumarins (I) and (III), which have been synthesised recently,[55] are structurally similar to psoralenes.



R = H(I), CH_3(II), C_2H_5(III)

The photophysical behaviour of these two groups of compounds also has much in common. Whilst exhibiting only a weak fluorescence ($\varphi_{fl} \simeq 10^{-2}$), pyrrolocoumarins phosphoresce intensely in the range 480–600 nm. The triplet–triplet absorption spectrum of compound (I) contains bands with maxima at λ_{max}^{T-T} = 380, 500, and ~600 nm.[55] The lifetimes of the excited triplet states of pyrrolocoumarins are typical for coumarins and amount to ~5 μs. Experimental data[55] indicate an intense intramolecular charge transfer on excitation of compounds (I)–(III) as a consequence of the pronounced electron-donating properties of the pyrrole ring.

4. Generation of singlet oxygen

An important characteristic of coumarins is the quantum yield in the generation of singlet oxygen by these compounds. It has been suggested that the phototherapeutic effects of furocoumarins, which are epidermal photosensitisers and are used in the phototherapy of many skin diseases, may be partly due to the formation of $^1\Delta_g$ singlet oxygen ($^1O_2$).[56,57] The lasing 7-aminocoumarins are oxidised by singlet oxygen via a self-sensitised oxidation mechanism.[58,59] For the quantitative estimation of the efficiency of both the processes listed above as well as others occurring with participation of $^1O_2$ generated by coumarins, it is essential to know the quantum yield of singlet oxygen ($\varphi_{^1O_2}$).

$^1O_2$ is usually formed when excitation energy is transferred from the T_1 level of the sensitiser (coumarin) to oxygen in the triplet ground state:

$$^3K^* + {}^3O_2 \rightarrow K + {}^1O_2 .$$

The energies of the triplet levels of coumarin and its derivatives (see above) exceed the energy of $^1\Delta_g$ singlet oxygen (94.4 kJ mol^{-1}), so that the energy transfer process considered is feasible. The quenching of the excited triplet states of coumarin by oxygen proceeds, like that of the majority of other compounds, with rate compounds close to the diffusion-controlled limit and leads to the formation of $^1O_2$.[60]

$\varphi_{^1O_2}$ for unsubstituted coumarin, which has been determined by a comparative method from the luminescence of the singlet oxygen generation, is ~0.015 in D_2O and 0.03 in CH_3OH.[61] Knox, et al.[34] determined the quantum yields in the generation of $^1O_2$ for a series of furocoumarins in benzene. The yields $\varphi_{^1O_2}$ for some of them are presented in Table 3, which shows that the efficiency of the generation of $^1O_2$ by furocoumarins may be various. It has been established that $\varphi_{^1O_2}$ is determined not only by the quantum yields of the excited triplet states of furocoumarins but also by the probability of the formation of $^1O_2$ when their T_1 states are quenched by oxygen ($\theta_{^1O_2}$), which varies in the range 0.1 to 1 for many of the furocoumarins investigated (Table 3).

Table 3. Characteristics of the generation of singlet oxygen by furocoumarins in benzene.[34]

Furocoumarin	$\varphi_{^1O_2}$ ±10%	$\theta_{^1O_2}$ ±25%
Psoralen	0.01	0.33
Angelicin	0.01	0.33
8-Methoxypsoralen	0.004	0.40
5,8-Dimethoxypsoralen	0.004	0.10
4,5′,8-Trimethylpsoralen	0.08	0.38
6,4,4′-Trimethylangelicin	0.02	0.16
3-Ethoxycarbonylpsoralen	0.30	1.00
3-Acetoangelicin	0.40	0.73

The quantum yields in the generation of $^1O_2$ by the lasing 7-aminocoumarins are low — the values for coumarins 1 and 102, determined using rubrene as the trapping agent for $^1O_2$, are 0.08–0.025 in benzene.[62]

III. Photochemical properties

1. Electron and proton phototransfer

The phototransfer of an electron is postulated as the primary elementary step in many photochemical reactions of coumarin derivatives. This aspect of the problem will be dealt with in the corresponding Sections of the review.

As noted above, the excited singlet[37–41] as well as triplet[41] states of coumarins are quenched by electron donors and acceptors. The acceleration of the destruction of coumarin and psoralene triplets in the presence of thymine and other DNA bases as well as aminoacids, in particular tryptophan, has also been interpreted as quenching via an electron transfer mechanism.[45] However, the attempts to detect coumarin radical-ions as the products of the total electron transfer were unsuccessful in these experiments.[41,45] Only in the study of the quenching of the excited triplet states of coumarin and 4′,5′-dihydropsoralen by tryptophan using pulsed laser photolysis was a relatively long-lived absorption detected and was tentatively

assigned to absorption by the mixture of the coumarin radical-anion and the tryptophan radical-cation.[45]

Reliable data for the absorption spectra of the radical-ions of coumarin derivatives were obtained by the pulsed radiolysis method.[45,53,63] The electronic absorption spectra of the radical-anions of coumarins and psoralens in water show an intense absorption peak in the vicinity of 360 nm and a broad structureless band in the wavelength range above 500 nm with a diffuse maximum near 600 nm ($\varepsilon \simeq 2000$ mol litre^{-1} cm^{-1}).[45,53] The radical-cations of coumarins absorb at shorter wavelengths: $\lambda_{max}^{abs} = 460$ nm for the coumarin 153 radical-cation in cyclohexane[63] and $\lambda_{max}^{abs} = 480-500$ nm for the radical-cations of psoralen and its derivatives in aqueous solution.[53]

Proton phototransfer has been investigated for many, mainly lasing, coumarin dyes. New ionic forms formed in this process exhibit an effective luminescence in a whole series of instances, which makes it possible to plan significantly the laser tuning range. The spectra and structures of photoprotolytic forms have been identified and the kinetics of the proton phototransfer reactions have been investigated for 7-hydroxycoumarin[22,64,65] and its 4-methyl[22,64] and 4-trifluoromethyl derivatives[23] as well as esculin (6,7-dihydroxy-coumarins to the S_1 state intensifies sharply the acid properties of the hydroxy-group and the basic properties of the carbonyl oxygen, which determines the direction of the proton phototransfer. Whereas the CH_3 substituent in the 4-position in the pyrone ring does not alter the efficiency of the formation of the various protolytic forms, the CF_3 group has a marked influence on this reaction with abstraction, addition and transfer of a proton in hydroxycoumarins. By virtue of the inductive effect of the trifluoromethyl group, in the excited singlet state there is an appreciable increase in the probability of the abstraction of a proton from the hydroxy-group, but its addition to the carbonyl group is hindered. In the case of 3-hydroxycoumarin, there is insufficient time for the attainment of the protolytic equilibrium in the excited state owing to the rapid degradation of the excitation energy.[67]

The acid–base forms of aminocoumarins luminesce much less effectively than the neutral forms.[14,25] We shall consider the characteristics of the photocatalytic reactions of the familiar lasing dye coumarin 102. On protonation of the coumarin 102 molecule, the amino group is the first to be protonated in the ground state and is followed by the carbonyl group.[24] In the fluorescent S_1 state, the proton-accepting capacity of the carbonyl group increases appreciably and the order in which the groups are protonated changes. It has been suggested[24] that, during the lifetime of the excited state in acidified solutions of coumarin 102, a proton is abstracted from the nitrogen atom of the amino-group and is added to the oxygen atom of the carbonyl group after transfer through the surrounding medium.

7-Aminocoumarins have been divided into three groups in terms of their photoprotolytic properties:[25] (1) coumarins 102 and 120 as well as others in which a proton adds adiabatically to the carbonyl oxygen; (2) 7-aminocoumarins containing a CF_3 substituent in the 4-position in the pyrone ring, where the proton phototransfer is accompanied by the loss of excitation; (3) 7-alkylaminocoumarins whose photoprotolytic forms do not luminesce owing to the disruption of the planar configuration of the cation by the mobile alkyl groups attached to the nitrogen atom.

It is noteworthy that the proton phototransfer reactions are fully reversible: the loss of excitation is accompanied by the rapid conversion of the dye into the initial form.

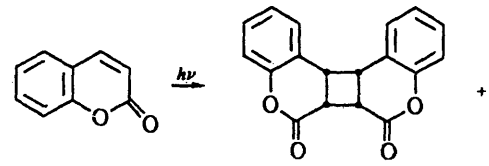
2. Phototransformation of the chromophore

Photochemical reactions leading to the disruption of the benzo-pyrone fragment, which serves as the chromophore in compounds of the coumarin type, are included among the phototransformations of the chromophore. The absorption and luminescence in the visible and near UV regions of the spectrum disappear under these conditions. This part of the review will deal with the reactions involving the opening of the pyrone ring, the photochemical reduction, as well as reactions involving the [2 + 2]photocyclo-addition to the double bond between the third and fourth carbon atoms, which are extremely characteristic of coumarins.

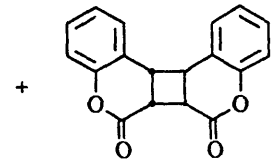
(a) [2 + 2]Photocycloaddition reactions

Photodimerisation. Coumarins, which are cyclic esters [lactones?] of α,β-unsaturated carboxylic acids, show an extremely great tendency to undergo reactions involving photocycloaddition to the 3,4-bond of the pyrone ring, in which cyclobutane adducts are formed. Such reactions include photodimerisation. The photo-dimerisation of coumarin has been the subject of numerous investigations.[68–71] The principal conclusions reached in such studies can be formulated as follows.

Mainly two out of the four possible stereoisomers are formed as the products of the photodimerisation of coumarin in solution:



(IV)



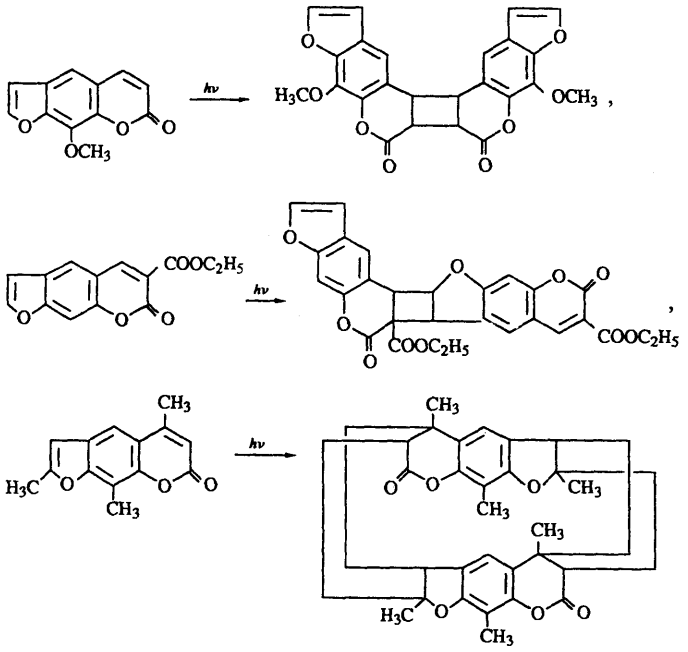
(V)

The "head to head" *endo*-dimer (IV) is the main product of the extremely inefficient reaction of coumarin in the excited singlet state ($\varphi \simeq 10^{-3}$ in water at a coumarin concentration of 0.01 M and $\varphi < 10^{-5}$ in methanol and benzene[70]). The "head to head" *exo*-adduct (V) is formed from the excited triplet state with an average efficiency ($\varphi \simeq 0.1$ on sensitisation with benzophenone[69]). The reaction in the excited singlet state is catalysed by Lewis acids. Thus the quantum yield of the *endo*-dimer in dichloromethane (coumarin concentration 0.2 M) increases from 10^{-3} to 0.16 in the presence of BF_3.[71]

The *endo*-orientation of the product obtained from the excited singlet state and the *exo*-orientation of the product obtained from the excited triplet state in the photodimerisation reaction persist also for substituted coumarins. Studies have been performed in relation to compounds containing alkyl, alkoxy-, acetoxy-, chloro-, phenyl, and cyano-substituents in the 3-, 4-, 6-, and 7-positions.[72,73] Depending on their structure, coumarin derivatives dimerise via both excited singlet and triplet states. Thus, whereas in the case of 4-substituted derivatives the photoreaction takes place via the triplet on direct excitation, the multiplicity of the reactive excited state of coumarins substituted in the 7-position depends on the nature of the

substituent. A dual behaviour is characteristic of 4,7-di-substituted derivatives—the reaction proceeds simultaneously via states of different multiplicity.[72–74] The methyl group in the 4-position in the pyrone ring does not prevent photodimerisation,[72,75] but the familiar lasing dye 7-diethylamino-4-methylcoumarin (coumarin 1) does not dimerise under the reaction conditions, undergoing another photochemical transformation involving the photochemical oxidation of the diethylamino-group.[75] 3,4-Disubstituted coumarins do not form dimeric cyclobutane photoadducts, probably as a consequence of steric hindrance.[75] In aqueous micellar solutions, the nature of the products has not changed but a decrease in the rate of photochemical reaction is observed for coumarin itself,[70] whereas in the case of its substituted derivatives the rate increases.[72]

Furocoumarins can dimerise via both the pyrone and furan fragments[76–79] to form dimers of different types, for example:

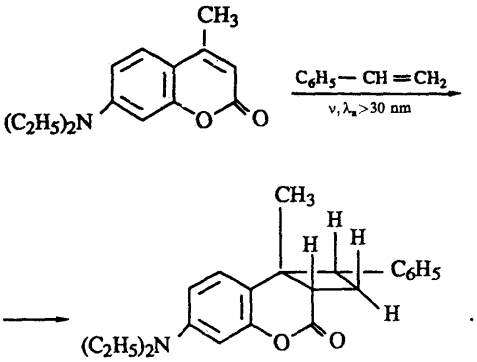


In contrast to the liquid phase, in the solid state coumarin exhibits a fairly high photostability and does not form dimeric cyclobutane adducts on irradiation.[80] A characteristic feature of the solid-phase reaction is the restriction of the movement of the molecules and a greater influence of their disposition in the crystal on the course of the process. The packing in individual crystals unfavourable for photodimerisation can be modified in mixed crystals, for example, with phenanthrene or antipyrine.[80] In mixed crystals, photodimerisation of this kind becomes geometrically feasible and a mixture of the photodimers (IV) and (V) is formed, containing mainly the "head to head" *endo*-dimer (IV).

The relation between the structure of the crystals and reactivity was investigated for a series of coumarin derivatives.[81,82] The limiting distance between the centres of the reaction bonds in the photoreactive crystals is 4.2 Å.[81] For small deviations from the disposition of molecules favourable for photodimerisation, of the kind which occur, for example, in the case of 7-chlorocoumarin where the distance between the reacting bonds in the crystals is 4.454 Å or 7-methoxycoumarin in the crystals of which the reacting bonds have been rotated by 65° relative to one another, the topochemical reaction can proceed with a high yield (~90%).[82]

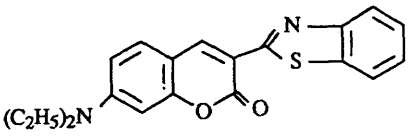
The photodimerisation of coumarin is reversible: on irradiation with short-wavelength light, the dimers are reconverted into the initial compounds, while on exposure to polychromatic sunlight a photostationary equilibrium is established between coumarin and its dimer.[83]

Photocycloaddition of olefins. The [2 + 2]photocycloaddition of olefins to coumarins usually takes place more effectively than the photodimerisation of the latter. In the presence of olefins, the photodimerisation can be actually inhibited as a consequence of the preferential reaction with olefins.[84] 7-Aminocoumarins, which do not tend to form photodimers,[75] react with olefins to form cyclobutane adducts.[85–88] As a result of the reaction occurring regiospecifically via the excited singlet state, mainly "head to tail" cyclic [2 + 2]adducts are formed. For example, coumarin 1 reacts with styrene in acetonitrile at reactant concentrations of 10 and 0.08 M respectively to form a "head to tail" type isomer with the *endo*-disposition of the phenyl substituent,[86] the quantum yield being 0.041:



The presence of an electron-donating group in the 4-position accelerates the process.[87,88] These results as well as the data of other workers concerning the reactivity of 4-hydroxycoumarin[89] and 3-acetylcoumarin[90] show that the substituents in the 3- and 4-positions in the pyrone ring do not prevent the formation of [2 + 2]photoadducts with olefins.

The lasing dye coumarin 6 in solutions in the presence of diphenylpolyenes generates stimulated radiation under the influence of a light pulse and is simultaneously decolorised in the [2 + 2]photocycloaddition reaction.

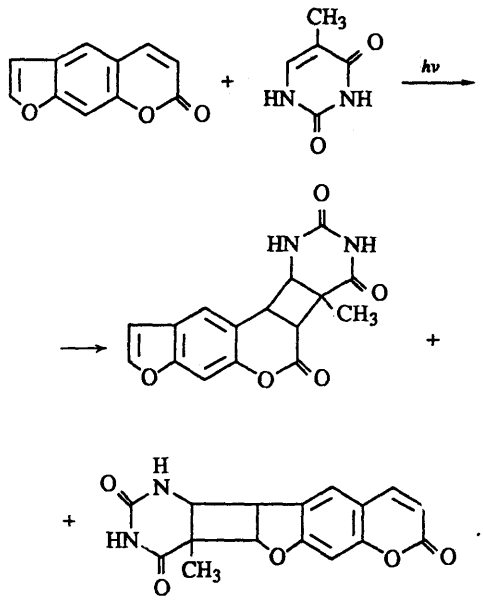


Coumarin 6

Active media having this composition have been proposed for lasers of a new type operating in the decolorisation wave regime with the lasing zone moving in the solution.[91]

Furocoumarins also form photoadducts with olefins,[92] while in biological systems they add under the influence of light to thymine in nucleic acids, to unsaturated acids, and to lipids and proteins,[93–96] and the reaction can involve not only the pyrone but also the furan

ring. Thus both types of psoralene–thymine monoadducts have been isolated:[97–99]



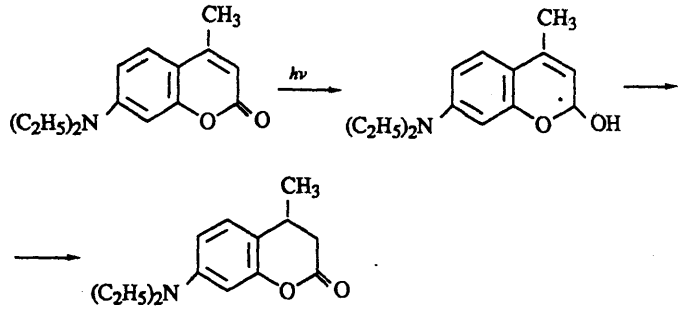
It is nowadays generally accepted that the therapeutic action of furocoumarin combined with irradiation by near UV light is due to the photochemical formation of interstrand cross-links in DNA via the successive cycloaddition of the furocoumarin to the pyrimidine bases of two DNA strands. The presence of such cross-links suppresses the hyperactive synthesis of DNA associated with psoriasis.[4] The breakdown of conjugation in the psoralen molecule on formation of a monoadduct via the pyrone ring induces a marked hypsochromic shift of the absorption, whereas the product of the addition of thymine to the furan ring absorbs radiation in almost the same way as psoralene—up to 380 nm.[97,98] Accordingly, it is clear that the interstrand cross-linking of DNA is possible only under the conditions of the initial addition of psoralene to the furan fragment, since only then can the system retain its ability to be activated by near UV light. It is noteworthy that in solution the reactivity of furocoumarins in the photocycloaddition reaction is much higher for the double bond of the pyrone ring than for that of the furan ring.[92] Since furocoumarins add to DNA in the opposite order in biological systems, it has been suggested that the mode of photocycloaddition is determined in this instant by non-valence interactions.

The [2 + 2]photocycloaddition of olefins to coumarins can occur, like the photodimerisation of the latter, both via the excited singlet and excited triplet states, depending on the structure of the substrate. Thus experimental data show that in the case of 7-aminocoumarins the excited singlet state is reactive,[85–87] while in furocoumarins it is the excited triplet state.[92,100]

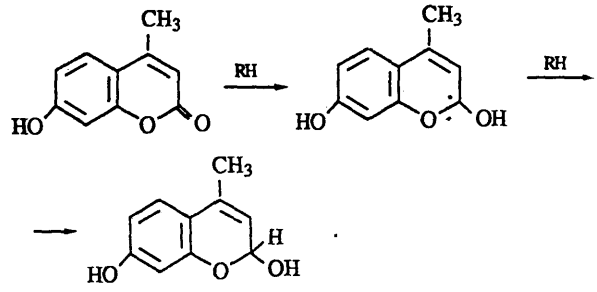
The similarity between the [2 + 2]photocycloaddition of olefins and [2 + 2]photocyclodimerisation is also manifested by the fact that both reactions are reversible—under the influence of short-wavelength light the cyclic adducts are reconverted into the initial compounds.[95,98]

(b) Other photochemical reactions of the chromophore

There are few data on the photodegradation of the chromophore in coumarin dyes in photochemical reduction reactions. When coumarin 1 is irradiated in deoxygenated acetonitrile, the product of the hydrogenation of one of the double bonds is formed, judging from mass-spectrometric data, in a low yield as a side-product.[49,101] Jones and co-workers[49,101] suggested that the 3,4-bond of the pyrone ring is reduced. In their view, the photochemical reaction proceeds via the excited singlet state by a bimolecular mechanism, which includes the ketyl radical disproportionation stage:

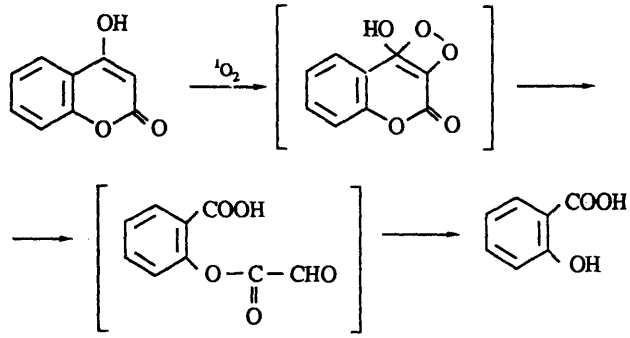


On the other hand, the reduction of the carbonyl groups has been postulated[102] for the analogous product of the photolysis of 4-methylumbelliferone:



The different views concerning the mode of photochemical reduction of the chromophore in coumarin derivatives indicate that the process has been studied inadequately and that a detailed analysis of the products is necessary in order to elucidate their structure unambiguously.

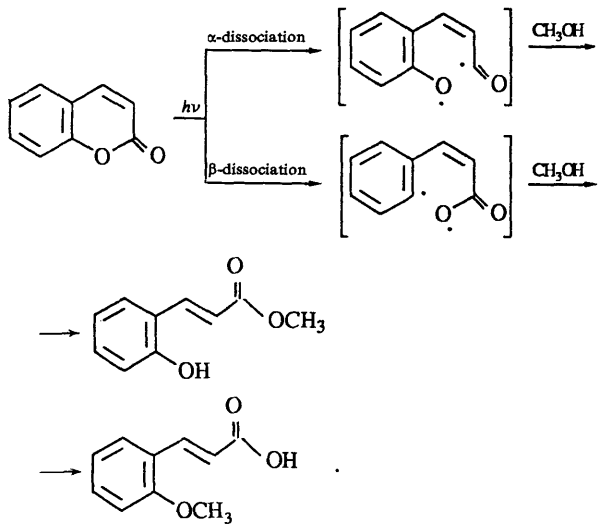
The photodegradation of the heterocycle with participation of singlet oxygen is known to occur for coumarins containing a hydroxy-group in the 4-position:[103]



The electron-donating hydroxy-group in compounds of this type activates the 3,4-double bond in reactions with $^1O_2$, which is particularly necessary for coumarins containing a carbonyl group, a powerful electron acceptor, next to the double bond. The hydroxy-group in the 3-position does not activate coumarin, since it forms an intramolecular hydrogen bond with the carbonyl oxygen. Like other

substituted derivatives, 3-hydroxycoumarins, with the exception of those containing a hydroxy-group in the 4-position, are not oxidised by singlet oxygen.[103]

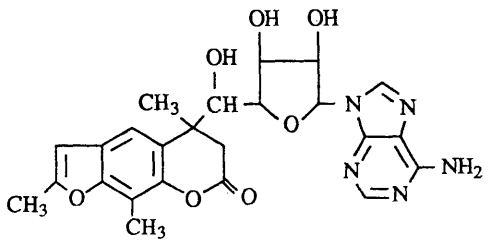
The opening of the pyrone ring can be initiated by the α- and β-dissociation of the C—O bond (relative to the carbonyl group).[104] The final products are formed in the reactions of biradicals with solvent molecules:



The α- and β-dissociation products are formed via states of different multiplicity—singlet and triplet respectively, α-dissociation being more probable.

The analogous ring opening reaction in derivatives of 3,4-dihydrocoumarin proceeds via α-dissociation. The quantum yield of this photochemical reaction is high and amounts to, for example, $(7.4 \pm 0.5) \times 10^{-2}$ for unsubstituted 3,4-dihydrocoumarin.[105]

The only known example of photoaddition to coumarins without the formation of cyclobutane derivatives is the photoaddition of adenosine to trimethylpsoralene.[106] The photoadduct has the following structure:

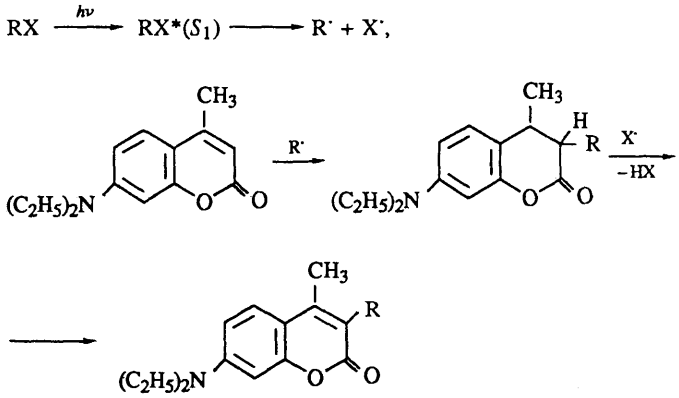


3. Photochemical reactions of the substituting groups

It was noted above that unsubstituted coumarin does not fluoresce and that the best phosphors of the coumarin series have electron-donating substituents in the 7-position. Other groups usually cause a shift of the fluorescence to the required spectral region and increase solubility, photostability, affinity for fibres, etc. In the light, the substituting groups can enter into various photochemical reactions. We shall consider the most important of these.

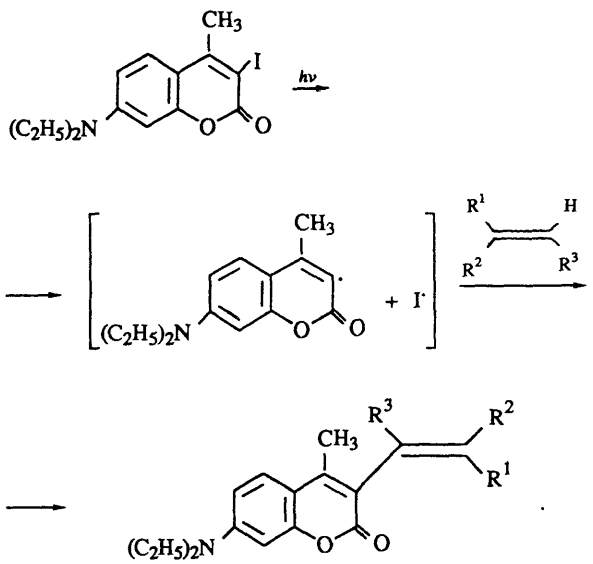
(a) Photosubstitution

The photosubstitution reactions of coumarin derivatives have been investigated in relation to the most readily available dye coumarin 1. Photosubstitution via a radical mechanism involves the 3-position when coumarin 1 is irradiated in the presence of reagents containing photolabile chemical bonds (alkyl and aryl halides, dioxane pyroxide, nitromethane):[107]



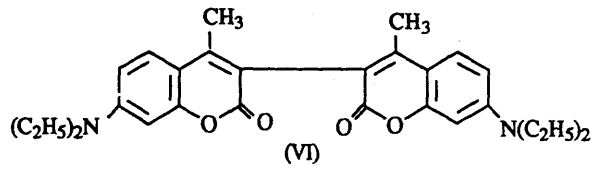
The yields of the photochemical reaction products are 10—30%. In conformity with the bond energies in the series of alkyl or aryl halides. the use of iodo-derivatives is most effective for substitution reactions. The study of the influence of the nature of the substituent in the 4-position in the pyrone ring showed that both electron-donating and electron-accepting substituents accelerate the process, apparently stabilising the radical centre in the intermediate.[108]

When 3-iodocoumarins containing the photolabile C—I bond were used in the presence of substituted benzene derivatives as well as olefins, a series of new 7-aminocoumarins were obtained containing an aryl[109] or unsaturated substituent[110] in the 3-position. The photochemical reaction proceeds via the excited singlet state of the substrate in accordance with the following most probable mechanism:



The reactions with monosubstituted benzenes result in the formation of *ortho*- and *para*-isomeric products, the efficiency of the photosubstitution decreasing on passing from electron-donating to electron-accepting substituents.[109]

The biscoumarin (VI) was obtained from coumarin 1 and its 3-iodo-derivative under similar conditions.[107]



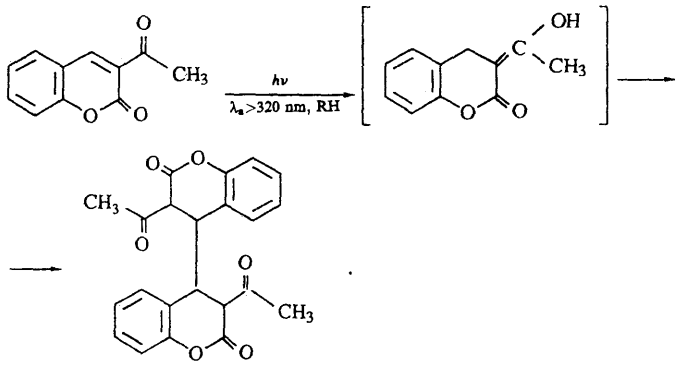
(VI)

On irradiation of 7-aminocoumarins in chlorine-containing solvents, 3-chloro-substituted derivatives are also formed via the radical photosubstitution mechanism with participation of chlorine atoms, which attack the unoccupied 3-position in the substrate molecule.[111]

Photosubstitution of coumarins by the radical-ion mechanism has not been investigated. According to preliminary data,[107] it is not selective and involves not only the 3-position but also other positions subjected to attack by the radical-ion.

The formation of a 3-hydroxy-derivative from coumarin 120 in the reactions of the latter with singlet oxygen has been postulated.[112,113]

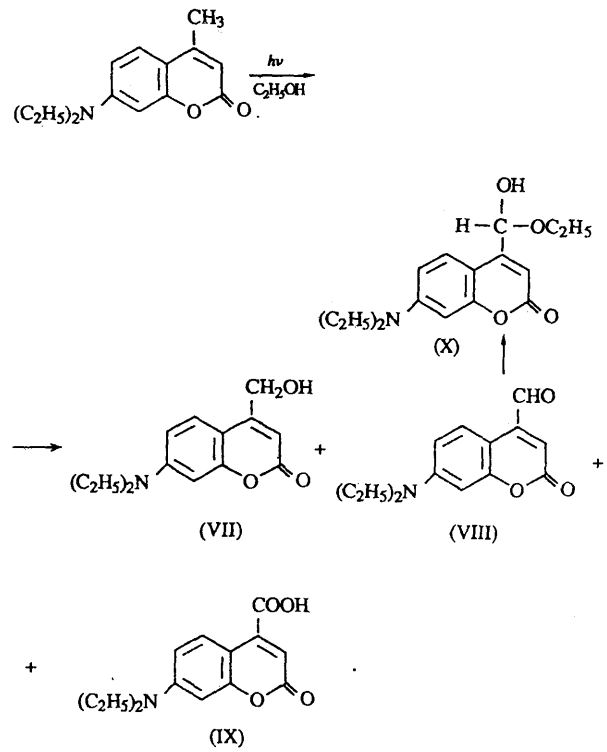
In connection with the discussion in this Section of the review of the mechanism of the formation of the biscoumarin (VI), we may note that 3,3'-diacetyl-3,3',4,4'-tetrahydro-4,4'-biscoumarin is formed in accordance with an unusual mechanism via the reduction of a substituent and the isomerisation and recombination of radicals:[90,114]



(b) Photochemical oxidation of alkyl substituents

Many coumarin phosphors contain a methyl group in the 4-position in the pyrone ring. Compounds of this type include coumarins 1 and 102, which have found extensive applications in the laser technique.

Winters, et al.[115] established for the first time that, when active lasing media based on alcoholic solutions of coumarin 1 are irradiated with light from pulsing pumping lamps, the methyl group in its structure is oxidised to the corresponding alcohol, aldehyde, and acid:

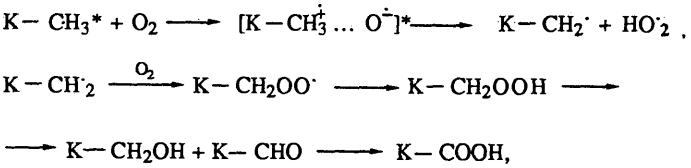


(VII) (VIII) (X) (IX)

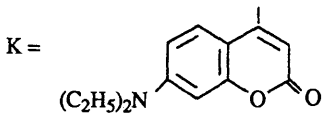
The accumulation in the solution of the products of the photochemical oxidation of the methyl group leads to an increase in the absorption by the lasing medium in the region corresponding to the luminescence of coumarin 1 and the impairment of lasing parameters. However, in alcohol only 4-carboxy-7-diethylamino-coumarin (IX) among the photoproducts (VII)–(IX) absorbs appreciably in the region corresponding to lasing by coumarin 1.[116] The aldehyde (VIII) likewise makes a significant contribution to the photoinitiated increase in the optical density of the active medium in the long-wavelength region, but subsequent interaction of compound (VIII) with the solvent leads to the formation of the hemiacetal (X), which does not absorb the luminescence radiation, is responsible for the dark relaxation of the optical density in the lasing region (Fig. 2), and determines the lasing energy in irradiated alcoholic solutions of coumarins.[116]

In order to seek ways of increasing the photostability of lasing media based on 4-methylcoumarins, the mechanism of the photochemical oxidation of these compounds was investigated by several groups of workers.[59,117–120] In air-saturated ethanol, the quantum yield of the photochemical reaction is 5×10^{-4}, is independent of the dye concentration, and in the range $10^{-4}-10^{-2}$ M the reaction constitutes the principal photodegradation pathway.[117] The efficiency of the photochemical oxidation of the methyl group increases with enhancement of the electron-donating properties of the substituent in the 7-position. The process is sensitised by triplet sensitisers and is almost independent of the energy of the absorbed quantum in the wavelength range 254–365 nm. The oxidation

reaction proceeds via a free-radical mechanism and is initiated by the bimolecular reaction between the excited coumarin and oxygen:[117]



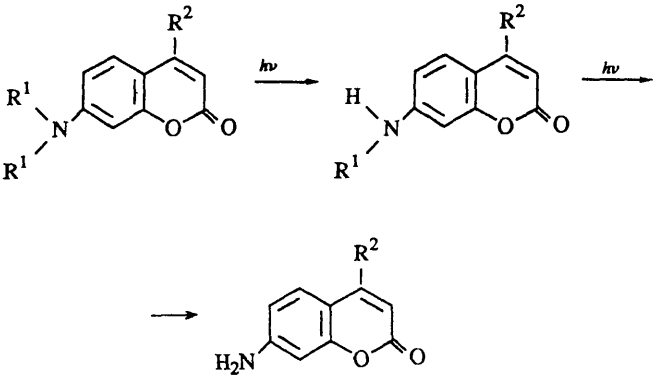
where



The study of the photochemical processes occurring in solutions of coumarins containing a methyl-group in the 4-position revealed the following pathways leading to the expansion of the stock of available active lasing media: removal of oxygen from the solution by bubbling the latter with an inert gas;[121,122] the use of coumarins not containing a CH_3 group[123] or containing the non-oxidisable CF_3 group in the 4-position'[124] inhibition of the radical oxidation reactions by photostabilisers;[125] adsorption of 4-carboxy-7-diethylaminocoumarin on the Al_2O_3 filter in the laser pumping system.[115]

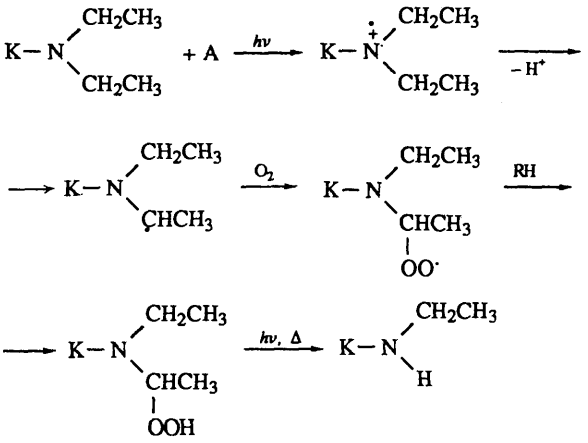
(c) Photochemical reactions of alkylamino-groups

The most numerous group of coumarin phosphors contain an amino- or alkylamino-group in the 7-position. 7-Alkylaminocoumarins are dealkylated under the influence of radiation, the dealkylation products being formed with a greater or small probability virtually under any photolytic conditions. They were first isolated and identified by Winters, et al.[115] after irradiating coumarin 1 in ethanol. In the latest studies,[59,101] it has been shown that the process is common to all 7-alkylamino-coumarins:

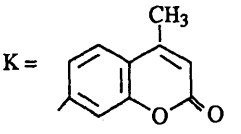


$R^1 = CH_3,\ C_2H_5;\quad R^2 = CH_3,\ CH_2OH,\ CF_3.$

7-Alkylaminocoumarins are dealkylated in accordance with the same mechanism as other tertiary and secondary amines—via α-aminoalkyl radicals, which are formed when electron acceptors abstract a hydrogen atom or an electron and a proton according to the following most probable scheme:



where



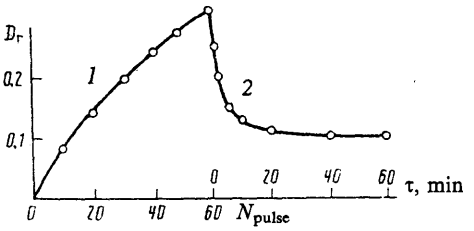


Figure 2. Variation of the optical density of an ethanol solution of coumarin 1 ($c = 10^{-3}$ M, $L = 5$ cm) in the lasing region at a wavelength of 460 nm during irradiation by light pulses (N_{pulse}) from an IFP=2000 lamp at a frequency of 0.3 Hz (curve *1*) and during the subsequent dark process (curve *2*).[116]

Various oxidants, for example aromatic nitro-compounds,[126] the solvent,[111] another coumarin molecule in an excited state,[49,127,128] and singlet oxygen,[58,59,62] can also function as electron (hydrogen atom) acceptors.

The role of the photochemical oxidation by singlet oxygen, which is extremely common in organic photochemistry, in the photodegradation of coumarins has been investigated in fair detail. It has been established[59,62] that the interaction of 7-alkylaminocoumarins with $^1O_2$ leads to the oxidative photo-*N*-dealkylation and does not usually involve the 3,4-bond in the pyrone fragment. With the exception of the 4-hydroxy-derivative,[103] coumarins without amino-groups do not react on treatment with $^1O_2$.

On direct photolysis in a number of solvents, the photo-*N*-dealkylation proceeds according to the self-sensitised photochemical oxidation mechanism, which consists in the initial activation of oxygen by the transfer to the latter of the excitation energy from the triplet level of coumarin and the formation of singlet oxygen, which oxidises the dye in the electronic ground state:

$$K \rightsquigarrow {}^3K^*,$$

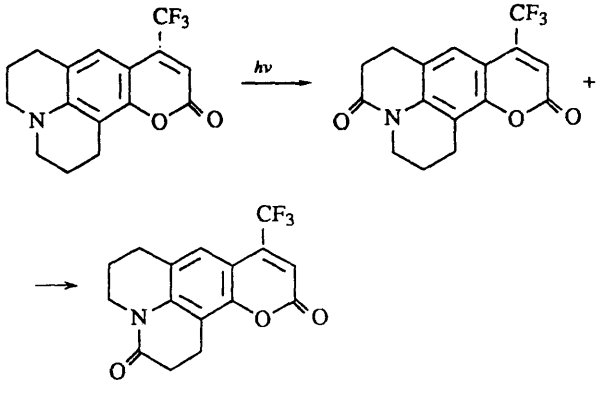
$${}^3K^* + {}^3O_2 \rightarrow K + {}^1O_2,$$

$$K + {}^1O_2 \rightarrow N\text{-dealkylation products}.$$

For example, in benzene the photo-*N*-dealkylation of coumarin 1 (the main photochemical reaction) via the mechanism of the self-sensitised photochemical oxidation by singlet oxygen proceeds to an extent greater than 70% for a $^1O_2$ generation quantum yield of ~ 0.1 and an overall rate constant for the physical and chemical quenching of singlet oxygen by coumarin of 10^6 litre mol^{-1} s^{-1}.[62] The formation of the clathrate complex between coumarin 1 and β-cyclodextrin increases the stability of the dye as regards the action of $^1O_2$ in aqueous solutions by an order of magnitude.[128]

On passing from dilute to concentrated ($c > 10^{-2}$ M) solutions, the mechanism of the photo-*N*-dealkylation changes to a bimolecular mechanism, which includes the abstraction of an electron (hydrogen atom) by an excited coumarin molecule from an unexcited one ($k = 10^7$ litre mol^{-1} s^{-1} in ethanol[128]). In this connection, one should note that in alcoholic solutions at low concentrations the main photochemical reaction of 7-dialkylamino-4-methylcoumarins is the photochemical oxidation of the methyl group, whereas at high concentrations the bimolecular photo-*N*-dealkylation predominates.

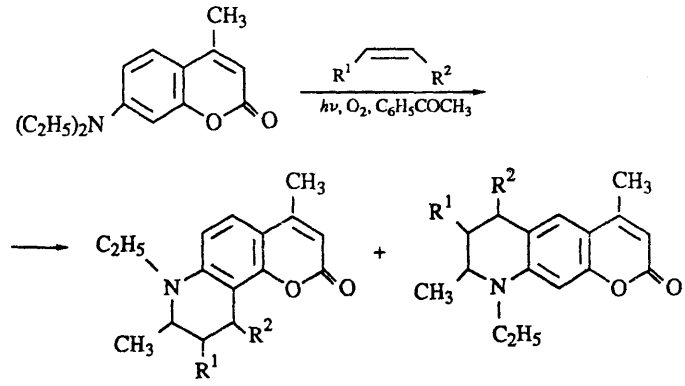
The formation of amides in the photochemical oxidation of alkylaminocoumarins has been reported in a number of communications.[59,101] Thus two isomeric amides are formed on irradiation of coumarin 153 in air-saturated acetonitrile:[102]



Evidently amides are formed as products of photo-*N*-dealkylation on oxidation of the intermediate α-aminoalkyl radicals by oxygen.

In deoxygenated solutions, the radicals undergo other dark reactions — they recombine with solvent molecules[129] and give rise to oligomers.[49,101] The role of radicals in the photodegradation of deoxygenated solutions has been confirmed by the inhibition of the reaction by divalent sulphur compounds.[127]

The heterocyclisation of alkylamino-groups in the 6- and 8-position in the coumarin ring is of interest. On photoirradiation in the presence of olefins containing more than one electron-accepting substituents, 7-aminocoumarins do not give rise to adducts resulting from the [2 + 2]cycloaddition to the 3,4-bond, but in the presence of acetophenone, a triplet sensitiser, they afford heterocyclisation products in a quantum yield of 0.01:[130]



The mechanism of the photochemical reaction proposed by Kirpichenok, et al.[130] involves the participation of acetophenone in the T_1 state as the oxidant in the formation of the α-aminoalkyl radical and the addition of the latter to the olefin.

It follows from the data presented in this Section of the review that the photochemical reactions involving the alkylamino-group are initiated by the formation of α-aminoalkyl radicals, the different dark reactions of which determine the nature of the final product.

- - - o0o - - -

The results considered show that during the last decade our knowledge about the photochemical reactions of coumarin derivatives has greatly expanded. Various photochemical reactions of compounds of this class have been investigated, but the available information about certain aspects of the photolysis, for example, about the irreversible photodegradation of the chromophore, is inadequate. Nevertheless, on the basis of the known values it is possible in many instances to predict the behaviour of coumarin derivatives on photoirradiation. The results described determine to a large extent the course of future studies, which will have to be carried out in the search for effective ways of increasing the photostability of the organic phosphors in this important class.

References

1. H Gold *Chemistry of Synthetic Dyes* (Edited by K Venkataraman) (Translated into Russian), Khimiya, Leningrad, 1977, Vol. 6, p. 329
2. K H Drexhage *Dye Lasers* (Edited by F P Schaefer) (Translated into Russian), Mir, Moscow, 1976, p. 172
3. R S Davidson, M M Hilchenbuch *Photochem. Photobiol.*, 1990, **52** 431
4. R V Bensasson, E J Land, T G Truscott *Flash Photolysis and Pulse Radiolysis in Biology and Medicine* (Translated into Russian), Mir, Moscow, 1987, p. 332
5. V A Barachevskii, G I Lashkov, V A Tsekhomskii *Fotokhromizm i Ego Primenenie* (Photochromism and Its Applications), Khimiya, Moscow, 1977, p. 54
6. I I Grandberg, L K Denisov, O A Popova *Khim. Geterotsikl. Soedin.*, 1987, 147

7. A R Reddy, D V Prasad, M Darbarwar *J. Photochem.*, 1986, **32** 69
8. A N Fletcher, D E Bliss *Optics Commun.*, 1983, **47** 57
9. I I Tkach, T A Mikhailova, A V Reznichesnko, et al. *Khim. Geterotsikl. Soedin.*, 1990, 321
10. N Yu Vasil'eva, I V Sokolova, A M Degtyarenko, A V Kropachev *Izv. Vyssh. Uchebn. Zaved. Zaved. Fiz.*, 1990, 123
11. M M Asimov, V N Gavrilenko, L Kozma, et al. *Zh. Prikl. Spektrosk.*, 1990, **53** 201
12. O A Ponomarev, Yu F Pedash *Zh. Fiz. Khim.*, 1989, **63**(2) 546 [English translation in *Russ. J. Phys. Chem.*, 1989(2)]
13. W Rettig, A Klock *Can. J. Chem.*, 1985, **63** 1649
14. R V Subba Rao, M Krishnamurthy, S K Dogra *J. Photochem.*, 1986, **34** 55
15. A Mangini, R Passerini *Gazz. Chim. Ital.*, 1957, **87** 243
16. U Brackmann *Lambdachrome Lazer Dyes, Lambda Physik. Gmbh*, Gottingen, D-3400, 1986
17. C E Weelock *J. Am. Chem. Soc.*, 1959, **81** 1348
18. M S A Abdel-Mottaleb, B A El-Sayed, M M Abo-Aly, M Y El-Kady *J. Photochem. Photobiol. A*, 1989, **46** 379
19. G Jones (II), W R Jackson, C Choi *J. Phys. Chem.*, 1985, **89** 294
20. O A Ponomarev, E R Vasina, V G Mitina, A A Sukhorukov *Zh. Fiz. Khim.*, 1990, **64**(4) 974 [English translation in *Russ. J. Phys. Chem.*, 1990(4)]
21. L K Denisov, L M Mel'nikova, M A Kirpichnok, I I Grandberg *Zh. Prikl. Spektrosk.*, 1991, **54** 135
22. T Moriya *Bull. Chem. Soc. Jpn.*, 1988, **61** 1873
23. L I Loboda, I V Sokolova, E A Postol, et al. *Zh. Fiz. Khim.*, 1984, **58**(10) 2462 [English translation in *Russ. J. Phys. Chem.*, 1984(10)]
24. R T Kuznetsova, I V Sokolova, R M Fofonova, et al. *Zh. Fiz. Khim.*, 1989, **63**(3) 747 [English translation in *Russ. J. Phys. Chem.*, 1989(3)]
25. E M Goryaeva, A M Gorelik, V F Donyagina, et al. *Zh. Prikl. Spektrosk.*, 1990, **52** 306
26. J A Barltrop, J D Coyle *Excited States in Organic Chemistry* (Translated into Russian), Mir, Moscow, 1978, p. 115
27. G Jones (II), W Jackson, A Halpern *Chem. Phys. Lett.*, 1980, **72** 391
28. I V Sokolova, N Yu Vasil'eva, L I Loboda, et al. *Izv. Vyssh. Uchebn. Zaved. Fiz.*, 1986, 79
29. M S A Abdel-Mottaleb, M S Antomous, M M Abo-Aly, et al. *J. Photochem. Photobiol. A*, 1989, **59** 259
30. G Chu, F Yangbo *J. Chem. Soc., Faraday Trans. 1*, 1987, **83** 2533
31. A Nag, T Chakrabarty, K Bhattacharyya *J. Phys. Chem.*, 1990, **94** 4203
32. J A Van Gompel, G B Schuster *J. Phys. Chem.*, 1989, **92** 1292
33. R W Yip, Y X Wen *J. Photochem. Photobiol. A*, 1990, **54** 263
34. K N Knox, E J Land, T G Truscott *J. Photochem. Photobiol., B*, 1988, **1** 315
35. T A Shakhverdov, V N Kalinin, V L Ermolaev *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1990, **54** 460
36. R F Kubin, A N Fletcher *Chem. Phys. Lett.*, 1983, **99** 49
37. T Moriya *Bull. Chem. Soc. Jpn.*, 1984, **57** 1723
38. T Moriya *Bull. Chem. Soc. Jpn.*, 1986, **59** 961
39. T Moriya *Bull. Chem. Soc. Jpn.*, 1987, **60** 3855
40. T Moriya *Bull. Chem. Soc. Jpn.*, 1988, **61** 753
41. G Jones, S Griffin, C Choi, W Bergmark *J. Org. Chem.*, 1984, **49** 2705
42. T G Pavlopoulos *Spectrochim. Acta*, 1986, **42** 47
43. B R Henry, R V Hunt *J. Mol. Spectrosc.*, 1971, **39** 466
44. P Crozet *Chem. Phys. Lett.*, 1974, **25** 114
45. E J Land, T G Truscott *Photochem. Photobiol.*, 1979, **29** 861
46. W W Mantulin, P-S Song *J. Am. Chem. Soc.*, 1973, **95** 5122
47. N K Ray, V K Ahuja *Photochem. Photobiol.*, 1973, **17** 347
48. K I Priyadarsini, D B Naik, P N Moorthy *Chem. Phys. Lett.*, 1989, **157** 525
49. G Jones, W Bergmark *J. Photochem.*, 1984, **26** 179
50. T G Pavlopoulos, D J Golich *J. Appl. Phys.*, 1988, **64** 521
51. K I Priyadarsini, D B Naik, P N Moorthy *J. Photochem. Photobiol. A*, 1990, **54** 251
52. K I Piyadarsini, D B Naik, P N Moorthy *J. Photochem. Photobiol. A*, 1989, **46** 239
53. R V Bensasson, O Chalvet, E J Land, J C Ronfard-Haret *Photochem. Photobiol.*, 1984, **39** 287
54. R Costalat, J Blais, J-P Ballini, et al. *Photochem. Photobiol.*, 1990, **51** 255
55. E Quenten, P Adriaens *Photochem. Photobiol.*, 1986, **43** 485
56. N J De Mol, G M Beijersbergen van Henegouwen *Photochem. Photobiol.*, 1979, **30** 331
57. N Singh, J A Vadasz *Photochem. Photobiol.*, 1978, **28** 539
58. O V Zin'kovskaya, N A Kuznetsova, O L Kaliya *Zh. Prikl. Spektrosk.*, 1984, **41** 626
59. R J Trebra, T H Koch *J. Photochem.*, 1986, **35** 33
60. W Poppe, L J Grossweiner *Photochem. Photobiol.*, 1975, **22** 217
61. S Yu Egorov, A A Krasnovskii, Jr., V L Sukhorukov, A Ya Potapenko *Biofizika*, 1986, **31** 154
62. O V Zin'kovskaya, N A Kuznetsova, A V Reznichenko *Khim. Vys. Energ.*, 1987, **21** 352
63. K I Priyadarsini, D B Naik, P N Moorthy *Chem. Phys. Lett.*, 1988, **148** 572
64. T Moriya *Bull. Chem. Soc. Jpn.*, 1983, **56** 6
65. L M Rubeko, A I Akimov, L K Denisov, B M Uzhinov *Zh. Prikl. Spektrosk.*, 1981, **35** 436
66. L D Derkacheva, A I Krymova, V A Petukhov, N S Platonov *Opt. Spektrosk.*, 1982, **53** 73
67. O S Wolfbeis *Z. Phys. Chem. (Munich)*, 1981, **125** 15
68. H H Morrison, H Curtis, T McDowell *J. Am. Chem. Soc.*, 1966, **88** 5415
69. R Hoffman, P Wells, H Morrison *J. Org. Chem.*, 1971, **36** 102
70. K Muthuramu, V Ramamurthy *J. Org. Chem.*, 1982, **47** 3976
71. F Lewis, D Howard, J Oxman *J. Am. Chem. Soc.*, 1973, **105** 3344
72. K Muthuramu, V Ramamurthy *Indian J. Chem., Sect. B*, 1984, **23** 502
73. D V Rao, H Ulrich, F A Stuber, A A R Sayigh *Chem. Ber.*, 1973, **106** 388
74. N Ramnath, V Ramamurthy *J. Org. Chem.*, 1984, **49** 2807
75. H Umemoto, T Kitao *Kogyo Kagaku Zasshi*, 1970, **73** 2200
76. J Gervais, F C De Schryver *Photochem. Photobiol.*, 1975, **21** 71
77. A Moysan, A Cazaussus, F Gaboriau, et al. *Photochem. Photobiol.*, 1988, **47** 327
78. S C Shim, S S Lee, S J Choi *Photochem. Photobiol.*, 1990, **51** 1
79. J P Y Kao, S T Isaacs, J E Hearst *Photochem. Photobiol.*, 1990, **51** 273
80. J Meng, D Fu, X Yao, et al. *Tetrahedron*, 1989, **45** 6979
81. K Gnanaguru, N Ramasubbu, K Venkatesan, V Ramamurthy *J. Photochem.*, 1984, **27** 355
82. K Gnanaguru, N Ramasubbu, K Venkatesan, V Ramamurthy *J. Org. Chem.*, 1985, **50** 2337

83. L A Holt, I H Leaver, B Milligan *Textile Research J.*, 1976, **46** 539
84. J W Hanifin, E Cohen *Tetrahedron Lett.*, 1966, 1419
85. M A Kirpichenok, L M Mel'nikova, L K Denisov, I I Grandberg *Khim. Geterosikl. Soedin.*, 1988, 1169
86. M A Kirpichenok, L M Mel'nikova, D S Yufit, et al. *Khim. Geterosikl. Soedin.*, 1988, 1176
87. M A Kirpichenok, D S Yufit, L M Mel'nikova, et al. *Khim. Geterosikl. Soedin.*, 1990, 1022
88. M A Kirpichenok, D S Yufit, L M Mel'nikova, et al. *Khim. Geterosikl. Soedin.*, 1990, 1319
89. R G Hunt, C J Potter, S T Reid, M L Roantree *Tetrahedron Lett.*, 1975, 2327
90. K-H Pfoertner *Helv. Chim. Acta*, 1976, **59** 834
91. Yu Yu Stoilov, S P Bazhulin *Kvantovaya Elektronika*, 1986, **13** 633
92. B D Ratiner, T Otsuki *Chem. Lett.*, 1989, 1035
93. J Cadet, P Vigny, W R Midden *J. Photochem. Photobiol. B*, 1990, **6** 197
94. S Caffieri, A W M Lefeber, F Dall'Acqua, G M J Beijersbergen van Henegouwen *J. Photochem. Photobiol., B*, 1990, **7** 347
95. S Caffieri, A Daga, D Vedaldi, F Dall'Acqua *J. Photochem. Photobiol., B*, 1988, **2** 515
96. F Dall'Acqua, P Martelli *J. Photochem. Photobiol., B*, 1991, **8** 235
97. G Rigatti *Photochem. Photobiol.*, 1967, **6** 711
98. L Musajo, F Bordin, R Bevilacqua *Photochem. Photobiol.*, 1967, **6** 927
99. J E Hearst *Chem. Res. Toxicol.*, 1989, **2** 69
100. R Bevilacqua, F Bordin *Photochem. Photobiol.*, 1973, **17** 191
101. G Jones (II), W R Bergmark, W R Jackson *Optics Commun.*, 1984, **50** 320
102. T P Zhestkova, G G Ryabchikova, A K Pikaev *Zh. Prikl. Spektrosk.*, 1980, **33** 934
103. S S Chibber, R P Sharma *Indian J. Chem., Sect., B*, 1979, **18** 538
104. O A Ponomarev, O E Bondarenko, V G Mitina, L A Sleta *Khim. Fiz.*, 1990, **9** 477
105. C D Gutsche, B A M Oude-Alink *J. Am. Chem. Soc.*, 1968, **90** 5855
106. S C Chim, S J Choi *Photochem. Photobiol.*, 1990, **52** 669
107. M A Kirpichenok, L M Mel'nikova, L K Denisov, I I Grandberg *Khim. Geterosikl. Soedin.*, 1989, 460
108. M A Kirpichenok, L M Mel'nikova, L K Denisov, I I Grandberg *Khim. Geterosikl. Soedin.*, 1990, 1028
109. N A Gordeeva, M A Kirpichenok, A I Chernyshev, et al. *Khim. Geterosikl. Soedin.*, 1990, 1172
110. N A Gordeeva, M A Kirpichenok, V S Yufit, et al. *Khim. Geterosikl. Soedin.*, 1990, 1033
111. N S Patalakha, M A Kirpichenok, N A Gordeeva, I I Grandberg *Izv. Timiryazev Sel'skokhoz. Akad.*, 1989, 157
112. J T Kunjappu, K N Rao *J. Photochem.*, 1987, **39** 135
113. J T Kunjappu *J. Photochem. Photobiol., A*, 1991, **56** 365
114. I Petkov, A Bojilova, P Markov *Monatsh. Chem.*, 1990, **121** 85
115. B H Winters, H I Mandelberg, W B Mohr *Appl. Phys. Lett.*, 1974, **25** 723
116. O V Zin'kovskaya, N A Kuznetsova, O L Kaliya, E A Luk'yanets *The Chemical Nature of the Dark Relaxation Processes in Lasting Media Based on Coumarin 47*, Minsk, 1986, 13 pp.—Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 29.1.86, No. 293-86
117. E A Kalmykova, N A Kuznetsova, O L Kaliya *Zh. Obshch. Khim.*, 1990, **60** 946
118. K I Priyadarsini, J T Kunjappu, P N Moorthy *Indian J. Chem., Sect. A*, 1987, **26** 899
119. E I Akimova, M I Snegov *Opt. Spektrosk.*, 1987, **63** 71
120. L Z Vinogradov, A A Krasheninnikov, V P Klindukhov, et al. *Zh. Prikl. Spektrosk.*, 1989, **50** 401
121. US P. 4479223, 1984
122. US P. 4562580, 1985
123. US P. 4051062, 1977
124. US P. 3891563, 1975
125. US P. 4428859, 1984
126. D Dopp, J Heufer *J. Photochem.*, 1986, **32** 243
127. R J Trebra, T H Koch *Appl. Phys. Lett.*, 1983, **42** 129
128. E A Kalmykova, N A Kuznetsova, O L Kaliya, M A Tavrizova *Zh. Obshch. Khim.*, 1991, **61** 1003
129. R J Trebra, T H Koch *J. Photochem. Photobiol., A*, 1987, **41** 111
130. M A Kirpichenok, L M Mel'nikova, L K Denisov, et al. *Khim. Geterotsikl. Soedin.*, 1989, 30

Received 25th June 1991

Translated from *Uspekhi Khimii* **61** 1268–1302 (1992) U.D.C. 547.221:539.194

The electronic structure and reactivity of alkenes

V G Barabanov, A V Golovin, A A Rodin, A A Ustenko
State Institute of Applied Chemistry, St. Petersburg, St. Petersburg State University,
Patrice Lumumba University of Friendship Among Peoples, Moscow

ABSTRACT. The modern methods for the calculation of the electronic structures of alkenes are examined. The photoelectron spectra of alkenes are analysed and the relation between the properties of molecules and their orbital structure is discussed on the basis of experimental data and quantum-chemical calculations. The corresponding structural parameters of alkenes are systematically compared with their reactivities. The ionisation energies of alkenes are presented.

The bibliography includes 86 references.

Contents

I. Introduction 697
II. Approximations used in the analysis of the electronic structures of alkenes 697
III. Results of quantum-chemical calculations of the electronic structures and ionisation energies of alkenes 700
IV. The reactivities of alkenes 707

I. Introduction

The method for the investigation of the electronic structures of molecules which yields most information is nowadays photoelectron spectroscopy (PES). As it developed, it became possible to test experimentally the adequacy of quantum-chemical calculations within the framework of the molecular orbital (MO) theory. On the other hand, quantum-chemical calculations play an important role in the interpretation of photoelectron spectroscopy data.

The aim of the present review was to survey the studies on the electronic structures of alkenes with the aid of quantum-chemical calculations and photoelectron spectroscopy and to compare the parameters of the electronic structures of alkenes with their reactivities, which are determined mainly by the presence of the π-bond.

II. Approximations used in the analysis of the electronic structures of alkenes

1. Approximations of the molecular orbital method

Since exact quantum-chemical calculations of the electronic structures of polyatomic molecules are impossible, it is necessary to carry out significant simplifications and approximations depending on the complexity of the system investigated, the nature of the problem, and the possibilities of the computer technique. In the development of computational methods, one usually begins with the stationary Schrödinger equation for a polyatomic molecule. The fact that the mass of electrons is significantly smaller than the mass of nuclei while the forces acting on nuclei and electrons are of the same order of magnitude makes it possible to separate approximately the motions of the nuclei and electrons in the wave function (the Born–Oppenheimer approximation), while in the analysis of the photoelectron spectrum one can consider separately the positions of the bands in the spectrum (they are determined by the electronic subsystem) and the band contours (they are determined by the nuclear subsystem).[1,2]

The next approximation usually introduced involves allowance for the Coulombic interaction between electrons in the form of an effective potential acting on an isolated electron in the molecule. The set of eigenfunctions of the one-electron equation is usually referred to as molecular orbitals. The wave function of a many-electron system is represented in terms of this approximation by a linear combination of derivatives of one-electron wave functions.

A set of a finite number of basis functions, for which one usually selects functions centred on the atoms in the molecule, is used as an approximation to one-electron wave functions. The molecular orbitals are then represented by linear combinations of atomic orbitals (the LCAO-MO approximation). Only $1s$ atomic orbitals (AO) are used for hydrogen atoms, while s, p_x, p_y, and p_z atomic orbitals are used for carbon and other atoms.

For planar molecules, the molecular orbitals can be subdivided in accordance with the principle of their transformation on reflection in a plane. The π MO change sign on reflection in a plane, while σ MO do not. π MO are formed mainly from the p_z atomic orbitals, where the z axis is perpendicular to the symmetry plane of the molecule. Molecular orbitals of another type, frequently manifested in photoelectron spectra in the form of narrow bands, are the orbitals of the lone electron pairs of the heteroatoms. Such orbitals are mainly localised on heteroatoms and the removal of electrons from them does not lead to significant changes in the molecular geometry.

The molecular orbitals of the molecules are classified in accordance with the characteristics of the irreducible representations of the point group to which the equilibrium configurations of the molecule refer.[3] For example, in the ethylene molecule, which belongs to the D_{2h} symmetry group, eight types of symmetry of the molecular orbitals are distinguished: A_g, A_u, B_{1g}, B_{1u}, B_{2g}, B_{2u}, B_{3q}, and B_{3u}. In order to determine the symmetry type of a specific molecular orbital, it is essential to discover in terms of which irreducible representation the LCAO coefficients of the given molecular orbital are transformed for different symmetry operations. Here one uses standard tables of characters of irreducible representations.

The molecules of the class of alkenes can belong to the D_{2h}, C_{2h}, C_{2u}, C_2, and C_s symmetry groups. These groups contain only one-dimensional irreducible representations and in alkene molecules there is therefore no degeneracy of molecular orbitals in terms of symmetry. Doubly degenerate molecular orbitals are encountered only in cumulenes with an even number of double bonds (molecules of the type of allene $H_2C=C=CH_2$) which belong to the D_{2d} symmetry group incorporating a two-dimensional irreducible representation.

The knowledge of the LCAO coefficients for occupied molecular orbitals makes it possible to analyse the electronic populations of atoms and bonds, i.e. to discover the electronic structure of the molecule. The partial charges on atoms, calculated as the difference between the number of electrons in the isolated atom and its population in the molecule, are usually quoted. The total charges on atoms, as well as their σ and π components, are used as quantitative characteristics of the inductive and mesomeric effects of substituents in alkenes. Comparative analysis of the populations of bonds makes it possible to infer their relative strengths.

In discussing the effect of substituents in alkenes and also the reactivities of alkenes, use is frequently made of Fukui's theory of frontier orbitals (this theory has been most fully described by Hochstrasser[3] and Fukui[4]), in which only the interactions between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecular fragments are considered. Here one analyses characteristics of frontier orbitals such as their energy, symmetry, bonding or antibonding character, and their overlap in space. For clarity, one frequently uses energy diagrams of orbital interactions for reacting systems. The approximation of frontier orbitals constitutes a simplified qualitative theory, which works successfully in alkenes, provided that the HOMO have energies appreciably different from those of the remaining molecular orbitals. In other cases, for example in HFC=C=CHF, where the HOMO and the occupied molecular orbital which follows it have the same energies,[5] it is essential to take into account several highest occupied or lowest unoccupied molecular orbitals. In those cases where the conclusions reached from the theory of frontier orbitals do not explain the experimental results, it is assumed that the given interaction is subject to charge and not orbital control.

In a qualitative description of alkenes with a complex structure, use is made in a number of instances of the model of group orbitals,[6–8] according to which the orbitals of individual fragments (methylene and methyl groups, amino-groups, etc.) can be transferred from molecule to molecule, and thus to construct the molecular orbitals of large molecules from the orbitals of these fragments. Here correlation diagrams for the orbital energies of the molecule and its fragments, referred to as Walsh diagrams, are widely used. The employment of the orbitals of fragments in discussing the effects of substituents proves to be extremely fruitful. For highly polar molecules, the predictions of this simple model may be of the usual kind.

In discussing the molecular orbital stabilisation or destabilisation effects under the influence of substituents, Dewar's theory of perturbations of molecular orbitals is sometimes invoked.[9] It makes it possible to estimate the contributions of the inductive and mesomeric effects of the substituents and also of hyperconjugation.

2. Non-empirical and semiempirical calculations within the framework of the molecular orbital method

In the theory of molecular orbitals, the orbitals are obtained as functions minimising the electronic energy of the molecule in terms of the fixed nuclei approximation. Here one solves a system of equations in which the interelectron repulsion is taken into account in the form of the interaction between the electron in the given orbital and the average field of the remaining electrons. This approach, known as the self-consistent field (SCF) method, leads to an unduly high electron repulsion energy because the electron in fact moves in the instantaneous and not the average field of the remaining electrons. The difference between the true energy of the molecule and the energy obtained in terms of the SCF approximation is called the correlation energy.

The overall estimate of the interelectron repulsion energy in the SCF method is approximately constant for each type of electron pairs and therefore has little effect in the study of processes where the number and type of electron pairs (bond electrons, lone pairs) are conserved. In processes accompanied by the separation of electron pairs (ionisation, dissociation), failure to take into account the correlation energy can lead to serious errors.

Both non-empirical (*ab initio*) and semiempirical methods are widely used in quantum-chemical calculations.

In non-empirical calculations, account is taken of all the electrons of the atoms and of all the molecular integrals encountered in the SCF equations. The accuracy of calculations of this type depends on the choice of the basis set of atomic orbitals for the construction of the molecular orbital. In calculations for alkenes, both minimal and extended sets are encountered. Minimal basis sets include only the Slater type orbitals (STO) which are necessary for the construction of the complete atomic shell. Each Slater atomic orbital is represented by the sum of several Gaussian functions (GF) the use of which simplifies the calculation of molecular integrals. The STO-3G minimal basis sets in which three Gaussian functions are used to represent each Slater atomic orbital has come to be most widely used. The minimal basis set, frequently employed for the optimisation of the molecular geometry, has the advantage that it requires relatively small amounts of computer time in the calculations. Non-empirical calculations for alkenes in terms of the STO-3G basis set have been carried out in a number of studies.[11–15] A significant deficiency of the minimal basis set consists in the absence of the possibility of altering the size of the atomic orbitals as a function of the molecular structure because the same set of atomic orbitals is used for all types of molecular orbitals. This deficiency is eliminated in the extended basis sets, such as 4-31GF, where the core orbitals are fitted by four Gaussian functions while the valence orbitals are divided into two components—the compact component comprising three Gaussian functions and the diffuse component represented by a single Gaussian function. The 4-31G basis set has been used in calculations for alkenes.[13,14,16] Further expansion of the basis set is achieved by including polarisation *d* orbitals for heavy atoms and *p* orbitals for hydrogen atoms, as is done in basis sets of type 6-31G (in calculations for haloethylenes[17]). Two-exponent function (double-zeta) basis sets have also been used in calculations for alkenes.[5,10,18–22] Other basis sets can also be encountered, for example, basis sets consisting of Hartree–Fock atomic orbitals (i.e. obtained for individual atoms by the SCF method).[22]

Non-empirical calculations by the SCF method, in which the electronic wave function of the molecule is represented by a single determinant made up of occupied molecular orbitals, do not permit allowance for the electronic correlation energy, as stated above. Therefore in a number of calculations for alkenes, the correlation correction is taken into account additionally using different methods—the configuration interaction,[10] perturbation theory,[5] and

many-particle Green's functions.[17,23] The number of such studies is relatively small, since allowance for the electronic correlation by the above methods constitutes a laborious computational procedure and requires the consumption of much computer time.

In non-empirical calculations, use is also made of the discrete-variational X_α method,[22] which, however, has not so far become quite so common in the quantum chemistry of alkenes as the molecular orbital method.

Together with non-empirical methods, semiempirical computational methods, in which account is taken only of the electrons of the valence shells of atoms, have found extensive application in calculations for alkenes. The use in these methods of the null differential overlap (NDO) approximation makes it possible to neglect all three- and four-centre two-electron integrals as well as most of the two-centre integrals encountered in SCF equations, which significantly accelerates the computational procedure. Such reduction in the accuracy of the treatment of the problem is compensated by the introduction of a series of empirical parameters for each type of atoms, the numerical values of which are calibrated against the experimental characteristics of the compounds, such as dipole moments, heats of formation, and ionisation energies.

The earliest semiempirical methods employing the NDO approximation, namely CNDO, INDO, and NDDO, were developed by Pople and co-workers.[24] In the simplest of these, the CNDO (complete neglect of differential overlap) method, all the two-electron integrals in which different atomic orbitals are encountered on a single centre are rejected. The INDO method (incomplete neglect of differential overlap) has an additional feature involving allowance for the exchange integrals between the atomic orbitals of the same atom. The most complete allowance for two-electron integrals is achieved in the NDDO method (neglect of diatomic differential overlap). There exist versions of these methods in spectroscopic parametrisation which are designed to reproduce the electronic absorption spectra (CNDO/S,[35] INDO/S [36]) or photoelectron spectra (SPINDO [25]). Subsequently Dewar proposed a modified version of the INDO method, namely MINDO/3,[26] in which one-centre repulsion integrals are not evaluated analytically (as in the initial INDO version) but are regarded as parameters. The MINDO/3 method has come to be widely used in the calculation of molecular geometries. However, it has been noted that the method greatly underestimates the repulsion of lone pairs. Subsequently, Dewar developed on the basis of the NDDO approximation the improved MNDO method,[27] which makes it possible to avoid a series of systematic errors of the MINDO/3 method and which yields more accurate values of the geometrical parameters, heats of formation, and ionisation energies of molecules. One of the important advantages of the MNDO method over MINDO/3 is that the former involves only the parameters of individual atoms, while the latter contains also the parameters of pair combinations of atoms (in recent years, Dewar also developed the AM1 (*Austun Model* 1) method,[28] which is based, like the MNDO method, on the NDDO approximation and which eliminates the inability of the MNDO and MINDO/3 methods to reproduce the properties of hydrogen bonds.

The simplest semiempirical valence approximation method, in which the interelectron repulsion is fully neglected, is the extended Hückel method (EHM),[29] which was used in earlier studies on alkenes[5,10,46] and was subsequently displaced by improved methods. A version of the NDO approximation, which takes into account only π electrons and which is applicable only in the case of systems with conjugated bonds, is used in the Pariser–Parr–Pople (PPP) method.[30]

In contrast to non-empirical methods, in semiempirical methods the problem of correlation energy has been partially solved as a result of the optimisation of parameters on the basis of experimental data. Therefore in many cases methods such as MINDO/3, MNDO, and AM1 yield more reliable results than non-empirical calculations even when extended basis sets are used in the latter. Nevertheless the MNDO/C method,[31] where correlation corrections are evaluated (and the parametrisation takes into account such corrections), is used in certain problems. When account is taken of correlation in semiempirical methods with the aid of configuration interaction, the relative values of the calculated energies in a series of similar compounds and not their absolute values are of interest.

Semiempirical methods require much less computer time than non-empirical methods and are therefore widely used in the study of alkenes having fairly complex structures.

In non-empirical calculations, the geometry is usually optimised in terms of the STO-3G basis set, whilst in semiempirical calculations different methods can be used for this purpose. The procedure for the optimisation of the geometry of alkenes is sometimes carried out by methods of molecular mechanics (see, for example, Werstiuk and Timmins[32]). The standard values of bond lengths and bond angles are also frequently used to specify the geometries of large molecules.[22,33]

3. Koopmans' theorem

In the case of molecules with closed shells, where each molecular orbital in the one-determinant wave function is occupied by two electrons, the molecular orbital theory yields a simple method for the calculation of the ionisation energy (IE). According to Koopmans' theorem,[34] the ionisation energy is equal to the energy ε_i of the corresponding occupied molecular orbital with the sign reversed ($\varepsilon_i < 0$):

$$IE_i = E_{ion} - E_{mol} = -\varepsilon_i. \quad (1)$$

Koopmans' theorem was obtained subject to the condition that the molecular ion formed on ionisation has the same geometrical parameters as the initial molecule. Eqn. (1) is therefore used to estimate the vertical ionisation energies and is inapplicable to adiabatic ionisation energies. Furthermore, in the derivation of Koopmans' theorem, it was assumed that during the removal of an electron the molecular orbitals remain unaltered (the "frozen orbitals" approximation), i.e. that the electron shell of the molecular ion is described by the same orbitals as that of the initial molecule. Thus Eqn. (1) does not take into account the effect of the reorganisation (relaxation) of the electron shell of the molecular ion, which reduces the energy of the ion by $-\Delta E_{reorg}$ ($\Delta E_{reorg} > 0$).

Since the molecular orbital method does not take into account the electronic correlation effects, in Eqn. (1) account must be taken also of the correlation energy of both the molecule and the ion, the correlation correction reducing the energy of the molecule to a greater extent than that of the ion, which contains one electron less. Thus the difference between the correlation energies of the ion and the molecule ΔE_{cor} is positive. When account is taken of both corrections (ΔE_{reorg} and ΔE_{cor}), Eqn. (1) becomes

$$IE_i = -\varepsilon_i - \Delta E_{reorg} + \Delta E_{cor}. \quad (2)$$

Evidently the corrections taken into account enter Eqn. (2) with opposite signs. In the case of the ionisation of valence electrons, ΔE_{reorg} and ΔE_{cor} are similar in absolute magnitude and therefore partly cancel out, which justifies the application of Koopmans' theorem to valence electrons. In the case of the ionisation of inner

electrons, ΔE_{reorg} can exceed ΔE_{cor} by a factor amounting to several tens and in this case the Koopmans' theorem is inapplicable.

Attempts have been made in recent years to improve the accuracy of the estimation of the ionisation energies within the framework of Koopmans' theorem. Thus an approach has been developed[37] to take into account the correlation correction to the orbital energies of the molecule based on the use of natural molecular orbitals, which are obtained on diagonalisation of the density matrix. The applicability of this approach, which the authors called the extended Koopmans' method, has been demonstrated in the calculation of the ionisation energies for a series of atoms[38] and the accuracy of the extended Koopmans' method has been analysed.[39] However, this method has not so far found applications in calculations for organic molecules.

The approximations used in the derivation of Koopmans' theorem impose fundamental limitations on its applicability. Firstly, Eqn. (1) is valid only for molecules with closed electron shells where there are no unpaired electrons. In the case of open shells, where the ground state of the molecule has a radical character (a doublet or triplet state), molecular Coulombic and exchange integrals must be included in Eqns. (1) for the orbitals forming part of the open shell.[40] In alkenes, ground states with an open shell are not encountered. Secondly, Koopmans' theorem is valid only for one-electron ionisation and is inapplicable when the ionisation process is of a many-particle kind. Thirdly, Koopmans' theorem ceases to be applicable if the excited state formed on ionisation of the molecular ion cannot be described in terms of the orbital model of the ionisation and its description requires the mixing of several configurations of identical symmetry within the framework of configuration interaction.[17] Finally, Koopmans' theorem does not hold if there is a vibronic interaction between the states of the molecular ion manifested in the photoelectron spectra, which is observed, for example, in the case of fully deuteriated ethylene,[41] tetrafluorobutatriene,[10] and certain allenes,[11, 13, 42–44] One should also note that, in the SCF X_α method, Koopmans' theorem does not hold because direct comparison of the one-electron energies obtained in this method with photoelectron spectroscopic data lacks significance.[45]

The wide scale employment of Koopmans' theorem, despite its approximate nature, can be explained by its evident advantage: within the framework of one SCF calculation for the molecule, all the ionisation energies are obtained at once. At the same time, studies may be encountered where the ionisation energies of alkenes have been calculated as differences between the total energies of the ground state of the molecule and the radical cation states, for each of which its own SCF calculation is performed.[21] The geometry of the ground state of the molecule is then retained for the calculated states of the cation. This method of calculation of ionisation energies, called the ΔSCF method, includes, in contrast to Koopmans' theorem, allowance for the reorganisation energy of the electron shell of the cation. However, it has been noted that convergence of the iterative SCF procedure cannot be achieved for all the states of the cation considered.[21]

The agreement between the ionisation energies obtained within the framework of Koopmans' theory and experimental data depends on the chosen method of calculation. The difference between IE_{exp} and IE_{theor} can vary in different calculations from a few to several tens of electron-volts. In some investigations,[6,11] the results of calculations of ionisation energies by different methods have been compared and it has been noted that the greatest differences between the calculated and experimental ionisation energies are observed when the minimal STO-3G basis set and the semiempirical CNDO/2 methods are used. Linear relations between the experimental ionisation energies and the ionisation energies calculated by the Koopmans' theorem have been considered in a number of studies:[20,47,48]

$$IE_{exp} = K \times IE_{calc} + a, \quad (3)$$

and the correlation coefficients K for these relations have been determined. In comparing the results of the calculation with experiment, some workers[17,49] shift the spectrum of the calculated IE_{calc} in such a way that the ionisation energy of the HOMO agrees with the first ionisation energy.

III. Results of quantum-chemical calculations of the electronic structures and ionisation energies of alkenes

The simplest alkenes, ethylene and its derivatives with different substituents at the double bond, will be considered initially, then the homologues of the polyene series with different numbers of double bonds, and finally cumulenes of different structure.

1. Ethylenes

The electronic structure of the ethylene molecule has been studied in fair detail both experimentally and theoretically and the results of these investigations have been included in earlier reviews and monographs.[1,2] We shall therefore refer only to a study[50] in which the most complete and accurate non-empirical calculations have been carried out for the ethylene molecule and its cation taking into account the correlation corrections and the reorganisation energy of the electron shell. The calculation was performed using an extended two-exponent basis set supplemented by polarisation d functions and Rydberg s and p functions of carbon as well as diffuse d functions centred on the midpoint of the C–C bond (altogether 52 basis functions). The correlation energy of the ground state of the molecule was taken into account using the formalism of the cluster expansion of the wave function with subdivision in terms of symmetry. The ionised states of ethylene were calculated in terms of the configuration interaction approximation taking into account doubly, triply, and quadruply excited configurations. The vertical ionisation energies, calculated as differences between the energies of the cation and the molecule, were evaluated for the experimental geometry of ethylene in the ground state. The difference between the calculated and experimental ionisation energies does not exceed 0.3 eV and the calculated intensities of the bands in the photoelectron spectrum also agree well with experimental data. The study of high-energy ionised states of ethylene revealed the presence of a large number of low-intensity satellite peaks in the range 23–33.5 eV, the majority of which correspond to ionisation processes accompanied by excitation from the σ and π bonding molecular orbitals with $1b_{3u}$ symmetry to the antibonding π molecular orbital $2b_{2g}$. The results obtained by earlier non-empirical calculations for ethylene, carried out taking into account the electronic correlation, were also compiled in the above study.[50]

Among ethylene derivatives, fluoroethylenes have been studied in greatest detail.[51–53] According to ideas established at the present time, the influence of fluorine on the electronic properties of olefins can be explained by the inductive and mesomeric effects. The inductive effect is associated with the greater electronegativity of the fluorine atoms and consists in the strong polarisation of the σ skeleton of the olefin. The mesomeric effect reduces to the repulsive

interaction of the lone pair of fluorine with the π system arising as a result of $p-\pi$ conjugation. The competing influence of these two effects is manifested, in particular, by the fact that substitution by fluorine of one or several hydrogen atoms located in the nodal plane of the π system of the alkene does not lead to a significant shift of the ionisation energies of the π orbitals but does induce an appreciable shift (up to 4 eV) of the ionisation energies of the σ orbitals. This phenomenon, which has been called the perfluoro-effect, can be explained by the fact that the stabilisation of both σ and π orbitals by the inductive effect of fluorine is compensated in the case of π orbitals by the destabilising mesomeric effect.

The results of non-empirical and semiempirical calculations for fluoroethylene published up to 1986 have been discussed critically in detail in a monograph[52] and we shall therefore confine ourselves to listing the studies of this period, concentrating attention on later investigations.

Attempts at the interpretation of the photoelectron spectra of fluoroethylenes with the aid of non-empirical methods have been undertaken.[14,18,20,54] For this purpose, calculations have been performed in terms of a two-exponent basis set for monofluoro-ethylene[18] as well as tetrafluoroethylene without[20] and with[54] optimisation of the geometry. Calculations have also been performed for monofluoroethylene using the STO-3G and 4-31G basis sets.[14] The ionisation energies of fluoroethylenes have been calculated by semiempirical SCF methods in a number of studies.[19,49,55,56] The first ionisation energies have been calculated[19] by the PPP method for mono-, di-, and tri-fluoroethylenes, while for tetrafluoroethylene calculation by the CNDO/S method has been carried out.[49] The ionisation energies of all the fluoroethylenes have been calculated in terms of the CNDO and INDO approximations[55,56] and the CNDO/2 method has also been used in a study[57] where it was noted that this procedure yields a satisfactory agreement with experiment only for the first two ionisation energies of fluoroethylenes.

The most complete non-empirical calculation for the entire series of fluoroethylenes has been performed in a study[21] where a two-component basis set was used and a complete optimisation of the molecular geometry was carried out. The vertical ionisation energies have been determined in two ways—within the framework of Koopmans' theorem and by the SCF method, i.e. as the difference between the energies of the molecule and the cation adjusted for self-consistency. In the latter case, a separate SCF calculation was performed for the ground and each of the excited states of the cation (with retention of the molecular geometry) and thus account was taken of the reorganisation energy of the electron shell. The ionisation energies obtained by means of Koopmans' theorem are found to be higher and those calculated by the SCF method are lower than the corresponding experimental values. The final ionisation energies were therefore determined as arithmetical means of the above two theoretical values, whereby a better agreement with experiment was achieved. The bands in the photoelectron spectra of fluoroethylenes were reliably assigned[21] on the basis of the calculated results as well as the data obtained in a more detailed investigation of these compounds by photoelectron spectroscopy.[57]

The first band in the photoelectron spectra of fluoroethylene arises, according to both calculated and experimental data, as a result of the removal of an electron from the HOMO, which is a π(C=C) orbital with an antibonding contribution by fluorine atoms. In monofluoroethylene, IE_2 refers to the highest occupied σ MO, which is antibonding for the C–C and C–F bonds and bonding for the C–H bonds, while IE_3 refers to the bonding σ MO localised on the C–C and C–H bonds. This assignment agrees with the conclusions drawn from the analysis of the photoelectron spectrum of this compound.[57] According to calculated data, none of the molecular orbitals in $CHF=CH_2$ has the character of a pure lone electron pair of fluorine.

In 1,1-difluoroethylene, IE_2 corresponds to the bonding σ MO localised on C–H bonds. It was concluded that the third band, whose assignment gave rise to difficulties in early studies, arises from two molecular orbitals: the bonding σ(C–C) orbital a_1 and the orbital b_2, which can be regarded as a combination of the lone pairs of fluorine atoms. On the basis of calculated data, the fourth band was assigned to the π MO a_2, which represents the antibonding combination of p_π orbitals of fluorine atoms. The region of the fifth band includes two ionisation transitions, one of which corresponds to the σ MO a_1, which is antibonding for the C–C bond and bonding for the C–F and C–H bonds, while the second corresponds to the bonding π MO with a contribution by fluorine atoms.

The *cis*- and *trans*-isomers of 1,2-difluoroethylene are characterised by a close similarity of the photoelectron spectra (the ionisation energies obtained from these spectra agree within the limits of experimental error, except for the IE_3, which differ by 0.2 eV). Only the vibrational structure of the second band exhibits characteristic differences. As postulated by Cell and Kupperman,[57] it is formed in both isomers by two molecular orbitals. However, Heaton and El-Talbi[21] concluded that, whereas this band does indeed correspond to two σ MO a_1 and b_2 in the spectrum of the *cis*-isomer, in that of the *trans*-isomer it corresponds to only one σ MO a_g. With the aid of the analysis of the bond populations, which reveals the bonding or antibonding character of these molecular orbitals, it was then possible to account for the differences in the vibrational structure of the second band in the spectra of the isomers. According to calculated data, IE_2 and IE_3 correspond in both isomers to two σ MO involving respectively antibonding contributions by the C–F and C–C bonds. IE_4 in the *cis*-isomer and IE_5 in the *trans*-isomer correspond to the antibonding π(C=C) orbital with a bonding contribution from fluorine atoms, while IE_4 in the *trans*-isomer and IE_5 in the *cis*-isomer correspond to the σ MO, which is bonding for the C–F and C–H bonds and antibonding for the C–C bond; IE_6 corresponds in both isomers to the bonding π MO. As in the case of monofluoroethylene, none of the molecular orbitals of 1,2-difluoroethylene can be rigorously assigned to the lone pair of fluorine.

In the case of trifluoroethylene, the Koopmans' theorem and the ΔSCF method lead to different orbital assignments of the bands in the photoelectron spectrum (the ionisation energies obtained by the ΔSCF method agree better with experimental data). The nature of the bands is therefore not discussed and only the sequence of the molecular orbital energies is quoted, according to which IE_2 and IE_4 correspond to two σ MO—bonding in the case of IE_4 and with an antibonding contribution due to the C–F bonds in the case of IE_2. IE_3 corresponds to an antibonding combination of the lone pairs of the fluorine atoms of the CF_2 fragment; IE_5 and IE_6 correspond to π MO with main contributions by fluorine atoms.

In the photoelectron spectrum of tetrafluoroethylene, the experimental assignment is available only for the first band,[57] while the interpretation of the nature of the remaining bands without invoking calculations is made difficult by the presence of a large number of close ionisation transitions. For $CF_2=CF_2$, Koopmans' theorem and the ΔSCF calculation yield identical orbital assignments of the ionisation energies. According to these data, IE_2 corresponds

to the σ MO a_g with an antibonding contribution by the C–F bond and IE_3 and IE_4 have been assigned respectively to the σ MO b_{3g} and b_{2u}, which can be regarded, with some approximation, as a combination of the lone pairs of the fluorine atoms; IE_5 and IE_6 are associated with π MO consisting of the p_π orbitals of fluorine.

A semiempirical calculation for fluoroethylenes (except $CF_2=CH_2$) has been carried out in a study,[58] where the MRINDO/S method was used. This is a modified version of the INDO/S approximation, in which the one-centre exchange integrals are taken into account only in the valence atomic orbitals and are rejected for the Rydberg 3*s* and 3*p* atomic orbitals. The sequence of the π and σ MO obtained is the same as in the study of Heaton and El-Talbi.[21] The difference between the calculated and experimental first ionisation energies is 0.5–1.1 eV. The remaining ionisation energies were not discussed.

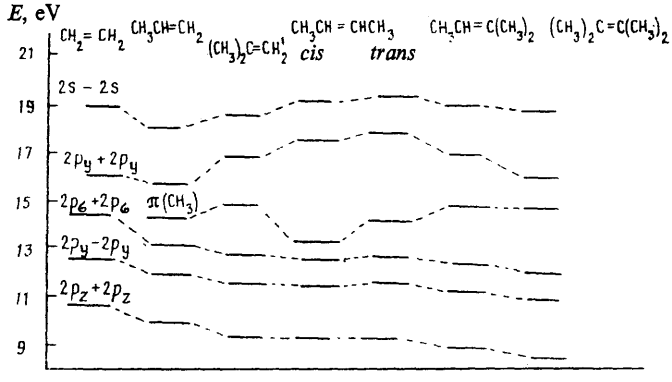


Figure 1. Correlation energy level diagram for the molecular orbitals of alkenes.

A theoretical study of the photoelectron spectra of chlorofluoroethylenes was undertaken in a study[17] where the 6-31G basis set, including the 4*s* and 4*p* atomic orbitals of Cl, the 3*s* and 3*p* atomic orbitals of C, and the 2*s* atomic orbital of H, was used in the non-empirical calculations for $CH_2=CFCl$, $CF_2=CHCl$, $CF_2=CFCl$, and $CF_2=CCl_2$. The experimental or optimised molecular geometry was employed. The ionisation energies were determined by means of Koopmans' theorem, the scale of the calculated ionisation energies being displaced for each molecule in such a way that the theoretical and experimental ionisation energies coincide. The ionisation energies thus obtained agree well with experiment. The ionisation energies of all the molecules for which calculations were made correspond to the highest occupied π MO having an antibonding contribution from the p_π atomic orbitals of chlorine atoms (the involvement of Cl in the formation of the HOMO has been confirmed by the analysis of the vibrational structure of the first band). IE_2 corresponds to the highest occupied σ MO localised on the C–C and CCl bonds, while IE_3 corresponds to a combination of the p_π atomic orbitals of chlorine atoms. An orbital assignment was given also for the remaining ionisation energies, calculated up to 22 eV. It was concluded that the ionisation of the inner electrons of haloethylenes in the range 20–75 eV cannot be described in terms of the orbital model.

The photoelectron spectra of mono-, di-, tri-, and tetra-methylethylenes have been compared in a study[7] where a quantum-chemical calculation by the method of group orbitals was carried out in order to assign the ionisation energies. The results of the calculation are presented in the form of a correlation energy level diagram for the molecular orbitals (Fig. 1), from which it is seen that the introduction of one methyl substituent into ethylene destabilises the ethylene molecular orbitals, which is associated with the transfer of electron density from the CH_3 group to these molecular orbitals.

A further increase in the number of substituting CH_3 groups intensifies this destabilising effect for the first three ionisation energies. In terms of the approximation of group orbitals, the fourth ionisation energy was assigned in all the methylethylenes to the π level of the CH_3 group. The nature of the change in the fifth and sixth ionisation energies under the influence of substitution was found to be more complex than for the first three ionisation energies.

The effect of the cyano-group on the first ionisation energy in ethylene has been examined in a study[46] where the Hückel approximation was used for the analysis of the nature of the HOMO of mono-, di-, tri-, and tetra-cyanoethylenes. The successive increase in the number of CN groups (*n*) induces an additive increase in the first ionisation energy, which is described satisfactorily by the relation

$$IE = 10.52 + 0.32n.$$

The effect of the cyano-group on IE_1 can be explained by the joint manifestation of both the inductive effect, where this group functions as an electron acceptor, and the conjugation effect, which has been shown to arise as a result of the mixing of the HOMO of ethylene with the π LUMO of the C≡N group. The mechanism of the joint effect of the methyl substituent and the cyano-group on IE_1, manifested by the fact that β-methylation of monocyanoethylene (acrylonitrile) causes a more marked decrease in IE_1 (by 0.69 eV) than α-methylation (0.55 eV), has also been explained. The point is that the orbitals of the CH_3 group interact more strongly with the π system in the β-position, since the HOMO coefficient is greater for the β-carbon atom than for the α-carbon atom. On the other hand, the effect of the introduction of the second cyano-group is greater in the α-position (0.46 eV) than in the β-position (0.23 eV), which can be explained by the smaller sensitivity of the inductive effect (compared with hyperconjugation) to the value of the HOMO coefficient at the substituted carbon atom. The destabilising effect of the acetyl group on the position of the HOMO has been demonstrated in relation to crotononitrile.

The influence of the mesomeric and inductive effects of substituents on the first ionisation energy of ethylene has been investigated[59] in relation to mono- and 1,2-di-substituted ethylenes with π-donor substituents [F, Cl, Br, I, OCH_3, SCH_3, $Si(CH_3)_2$] and monosubstituted ethylenes with π-acceptor substituents (CHO, $COCH_3$, CN, NO_2). The approximation of group (fragment) orbitals (LCFO-MO), in which the HOMO of the substituted ethylenes is represented by a linear combination of the HOMO of ethylene and either the π or *p* orbital of the substituent X, was used:

$$\Psi_{CH_2=CHX} = a_1\Psi_{CH_2=CH_2} + a_2\Psi_X.$$

The coefficients a_1 and a_2 characterise the contributions of the π MO of ethylene and the π MO of the substituent to the combined orbital. In this representation, the mesomeric effect (i.e. π conjugation) of the substituent is taken into account automatically. The inductive effect of the substituent X on the ionisation energy is

treated[59] as a result of the electrostatic interaction of the positive charge, delocalised over the π-system and arising when an electron is removed from the molecule, with the dipole of the C–X fragment. The vertical ionisation energy of the compound HX was used as the parameter characterising the inductive effect of the substituent X. The ionisation energies calculated in this way for mono- and di-substituted ethylenes differ from the experimental values by not more than 0.2 eV. It was concluded that the resonance effect of the nitro-group may be neglected because of the considerable difference between the HOMO and LUMO energies of this group and the HOMO energy of ethylene.

The influence of the σ–π conjugation, the inductive effect, and the $p_\pi - d_\pi$ interaction on the first ionisation energy in monosubstituted ethylenes with the organosilicon substituents SiH_3, $SiH(CH_3)_2$, $Si(CH_3)_3$, CH_2SiH_3, and $CH_2Si(CH_3)_3$ has been studied.[60] The ionisation energies were calculated in accordance with the Koopmans' theorem by the semiempirical CNDO/2 method using *sp* and *spd* basis sets. The contribution of the σ–π conjugation ($\delta IE_{\sigma,\pi}$) to the change in the ionisation energy of ethylene under the influence of the substituent (ΔEI) was estimated on the basis of the perturbation theory and the contribution of the $p_\pi - d_\pi$ interaction ($\delta IE_{p,d}$) was found from the difference between the HOMO energies of the substituted molecule calculated in terms of the *spd* and *sp* basis sets (in the calculation using the *sp* basis set, the influence of the *d* orbitals is not taken into account). The contribution of the inductive effect was determined from the residual, having subtracted $\delta IE_{\sigma,\pi}$ and $\delta IE_{p,d}$ from ΔIE. It was concluded that in the majority of ethylene derivatives σ–π conjugation predominates over other effects. The extent of the $p_\pi - d_\pi$ interaction diminishes in the sequence $SiH_3 > SiH(CH_3)_2 > Si(CH_3)_3$, i.e. with increase in the number of CH_3 groups at the silicon atom. The extent of the σ–π conjugation diminishes in the sequence $C(CH_3)_3 > Si(CH_3)_2 > CH_3 > SiH_3$, while the inductive effect diminishes in the sequence $Si(CH_3)_3 > SiH_3 > CH_3 > C(CH_3)_3$, which agrees with the concept of the electronegativity of the substituents.

A number of theoretical studies have been devoted to ethylenes with cyclic substituents.[33,61–64] The influence of the substituents F, Cl, CH_3, and OCH_3 in the *meta*- and *ortho*-positions on the ionisation energies of styrene has been studied[61] with the aid of photoelectron spectra and calculations by the CNDO/2 method. The calculations were performed using the standard bond lengths and bond angles. The photoelectron spectra of styrene and its derivatives exhibit in the range 8–11 eV three well resolved bands, which correspond, according to the calculated data, to the π MO arising as a result of the interaction of one of the two degenerate benzene molecular orbitals of the e_{1g} type and the π MO of the vinyl group (π_1 and π_3 MO) and to the second degenerate molecular orbital of benzene e_{1g}, which does not interact with the vinyl group (π_2 MO). The influence of the inductive effect of the substituents has been investigated on the basis of the change in IE_2 corresponding to the ionisation of π_2 MO, which is not involved in conjugation with the π-system of the vinyl group; the maximum inductive effect is manifested by the F atom; IE_1 and IE_3 are acted upon by both the inductive and resonance effects. The difference $IE_3 - IE_1$ varies about 1.93 eV, which indicates the similarity of the effects of substituents on the π_1 and π_3 MO. The resonance effect of substituents was estimated from the difference between IE_1 and IE_2. For *para*-substituted styrenes, this difference is greater than for the *meta*-substituted derivatives; the greatest resonance effect is observed for the OCH_3 substituent.

The effect of Cl, NH_2, and NO_2 on the ionisation energies of *trans*-2,2-disubstituted stilbenes has been studied.[62] Derivatives containing identical substituents in the *ortho*-positions of the phenyl fragment were examined. The presence of the NH_2 group leads to an appreciable decrease in all the ionisation energies of stilbene (by 1.0 eV for IE_1), while the presence of the NO_2 group entails an appreciable increase in all the ionisation energies (by 0.9 eV for IE_1), which can be explained by the strong inductive effect of these substituents. The presence of Cl leads to some decrease in the ionisation energies of stilbene (by 0.2 eV for IE_1). The assignment of the photoelectron spectra based on calculations of ionisation energies by the Hückel method made it possible, in particular, to identify bands referring to the ionisation of the lone pairs of the chlorine atoms in 2,2-dichlorostilbene (11.19 and 11.53 eV) and in 2-amino-2-chlorostilbene (11.03 and 11.52 eV).

The INDO/S semiempirical method has been used[33] to interpret the photoelectron spectra of stilbene, α-cyanostilbene, 2-styryl-thiophene, and α-cyanostyrylthiophene. An idealised geometry was specified for the phenyl fragment and the experimental geometry was used for the thienyl fragment. Calculation showed that the first five ionisation energies of these compounds are associated with molecular orbitals consisting of a combination of the π orbital $1e_{1g}$ of benzene, the π orbitals $1a_2$ and $2b_1$ of thiophene, and the π MO of ethylene with a perturbing effect of the cyano-group. The doubly degenerate π MO of the C≡N group have energies which are too low and they do not enter into this combination, so that the influence of the cyano-group reduces to the inductive and steric effects. The first band in the photoelectron spectra of the cyano-derivatives and 2-styrylthiophene is generated on ionisation of the delocalised π MO, which is an antibonding combination of the b_1 MO of benzene and π MO of ethylene. The second band corresponds to three molecular orbitals localised on benzene rings. The third band corresponds to the π MO of the ethylene bond. The calculation reproduces satisfactorily the difference between IE_1 and IE_2.

3-Methyl-3-vinylcyclopropene (I) as well as its α-methyl and β-methyl derivatives [compounds (II) and (III)] have been investigated[63] with the aid of the semiempirical AM1 method. The calculation was performed with complete optimisation of the geometrical parameters for different values of the dihedral angle θ between the planes of the ethylene and cyclopropene fragments (θ = 0°, 60°, 90°, 120°, and 128°). One minimum was observed on the potential curve as a function of θ for compound (III) and two minima were observed for compounds (I) and (II). According to the calculated data, the ionisation energy of compound (I) corresponds to the ionisation of the cyclopropene π(C=C) MO whereas the ionisation energies of compounds (II) and (III) correspond to the ionisation of the ethylene bond. The presence of the methyl substituent at the ethylene bond lowers IE_1, the effect of one CH_3 group introduced in the α-position proving to be stronger than the effect on IE_1 of two CH_3 groups introduced in the β-position.

2. Polyenes

Numerous theoretical studies have been devoted to the electronic structure and the photoelectron spectra of polyenes. Some of them dealt with individual compounds—butadiene,[65,66] hexatriene,[66] and octatetraene,[12] whilst others were concerned with the general characteristics of the polyene series.[22,67] The influence of substituents has been traced in relation to monomethyl- and polymethylbutadienes[8,32,67] and decapentaene with different substituents at the C(5) and C(6) atoms.[68]

According to the results of a non-empirical calculation in terms of a grouped two-exponent basis set, the first band in the photoelectron spectrum of butadiene corresponds to the π HOMO b_g, whilst the second band corresponds to the second occupied π MO a_u.[66] The same result has been obtained in terms of a two exponent basis set supplemented by two diffuse *p* functions of carbon.[65] In both calculations, the first two ionisation energies agree with the experimental values to within 0.05–0.2 eV. The same assignment of the bands is given by the semiempirical SPINDO method.[67] The first three ionisation energies of hexatriene have also been calculated[66] (differing from the experimental values by −0.1 eV) and it was concluded that the first three bands in the photoelectron spectrum of this compound refer to π-type molecular orbitals, but, according to the calculation by the SPINDO method, the third band refers to σ-type molecular orbitals.[67] A comparative analysis of the orbital structures of the *cis*- and *trans*-isomers of hexatriene has been carried out (using the SPINDO method). The geometry of the *trans*-isomer (with C_{2h} symmetry) was specified on the basis of electron diffraction data, while in the *cis*-isomer (C_{2v}) the same bond lengths were used as in the *trans*-isomer. A satisfactory agreement with experiment was obtained for all the nine calculated ionisation energies. In the *cis*–*trans* transition, the energies of all three occupied π MO hardly change (like the experimental ionisation energies). A different picture is observed for this transition in the three highest occupied σ MO $9b_2$, $10a_1$, and $9a_1$, the energies of two of which ($10a_1$ and $9a_1$) increase, whilst that of the third ($9b_2$) falls, which leads to an appreciable narrowing of the energy range in which these orbitals are located in the *trans*-isomer. This result of the calculation made it possible to explain the differences in the shape of the photoelectron spectra of the hexatriene isomers in the region of 12 eV, where a broad gap is observed between the bands in the case of the *cis*-isomer (the σ MO lie within a wide range), being absent from the spectrum of the *trans*-isomer (the σ MO lie within a narrow range). It was concluded that the shift of the energies of the σ MO in hexatriene isomers is caused by the interaction through space between the C–H and C–C σ-bonds, which stabilises the orbitals with the a_1 symmetry and destabilises b_2 orbitals in the *cis*-isomer. Calculations by the non-empirical method using the minimal STO-3G basis set and by the SPINDO method led to the conclusion that the first three ionisation energies in octatetraene refer to π-type molecular orbitals.[12]

Calculations have been carried out for the polyenes $C_{2n}H_{2n+2}$ with $n = 1-6$ by the discrete-variational X_α method using a two-exponent basis set and a basis set comprising Hartree–Fock atomic orbitals.[22] The experimental geometry was used for the first members of the polyene series ($n = 1-3$), while for the remaining molecules the idealised geometry was employed. The first ionisation energies of butadiene, hexatriene, and octatriene, obtained in terms of a two-exponent basis set, differ from the experimental values by not more than 0.2 eV (photoelectron spectroscopic data are lacking for $C_{10}H_{12}$ and $C_{12}H_{14}$). The deviations of the remaining ionisation energies from the experimental values are on average ~0.5 eV for the two-exponent basis set and ~1 eV for the Hartree–Fock basis set. According to the calculations, the highest σ-type level (a_u or b_g) in all polyenes is close to the π-type level (a_u or b_u). It was suggested that for long polyene chains one may expect either a slight overlap of the σ and π zones in the photoelectron spectrum or these zones can be separated by a small gap amounting to several tens of electron-volts.[22,69]

For the theoretical study of the effect of methyl substituents on the π bands in the photoelectron spectra of polyenes, Beez et al.[67] used a model in which the π MO of the polyene is represented by a linear combination of the bonding orbitals (LCBO) of individual π-bonds (it was shown that the mixing of the bonding and antibonding orbitals of π-bonds leads to incorrect results in the calculation of ionisation energy), while the effect of the methyl substituent on the π-system of the polyene is considered as an inductive and hyperconjugation perturbation within the framework of the Hückel method. In this procedure, the CH_3 group is described by two degenerate pseudo-π orbitals made up of the σ orbitals of the C–H bonds. This simple and clear model makes it possible to reproduce the π-orbital ionisation energies with a satisfactory accuracy (to within not more than 0.1 eV for hexatriene, for example) and leads naturally to the sums rule, according to which the sum of the changes in all the π-orbital ionisation energies ($\sum_i \delta IE_i^\pi$) in the polyene under the influence of the CH_3 group is constant for the entire polyene series and is equal to δIE for ethylene (0.78 eV). The validity of the sum rule has been demonstrated in relation to monomethyl-substituted butadiene and hexatriene. Comparison of the experimental ionisation energies and the ionisation energies calculated within the framework of the LCBO model for mono-, di-, and tetra-methylbutadienes showed that the sums rule holds, provided that the substituting CH_3 groups are attached to different double bonds, i.e. the additivity of the effects of the CH_3 groups on the π ionisation energies holds in this case. On the other hand, if the substitution takes place at the same double bond, then the specific quantity $\sum_i \delta IE_i^\pi$, recalculated per CH_3 group, diminishes with increase in the degree of substitution—for example, we have the series $CH_2=CHCH_3$ (0.78 eV), $CH_3CH=CHCH_3$ (0.69 eV), $(CH_3)_2C=CH_2$ (0.64 eV), $(CH_3)_2C=CHCH_3$ (0.61 eV), and $(CH_3)_2C=C(CH_3)_2$ (0.55 eV). It has been shown that the terminal methyl substituents in the polyene do not alter the gap between IE_1 and IE_2. Substitution by CH_3 groups in the central positions leads to the mutual approach of IE_1 and IE_2, which can be explained, as demonstrated in relation to butadiene, by the interaction through space between the pseudo-π orbitals of the CH_3 group in the 2- or 3-position with the π orbital of the vicinal (unsubstituted) double bond. Allowance for this interaction in the LCBO model shows that it stabilises the HOMO in the polyene and destabilises the next occupied π MO. The same conclusion was reached in a study[8] where the investigation of the effect of methyl substituents was extended to non-planar cases when there is rotation about a single C–C bond in the polyene. Tetramethylbutadiene, containing one methyl group at each carbon atom, was investigated. This structure exists in the form of three isomers, namely (*E*, *E*), (*E*, *Z*), and (*Z*, *Z*), and can be regarded as two identical fragments interacting via the C(2)–C(3) single bond and rotated relative to this bond by an angle θ. Then, in terms of the first approximation of the perturbation theory, the gap $\Delta IE = IE_2 - IE_1$ depends on θ in accordance with the formula

$$\Delta IE = \Delta IE_0 - \cos\theta, \qquad (4)$$

where ΔIE_0 is the value of ΔIE for the planar case with θ = 0. This dependence of ΔIE on θ has been confirmed by a non-empirical calculation in terms of the minimal STO-3GF basis set in relation to unsubstituted butadiene. Using the ionisation energies found from the photoelectron spectra and Eqn. (4), the authors[8] obtained estimates of θ for the isomers; 0° ± 30° for (*E*, *E*), 80° ± 15° for (*E*, *Z*), and 80° ± 105° for (*Z*, *Z*). It has been shown[32] by calculations using the molecular mechanics method and the

semiempirical AM_1 method that the (*Z*)-conformer of the 1,3-disubstituted butadiene (2-methylpenta-1,3-diene) exists preferentially in the twisted form, while the (*E*)-conformer exists in a planar form. This made it possible to explain the differences between the photoelectron spectra of the (*Z*)- and (*E*)-conformers. It was noted that the AM_1 method overestimates the steric interaction between the CH_3 groups in the 1- and 3-positions and underestimates the stabilisation of the π-system due to the resonance effect.

The influence of electron-donating and electron-accepting substituents on the ionisation energies of polyenes has been studied theoretically[68] in relation to 5,6-disubstituted decapentaenes ($C_{10}H_{10}X_2$). The calculations were performed by the discrete-variational X_α method using a basis set of Hartree–Fock atomic orbitals. The idealised geometry was used for the hydrocarbon skeleton of the molecule. The geometrical parameters for the substituents and the C–X bond were selected on the basis of experimental data or the results of non-empirical calculations. In the unsubstituted polyene $C_{10}H_{12}$, the energies of the valence σ levels lie below those of the set of π levels. The introduction of lithium as a strong σ-donor does not destabilise the σ levels, which fall as a result into the region of the π levels. As a weaker σ-donor, BeH does not lead to the overlap of the σ and π sets of molecular orbitals and the energy IE_1 in the BeH-polyene is almost identical with IE_1 in $C_{10}H_{12}$. The introduction of F as a σ-acceptor lowers IE_1 by only 0.1 eV. The nature of the interaction of the NH_2 group, which is a π-donor, with the π-system of the polyene depends on its rotation relative to the plane of the polyene: the $2p_\pi$ atomic orbital of nitrogen is involved in conjugation with the π-system of $C_{10}H_{12}$ when the NH_2 group is in the plane of the polyene and interacts with the σ-system when the plane of the NH_2 group is perpendicular to that of the polyene. In the former case, the interaction indicated leads, as shown by the calculation, to a decrease in IE_1 by 1.2 eV, while in the latter IE_1 hardly changes. When BH_2, which acts as a π-acceptor, is introduced, IE_1 scarcely changes, provided that BH_2 is located in the plane of the polyene, and diminishes by 0.4 eV if the planes of BH_2 and the polyene are mutually perpendicular.

3. Cumulenes

The simplest representation of the cumulene series is allene $CH_2=C=CH_2$ where there are two mutually perpendicular π-systems between which there is no conjugation; the CH_2 groups are also located in mutually perpendicular planes. The allene molecule belongs to the D_{2d} symmetry group, which has a two-dimensional irreducible representation and gives rise to doubly degenerate molecular orbitals of the *e* type. In particular, in conformity with non-empirical[23,70] and semiempirical[15] calculations, the π HOMO 1*e* and the σ MO 2*e* which follows it are doubly degenerate in allene. The HOMO splits into two molecular orbitals, each of which is localised in one of the $CH_2=C$ fragments and represents an antibonding combination of the π orbital of the C=C bond with the pseudo-π orbital of the CH_2 group.[16] All the other homologues of the cumulene series with an even number of double bonds, for example, pentatetraene $CH_2=C=C=C=CH_2$, the π HOMO of which is likewise doubly degenerate, also belong to the D_{2d} symmetry group.[15] Analysis of the first band in the photoelectron spectra shows that the degeneracy is removed in the allene[23] and pentatetraene[15] radical-cations as a result of geometrical distortions arising in the ionisation of the molecule and reducing its symmetry (the Jahn–Teller effect). For example, the removal of the degeneracy of the HOMO in allene leads to the splitting of the first band in the photoelectron spectrum into two peaks with ionisation energies of 10.0 and 10.6 eV.[23] A simple molecular-orbital model shows that such splitting is a result of a twisting deformation which reduces the symmetry of the allene radical-cation from D_{2d} to D_2.[72] Cumulenes with an odd number of double bonds belong to the D_{2h} symmetry group and contain no molecular orbitals degenerate as regards symmetry. However, in this case ionisation may entail the appearance of a distortion in the molecule, which reduces its symmetry, as indicated, for example, by data obtained as a result of the optimisation of the geometry of the butatriene $CH_2=C=C=CH_2$ radical-cations in terms of the STO-3GF basis set.[75]

When the π-electronic structure of cumulenes is considered, the isolated ethylene-like π orbitals (2*e* in allene and $2b_{3u}$ in butatriene) and butadiene-like four-centre π MO, which are combinations of two ethylene orbitals—bonding ($1b_{2u}$ in butatriene and 2*e* in pentatetraene) and antibonding ($1b_{3g}$ in butatriene and 3*e* in pentatetraene)—are distinguished.[15] In the ethylene–allene–butadiene series, a gradual destabilisation of the isolated π MO (and a decrease in the corresponding ionisation energies) has been observed, which can be accounted for by the destabilising effect of the CH_2 group, which is in the nature of hyperconjugation.[15] This effect is manifested most strongly in butatriene, where the CH_2 groups are located in one plane and both interact with the π MO of the central C=C bond. On passing from butatriene to pentatetraene, where the isolated π MO are no longer encountered, the destabilising effect of the pseudo-π orbitals of the CH_2 group is weakened. In order to interpret the photoelectron spectra of allene, both non-empirical calculations, using the minimal STO-3GF basis set,[13,15] the 4-31GF basis set,[16] and a two-exponent basis set,[5,23] and semiempirical calculations by the SPINDO method,[15] have been resorted to. The most accurate calculation for the allene molecule using the experimental geometry, carried out in terms of a grouped two-exponent basis set with inclusion of polarisation *d* functions of carbon and taking into account the correlation corrections by the method of Green's functions, shows that the first band in the photoelectron spectrum (exhibiting Jahn–Teller splitting) corresponds to the π HOMO 1*e*. The second band (14–16 eV) is generated by the ionisation transition from two σ MO—2*e* and $2b_2$, while the third band corresponds to the σ MO $2a_1$.[23] A similar band assignment was obtained from calculations by the SPINDO method.[15]

Quantum-chemical calculations have shown[10,15,23,73] that the π-system of butatriene consists of two butadiene-like MO $1b_{2u}$ and $1b_{2g}$, the nodal plane of which coincides with the molecular plane, and the MO $2b_{3u}$ located on the central C=C bond in the molecular plane. When an attempt is made to interpret the photoelectron spectrum of butadiene with the aid of the ionisation energies obtained on the basis of Koopmans' theorem even in a very effective non-empirical calculation (two-exponent basis set with polarisation *d* functions as well as allowance for correlation corrections by the method of Green's functions),[23] a difficulty arises. It is associated with the fact that in the range 9–10 eV, where three bands are observed, there are only two ionisation processes, corresponding to the two highest π MO b_{3g} and b_{3u}. It has therefore been postulated that the middle band, with a maximum at 9.6 eV, is a satellite band. In order to elucidate the nature of the satellite band, the vibronic problem has been solved for butatriene with the aid of the formalism of Green's functions.[73] It was established that the band arises as a result of the vibronic interaction between the ground $^2B_{3g}$ state and the first electronically excited $^2B_{3u}$ state of the radical-cation, which are separated by a small gap (~0.7 eV). The intensities, calculated

taking into account the vibronic interaction, made it possible to reproduce closely the form of the first three bands in the photoelectron spectrum of butatriene. For an accurate prediction of the position of the above satellite band, the multiconfiguration SCF method has been used.[10] The geometry of the butatriene molecule was optimised in terms of the STO-3G basis set and the calculation for the molecule and the radical-cation was performed in terms of a grouped exponent basis set with inclusion of all the singly and doubly excited configurations (the excitations were considered only for π MO). It was concluded that non-empirical calculations of different types (SCF) in terms of the STO-3G and 4-31G basis sets, the method of Green's functions, and allowance for configuration interaction lead to the same conclusion, namely that the first three bands in the photoelectron spectrum of butatriene (not counting the satellite band) correspond to the ionisation of the highest π MO—b_{3g}, b_{3u}, and b_{2u} respectively.

As examples of two accumulated π-systems linked by a single bond,[6] 1,2,4,5-hexatetraene $CH_2=C=CH-CH=C=CH_2$ (I) (C_{2h} symmetry) and 1,3,4-pentatriene $CH_2=CH-CH=C=CH_2$ (II) have been investigated. Calculation of the ionisation energies in accordance with Koopmans' theorem with the aid of various semiempirical methods—EHM, CNDO/2, MINDO/3, and SPINDO—leads to the same sequence of the highest occupied π MO, namely $\pi_z - \pi'_z$ (b_g), $\pi_x - \pi'_x$ (a_g), $\pi_x + \pi'_x$ (b_u), and $\pi_z + \pi'_z$ (a_u), which are involved in the generation of the first four bands in the photoelectron spectrum of compound (I). It follows from the experimental ionisation energies that the energy splitting of the bonding and antibonding combinations for the $\pi_z - \pi'_z$ and $\pi_z + \pi'_z$ pair (π_z and π'_z are the orbitals of the allenyl fragments whose nodal plane coincides with the molecular plane) is much greater than for the $\pi_x - \pi'_x$ and $\pi_x + \pi'_x$ pair (π_x and π'_x are the orbitals of the allenyl fragments located in the molecular plane). It was noted that the best agreement between the calculated and experimental ionisation energies is afforded by the SPINDO method. In the photoelectron spectrum of compound (II), the first three bands correspond to the ionisation of the three highest occupied molecular orbitals. The study of the photoelectron spectrum and calculation of the ionisation energies of the 3-methyl derivative of compound (I) showed that the introduction of the CH_3 group has only a slight effect on the π_x type orbitals but causes an appreciable shift of the π_z-type orbitals. The effect of various substituents on the electronic structures and ionisation energies of cumulenes has been studied in a number of investigations.[5,10,11,16,57,74,75] Mono-, di-, tri-, and tetrafluoroallenes have been investigated in a study,[5] where the molecular geometry was optimised in terms of a biexponential basis set with polarisation *d* functions of carbon, which yields a correct description of the C—F bond; the ionisation energies were calculated in terms of the same basis set supplemented by the *d* functions of fluorine and the *p* functions of hydrogen, taking into account the correlation corrections by the method of perturbation theory. The high quality of the calculation is confirmed by the fact that the calculated dipole moments of the molecules reproduce satisfactorily the experimental values (the differences are on average 15%). According to the calculated data, as carbon atoms are substituted by fluorine, the negative charge on the central carbon atom increases, varying from +0.12 in allene to −0.43 in perfluoroallene; this effect is attributed to the π-donor capacity of fluorine. The calculation predicts a gradual increase in the first ionisation energy with increase in the number of substituting fluorine atoms, which agrees with photoelectron spectroscopic data (available only for some fluoroallenes). A large difference between the values of IE_1 (0.5 eV) of the difluoroallene isomers $H_2C=C=CF_2$ and $HFC=C=CHF$ has been noted. The random degeneracy in the latter compound, where the HOMO and the molecular orbital which follows it have the same energies, is striking.

The results of the non-empirical calculation in terms of the 4-31G basis set for 1,1-difluoroallene and tetrafluoroallene have been published.[16] Calculation showed that IE_1 for 1,1-difluoroallene corresponds to the π[C(1)=C(2)] orbital with an antibonding contribution by the electron pair of fluorine, while IE_2 corresponds to the π[C(2)=C(3)] orbital with a hyperconjugation contribution by the σ orbitals of the C—F bonds. The fluorine atom has only a weak effect on the energy of the π[C(1)=C(2)] HOMO, since in this case the stabilising inductive effect of fluorine is compensated by the destabilising resonance effect and lowers markedly the energy of the π[C(2)=C(3)] MO, where there is also a stabilising influence of the inductive effect and of the effect of the hyperconjugation of the CF_2 group.

The non-empirical calculation for perfluorobutatriene, carried out using a two-exponent basis set and the standard geometry of the molecule, may serve as an example of the study of the perfluoro-effect in cumulenes.[10] According to the calculated data, the first three bands in the photoelectron spectrum of this compound correspond to the ionisation of the highest occupied π MO b_{3g}, b_{3u}, and b_{2u}, while the fourth band (whose position and shape are similar to those of the corresponding band in the spectrum of tetrafluoroallene) is due to a linear combination of the unshared pairs of the fluorine atoms. All the fluorine atoms are located in the nodal plane of the HOMO b_{3g} and the orbital b_{2u}, corresponding to IE_3, and for this reason they give rise to only a slight change in the energies of these molecular orbitals compared with unsubstituted butatriene: IE_1 does not change at all, while IE_3 changes by 0.4 eV. A strong stabilising effect of fluorine is observed in the case of the molecular orbital b_{3u}, which lies in the same plane as the fluorine atoms: IE_2, corresponding to this molecular orbital, shifts by 2.6 eV on perfluorination.

Monosubstituted allenes have been investigated by Sinegovskaya et al.[74] (with substituents OAlk, where Alk = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9, and t-C_4H_9) and by Kamphuis et al.[11] with the substituents t-C_4H_9, OCH_3, OC_2H_5, OC_4H_9-t, $N(CH_3)_2$, SCH_3, SC_2H_5, and SC_4H_9-t). Sinegovskaya et al.[74] calculated the ionisation energy of alkyl allenyl ethers by the MNDO method with complete optimisation of the geometry. IE_1 and IE_3 for allenyl methyl ether correspond to a linear combination of the π[C(1)=C(2)] orbitals with the *p* atomic orbitals of ether oxygen (in the case of IE_1, the contribution of the *p* atomic orbitals of oxygen is antibonding, while in the case of IE_3 it is bonding), IE_2 corresponds to the unperturbed π[C(2)=C(3)] orbital, and IE_4 corresponds to the almost pure *n* orbital of oxygen (n_O). It was shown that this sequence of the four highest occupied molecular orbitals in allenyl methyl ether can be readily obtained from the consideration of the Walsh correlation diagram constructed from the two highest molecular orbitals of allene and of the $(CH_3)_2O$ molecule. Successive substitution of CH_3 by C_2H_5, n-C_3H_7, and iso-C_3H_7 in allenyl methyl ether leads to a shift of IE_1 and IE_2 by 0.1—0.3 eV and of IE_3 and IE_4 by 0.3—0.8 eV towards lower values. Calculation shows that, with increase in chain length and in the degree of branching of the alkyl substituent, the efficiency of the mixing of the n_O orbital and the σ_{CC} orbitals of the substituent increases.

It has been established[11] that the effect of bulky electron-donating substituents containing alkyl groups on the photoelectron spectra of allenes is determined not only by electronic effects (inductive,

conjugation, and hyperconjugation effects) but also by conformational effects. Calculations by the MINDO/3 method with complete optimisation of the geometry showed that the radical-cations in the ground state can have a geometry differing markedly from that of the corresponding molecules. For example, in allenes with the $N(CH_3)_2$ and t-C_4H_9 substituents, the C=C=C fragment in the cations has a bent structure. For the radical-cations where the substituting OAlk or SAlk group includes CH_3 and C_2H_5, the *S-cis*-form is preferred, while in the case of OC_4H_9-t and SC_4H_9-t the *S-trans*-form is preferred. The non-planar *gauche*-form, in which there is strong $\sigma-\pi$ mixing, is preferred for the $N(CH_3)_2$ group and the effect of the substituents can no longer be interpreted in terms of separate π and σ interactions.

The influence of the CF_3 group on the ionisation energies in cumulated systems was investigated separately in a study[75] where calculations were performed by the MINDO/3 method for tetrasubstituted allenes with the CF_3, OCH_3, and OC_2H_5 substituents. It was shown that the inductive effect predominates when the CF_3 group is introduced. It is additive and stabilises the HOMO to the extent of 0.5 eV per CF_3 group.

The effect of methylation on the photoelectron spectra of more complex cumulenes was investigated in relation to mono- and dimethyl-derivatives of penta-1,2,4-triene (vinylallene).[47] The CNDO/S method used for the calculation reproduced satisfactorily the dependence of the ionisation energies on the position of the CH_3 group. The methyl group at the terminal atom of the allene fragment affects appreciably the energy of the orbital localised on the terminal allene bond and corresponding to IE_2. The methyl group bound to the central carbon atoms C(3) and C(4) interacts through space with the orbitals of the vicinal C=C bonds. This interaction stabilises the HOMO and destabilises the molecular orbital corresponding to IE_3.

IV. The reactivities of alkenes

In the study of the reactivities of alkenes in relation to electrophiles, the first ionisation energy may serve as a measure of the electron-donating capacity. The electron-accepting capacity of the alkene in reactions with nucleophiles can be characterised by the electron affinity (EA). The correlation between the rate of reaction and the ionisation energy or the electron affinity, observed in series of related alkenes, makes it possible to predict fairly accurately the reactivity on the basis of the ionisation energies or electron affinities obtained experimentally or from quantum-chemical calculations. The quantum-chemical calculations, performed within the framework of the molecular orbitals model, not only yield the numerical values of the ionisation energy and the electron affinity, determined respectively as the HOMO and LUMO energies, but also make it possible to determine the nature of the location of these frontier orbitals on individual atoms and bonds, which makes it possible in its turn to explain the regioselectivity of the electrophilic or nucleophilic reaction. The calculation also enables one to model the intermediate state generated by the reacting species in the rate-limiting stage of the reaction.

The study of the relation between the first ionisation energies and the relative rates of electrophilic addition enabled Nelson et al.[48] to separate the electronic and steric factors in alkene bromination, hydroxymercuration, and hydroboration reactions. Olefins with sterically unlike electron-donating and electron-accepting groups Alk, OAlk, SCH_3, SC_6H_5, $Si(CH_3)_3$, Cl, Br, I, CN, and OAc, which were present both at the double bond and in the alkyl chain of the olefin (altogether 21 compounds) were investigated. In the bromination reaction, the dependence of $\lg k_{rel}$ (k_{rel} is the relative reaction rate constant) on the ionisation energy is described by one linear relation (with a correlation coefficient of 0.96), embracing the compounds of the entire series, the rate of reaction being independent of the degree of substitution at the double bond. On the other hand, in the case of hydroxymercuration and hydroboration it is not possible to obtain a single linear relation with the ionisation energy: for each reaction, there are two groups of alkenes, each of which is described by its own linear relation. One group includes alkenes substituted only at one of the atoms involved in the double bond, whilst the other comprises alkenes with substituents at both atoms of this bond, i.e. each group combines sterically similar compounds, the alkenes with smaller steric hindrance reacting faster. Thus it has been possible to show that the rate of bromination of the alkene is independent of the steric factor and is determined solely by the electronic effect of the substituent, i.e. by the ionisation energy of the alkene, while in hydroxymercuration and hydroboration the steric factors predominate over the electronic factors. However, satisfactory linear correlations have been obtained between the ionisation energies and relative reactivities for both experimental ionisation energies and ionisation energies calculated by the MNDO method on the basis of Koopmans' theorem, which justifies the prediction of the reactivities of alkenes by a computational procedure. The overall rule is that the rate of electrophilic addition falls with increase in ionisation energy. Analysis of the nature of the HOMO on the basis of data obtained by the MNDO calculation makes it possible to explain the regioselectivity of the hydroxymercuration and hydroboration reactions, where Hg and B atoms add preferentially to the unsubstituted carbon atom involved in the double bond. This has been demonstrated for the compounds $H_2C=CHCH_2X$ with different substituents X. In the hydroboration reaction of these compounds, the addition of boron to the unsubstituted carbon atom of the double bond is more preferred the greater the coefficient of the HOMO at this atom compared with the substituted carbon atom. The MNDO calculation also made it possible to establish that the transition states in the rate-limiting stages of the hydroxymercuration and hydroboration reactions are similar and both differ from the transition state in the bromination reaction. The transition state was modelled by a three-centre intermediate, for which the calculation was performed with complete optimisation of the geometry.

The relation between the electron affinities and reactivities of alkenes with an electron-deficient double bond, which function as electrophiles in the Diels–Alder cycloaddition reaction as well as other reactions involving the addition of nucleophilic species, has been traced.[46] The electron affinity was regarded as a measure of the electrophilic reactivity of the alkene. Mono-, di-, tri-, and tetracyanoethylenes as well as ethylenes containing, together with the cyano-group, also another electron-accepting substituent (CF_3, OAc, CO_2, CH_3, and certain others) have been investigated. Since the experimental electron affinities are available only for a small number of the test compounds, those of alkenes were estimated from the known ionisation energies. The method used for such estimations is based on the fact that, according to data calculated by the CNDO/2 method, the HOMO and LUMO energies (characterising the ionisation energy and the electron affinity respectively) in cyanoethylenes are linearly related: an increase in the HOMO energy under the influence of the cyano-groups is accompanied by a

proportional decrease in the LUMO energy. The following linear relation then holds:

$$EA = 3.3IE - 36 \text{ (eV)},$$

from which the electron affinities were in fact determined. The reliability of the electron affinities obtained is confirmed by their correlations with the polarographic potentials for the reduction of cyanoalkenes. For the cycloaddition reaction, where the alkene and the nucleophile (for example, NH_2 of OH) form only one bond with the alkene in the intermediate, the electron affinity (or the LUMO energy) is the controlling factor only for a nucleophile with a low ionisation energy ($\leqslant 8$ eV). The reactivity of the cyanoalkene in relation to a nucleophile with a high ionisation energy ($\geqslant 12$ eV) is controlled by the maximum orbital coefficient of the LUMO, which always corresponds to the least substituted carbon atom involved in the double bond and which in fact proves to be most susceptible to nucleophilic attack. By analysing the nature of the interactions between the frontier orbitals of the alkene and the nucleophile (interactions of the type alkene HOMO–nucleophile LUMO), the authors were able to differentiate pairs of frontier orbitals which determine both the relative rate and the regioselectivity of the reaction between the alkene and the nucleophile as a function of the type of nucleophile.

It has been suggested,[61] in relation to *meta*- and *para*-substituted styrenes with the F, Cl, CH_3, and OCH_3 substituents, that the ionisation energy be used as a measure of the gas-phase affinity of an alkene for a proton or a hydrogen atom (in hydrogenation reactions). The numerical values of the ionisation energies were determined from the photoelectron spectra and by calculations in terms of the CNDO approximation.

Substituted derivatives of allene, whose molecule contains two mutually perpendicular π-systems, are interesting objects for the study of reactivity.

In order to investigate the effects of the substituent on the reactivity of the allene fragment, Taber et al.[71] carried out calculations by the EHM method for monosubstituted allenes $H_2C=C=CRX$ as well as $H_2C=C=CF_2$. The results of the calculations showed that the ionisation energy, determined on the basis of the Koopmans' theorem from the HOMO energy, decreases in the following sequence of substituents X: H > CN > F > Cl > F_2 > Br > CH_3, while the electron affinity, estimated as the LUMO energy decreases in the following sequence: CN > F > F_2 > H > NH_2 > Cl > CHO > CH_3 > Br. Analysis of the composition of the frontier molecular orbitals showed that, when X = CH_3, F, Cl, Br, and NH_2, the HOMO is to a large extent localised on the substituted double bond while the LUMO is localised on the unsubstituted double bond. In the case where X = CN and CHO, the opposite situation is observed: the HOMO and the LUMO are localised on the unsubstituted and substituted double bonds respectively. Therefore, the reaction, accompanied either by the loss of an electron (with participation of the HOMO) or the acquisition of an electron (with participation of the LUMO), can proceed, depending on the nature of the substituent, via both the substituted and the unsubstituted double bond of the allene.

In the [4 + 2]cycloaddition reaction (diene synthesis), which takes place as a result of the interaction of the HOMO of the diene (the electron-donating agent) with the LUMO of the dienophile (the electron-accepting agent), the substituted allene can function both as a diene and as a dienophile depending on the substituent and the nature of the other reactant. A number of studies have been devoted to this reaction of fluoroallenes.[5,16] Dommelsmith et al.[16] studied mono- and 1,1-difluoroallenes, for which calculations were made by the non-empirical method in terms of the 4-31G basis set. For the asymmetric substitution of hydrogen by fluorine in the allene, the degeneracy of the HOMO is removed because the fluorine atoms act differently on the two π MO, one of which is localised on the substituted C(1)=C(2) bond, while the other is localised on the unsubstituted C(2)=C(3) bond. As a result, the HOMO in the $CH_2=C=CHF$ and $CH_2=C=CF_2$ molecules is localised on the fluorinated π bond and is influenced little by the fluorine atom located in the same nodal plane. Therefore the C(1)=C(2) bond can be characterised, as in the unsubstituted allene, as an electron-enriched double bond.

The next occupied molecular orbital as well as the LUMO are localised on the non-fluorinated C(2)=C(3) bond and are strongly stabilised as a result of the inductive effect of fluorine. Thus this bond can be regarded as electron deficient. The concerted [4 + 2]cycloaddition reaction involving the enrichment of the species in electrons proceeds therefore with participation of a non-fluorinated bond in fluoroethylenes, while the non-concerted [2 + 2]cycloaddition involves the fluorinated bond. Dixon and Smart,[5] who used an expanded two-exponent basis set for the non-empirical calculation and studied mono- and 1,1-difluoroallenes as well as trifluoroallene, arrived at similar conclusions about the nature of the HOMO and LUMO in fluoroallenes and about the influence of these frontier molecular orbitals on the regioselectivity of the cycloaddition reactions.

Table 1 presents a compilation of the ionisation energies of 243 compounds with a C=C bond. The first column lists the empirical formulae of the compounds, which are arranged in order of increasing numbers of C, H, N, O, F, Si, S, Cl, Br, Sn, and I atoms. The second column presents the structural formulae (conventional representations of the carbon skeleton for complex hydrocarbons) and in some cases the names of the compounds. The third column lists the first two vertical and adiabatic (in brackets) ionisation energies. In addition, the symmetry and the nature of the corresponding ionisation energy are also indicated in brackets.

Table 1.

Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
C_2H_4	$H_2C=CH_2$	10.55(10.51) ($1b_{2u}$)	12.85(12.45) ($1b_{2g}$)	[76]
C_2D_4	$C_2D=CD_2$	10.53($1b_{2u}$)	12.47($1b_{2g}$)	[77]
C_3H_4	$H_2C=C=CH_2$	9.62(2e)	10.2	[78]
C_3H_6		10.01(9.74) (a'', $\pi_{C=C}$)	12.4(11.82) (σ_1)	[76]
C_4H_4	$H_2C=C=C=CH_2$	9.15($1b_{3g}$)	9.98($2b_{3u}$)	[78]
C_4H_4		9.58(9.58) ($2a''$, π)	10.58(10.58) ($12a'$, π)	[78, 80]
C_4H_6		9.33($3a''$)	10.06($12a'$)	[78]
C_4H_6		9.20(9.03) ($1b_g$)	11.5($1a_u$)	[79]

Table 1 (contd.).

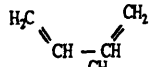
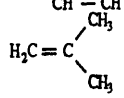
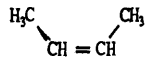
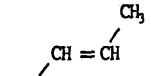
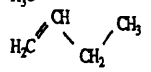
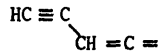
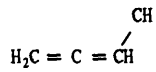
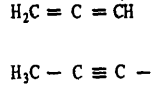
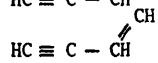
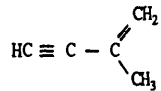
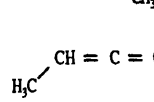
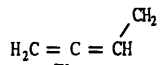
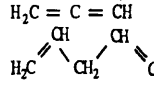
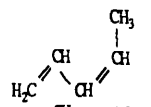
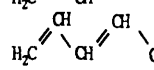
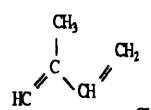
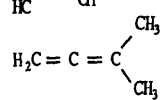
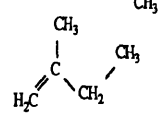
Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
C_4H_6		9.06(9.06) ($1b_g$, π)	11.47(11.22) ($1a_u$, π)	[77]
C_4H_8		9.44(9.21) (a'', $\pi_{C=C}$)	11.59(11.35) (a')	[76]
C_4H_8		9.12(9.07) ($2b_1$)	11.7(11.27) ($6b_2$)	[7, 78]
C_4H_8		9.37(9.09) (a'', $\pi_{C=C}$)	11.96(a')	[76]
C_4H_8		9.72(9.59) ($3a''$, $\pi_{C=C}$)	11.75(11.30) ($9a'$)	[76]
C_5H_4		9.65 (a'', π)	10.30 (a', π)	[6]
C_5H_4	$H_2C{=}C{=}C{=}C{=}CH_2$	8.67 ($3e$)	9.2	[78]
C_5H_6		8.88 (a'', π)	10.04 (a', π)	[6, 78]
C_5H_6		8.94(8.94) ($6a''$, π)	9.51(9.51) (a', π')	[80]
C_5H_6		9.17 ($3a''$)	10.44 ($15a'$)	[78]
C_5H_6		9.11 ($3a''$)	10.38	[78]
C_5H_6		9.27 ($3a''$)	10.43 ($15a'$)	[78]
C_5H_8		9.13	9.65	[78]
C_5H_8		9.25	10.0	[78]
C_5H_8		9.62 ($2a_u$)	10.12 ($1b_g$)	[78]
C_5H_8		8.67 ($3a''$)	11.1 ($2a''$)	[78]
C_5H_8		8.61(8.61) ($3a''$, π)	11.10 ($2a''$, π)	[8, 77, 78]
C_5H_8		8.89(8.89) ($3a''$, π)	10.9 ($2a''$, π)	[77]
C_5H_8		8.95	9.9	[77]
C_5H_{10}		9.15 ($4a''$)	—	[78]

Table 1 (contd.).

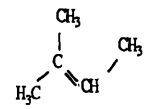
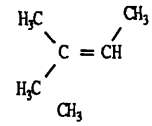
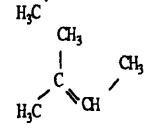
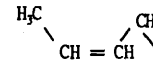
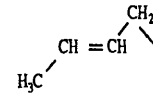
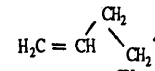
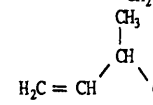
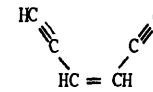
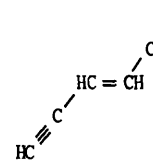
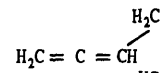
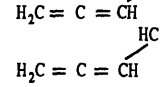
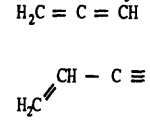
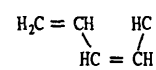
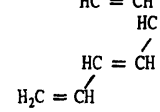
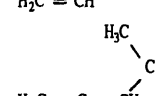
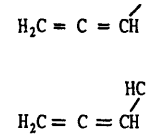
Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
C_5H_{10}		8.68 ($4a''$)	11.3 ($16a'$)	[78]
C_5H_{10}		8.92(8.72) ($\pi_{C=C}$)	11.23(11.08)	[8, 76]
C_5H_{10}		9.15	—	[76]
C_5H_{10}		9.04 ($4a''$)	—	[78]
C_5H_{10}		9.04 ($4a''$)	—	[78]
C_5H_{10}		9.52 ($4a''$)		[78]
C_5H_{10}		9.7(9.52) (π_1)	11.2(11.0) (σ)	[76, 77]
C_6H_4		9.10(9.10) ($2b_1$, π)	10.54 ($9a_1$, π')	[80]
C_6H_4		9.07(9.07) ($2a_u$, π)	10.55(10.55) ($9a_g$, π')	[78, 80]
C_6H_6		9.65 (a'')	10.3 (a')	[78]
C_6H_6		8.53 (b_g, π)	9.78 (a_g, π)	[6]
C_6H_6		8.71(8.50) ($2a_u$, π)	9.97 ($9b_u$, π')	[80]
C_6H_8	$H_3C{-}CH{=}C{=}C{=}CH{-}CH_3$	8.09(8.09) ($2b_g$, π)	10.6 ($2a_u$, π)	[77]
C_6H_8		8.32(8.32) ($2b_1$, π)	10.27(10.27) ($1a_2$, π)	[67, 77]
C_6H_8		8.29(8.29) ($2a_u$, π)	10.26(10.26) ($1b_g$, π)	[67, 77]
C_6H_8		8.54(8.54) (π_1)	9.79 (π_2)	[47]
C_6H_8		8.32 (π_1)	9.73 (π_2)	[47]

Table 1 (contd.).

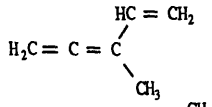
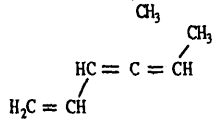
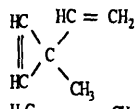
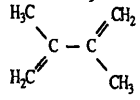
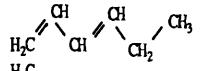
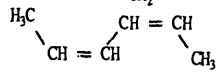
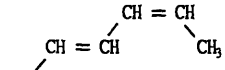
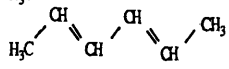
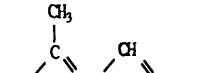
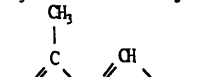
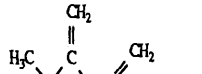
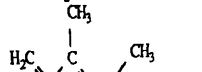
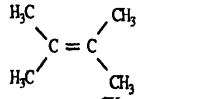
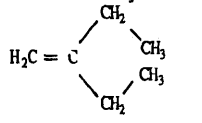
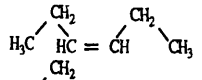
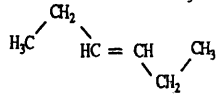
Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
C_6H_8		8.54 (π_1)	9.73 (π_2)	[47]
C_6H_8		8.56 (π_1)	9.47 (π_2)	[47]
C_6H_8		8.29	—	[63]
C_6H_{10}		8.62(8.62) ($2b_g$, π)	10.18 ($2a_u$, π)	[8, 77]
C_6H_{10}		8.63 ($3a''$)	11.1 ($2a''$)	[78]
C_6H_{10}		8.18 ($2b_g$)	10.7 ($2a_u$)	[78]
C_6H_{10}		8.25 ($4a''$)	10.7 ($3a''$)	[78]
C_6H_{10}		8.22 ($2b_g$)	10.7 ($2a_u$)	[8, 78]
C_6H_{10}		8.28 ($4a''$)	10.8 ($3a''$)	[78]
C_6H_{10}		8.47 ($4a''$)	10.5 ($3a''$)	[78]
C_6H_{10}		8.79 ($4a''$)	10.8 ($3a''$)	[78]
C_6H_{10}		8.39 ($4a''$)	10.6 ($3a''$)	[78]
C_6H_{12}		8.41(8.26) (b_{3u})	10.83(10.69) (b_{3g})	[76, 78]
C_6H_{12}		9.06	—	[76]
C_6H_{12}		8.95	—	[48]
C_6H_{12}		8.97	—	[48]

Table 1 (contd.).

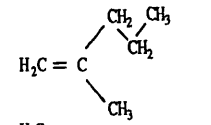
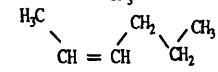
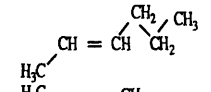
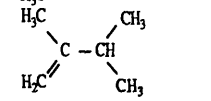
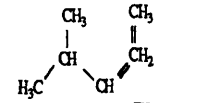
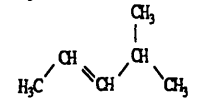
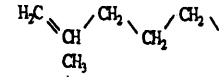
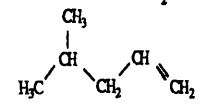
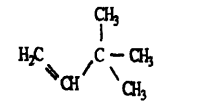
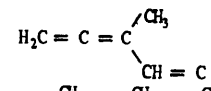
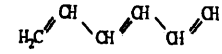
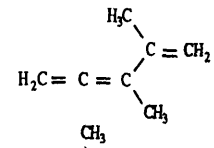
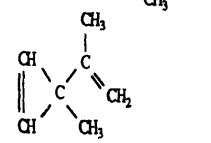
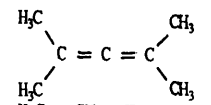
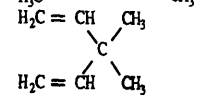
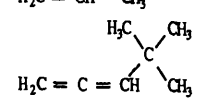
Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
C_6H_{12}		9.08	—	[48]
C_6H_{12}		8.97	—	[76]
C_6H_{12}		8.97	—	[76]
C_6H_{12}		9.07	—	[76, 78]
C_6H_{12}		8.98	—	[76, 78]
C_6H_{12}		8.97	—	[76]
C_6H_{12}		9.48	—	[76]
C_6H_{12}		9.45	—	[76, 78]
C_6H_{12}		9.7 (π_1)	11.1 (σ_1, C(CH$_3$)$_3$—C)	[76]
C_7H_8		8.39 (a'', π)	9.59 (a', π)	[6]
C_7H_{10}		8.07(8.07) (π)	10.07(10.07) (π)	[77]
C_7H_{10}		8.10 (π_1)	9.56 (π_2)	[47]
C_7H_{10}		7.84	—	[63]
C_7H_{12}		8.53(8.53)	—	[81]
C_7H_{12}		9.55 (b_1, π)	9.95 (a_2, π)	[77]
C_7H_{12}		9.32	—	[11]

Table 1 (contd.).

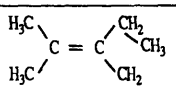
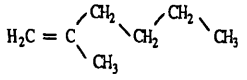
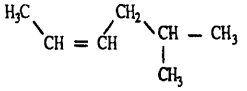
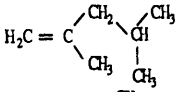
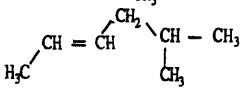
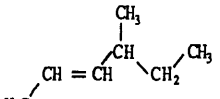
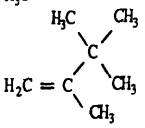
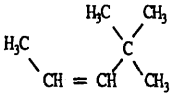
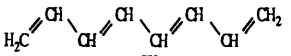
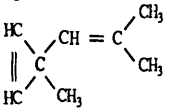
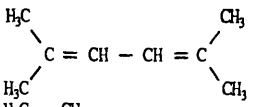
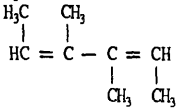
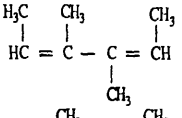
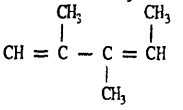
Empirical formula	Name, structural formula	IE(IE_{ad})(symmetry)		Refs.
		IE_1	IE_2	
C_7H_{14}		8.21	—	[76]
C_7H_{14}		9.04	—	[76]
C_7H_{14}		8.92	—	[76]
C_7H_{14}		9.03	—	[76]
C_7H_{14}		8.92	—	[76]
C_7H_{14}		8.91	—	[76]
C_7H_{14}		9.02	—	[76]
C_7H_{14}		8.92	—	[76]
C_8H_8	Styrene $C_6H_5CH=CH_2$	8.48(8.42) (b_1, π)	9.28(9.13) (a_2, π)	[33, 77]
C_8H_{10}		7.79(7.79) (b_g)	9.61(9.45) (a_u)	[12]
C_8H_{12}		8.08	—	[63]
C_8H_{14}		7.83(7.65) ($3b_g, \pi$)	10.12 ($3a, \pi$)	[8, 77]
C_8H_{14}		8.1 (*E, E*)	—	[8]
C_8H_{14}		8.6(*E, Z*)	—	[8]
C_8H_{14}		8.7(*Z, Z*)	—	[8]
C_9H_{10}	Allylbenzene $C_6H_5CH_2CH=CH_2$	8.65(8.60) (b_1)	9.27 (a_2)	[77]

Table 1 (contd.).

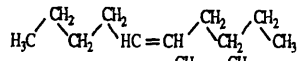
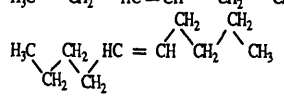
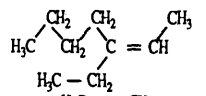
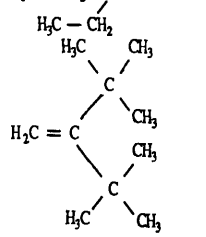
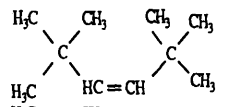
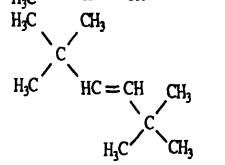
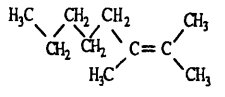
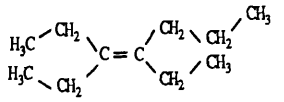
Empirical formula	Name, structural formula	IE(IE_{ad})(symmetry)		Refs.
		IE_1	IE_2	
C_9H_{10}	α-Methylstyrene $C_6H_5C(CH_3)=CH_2$	8.50(8.20) (b_1, π)	9.13 (a_2, π)	[77]
C_9H_{10}	*trans*-β-methylstyrene $C_6H_5CH=CHCH_3$	8.37(8.20) (b_1, π)	9.14 (a_2, π)	[77]
C_9H_{10}	*o*-Methylstyrene $CH_3C_6H_4CH=CH_2$	8.50(8.20)	9.00 (a_2, π)	[77]
C_9H_{10}	*m*-Methylstyrene $CH_3C_6H_4CH=CH_2$	8.36(8.15)	8.97 (a_2)	[77]
C_9H_{10}	$C_6H_5CH=CHCH_3$	8.48	—	[82]
C_9H_{12}	—	9.52–10.06 (e, π)	9.67 (a_2, π)	[77]
$C_{10}H_{10}$	1-Phenylbutadiene $C_6H_5CH=CHCH=CH_2$	8.16(7.95) ($\pi_{C=C}$)	9.27 (a_2)	[77]
$C_{10}H_{10}$	2-Phenylbutadiene $H_2C=C(C_6H_5)CH=CH_2$	8.77(8.57) ($\pi_{C=C}$)	9.3 ($a_2 + b_1$)	[77]
$C_{10}H_{12}$	*cis*-β-Ethylstyrene $C_6H_5CH=CH_2H_5$	8.54	—	[82]
$C_{10}H_{12}$	*trans*-β-Ethylstyrene $C_6H_5CH=CHC_2H_5$	8.30	—	[82]
$C_{10}H_{12}$	*o,m*-Dimethylstyrene $(CH_3)_2C_6H_3CH=CH_2$	8.30(8.00)	8.76 (a_2)	[77]
$C_{10}H_{20}$		8.77	—	[76]
$C_{10}H_{20}$		8.76	—	[76]
$C_{10}H_{20}$		8.10	—	[76]
$C_{10}H_{20}$		8.98	—	[76]
$C_{10}H_{20}$		8.69	—	[76]
$C_{10}H_{20}$		8.74	—	[76]
$C_{10}H_{20}$		8.13	—	[76]
$C_{11}H_{22}$		8.04	—	[76]

Table 1 (contd.).

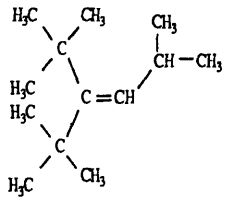
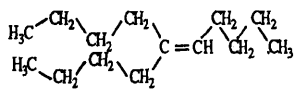
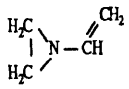
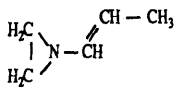
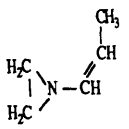
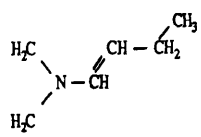
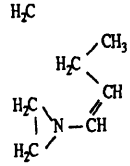
Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
$C_{12}H_{16}$	*cis*-t-Butylstyrene $C_6H_5CH=CHC(CH_3)_2$	8.85	—	[82]
$C_{12}H_{16}$	*trans*-β-t-Butylstyrene $C_6H_5CH=CHC(CH_3)_3$	8.18	—	[82]
$C_{13}H_{26}$		8.31	—	[76]
$C_{14}H_{12}$	*trans*-Stilbene $C_6H_5CH=CHC_6H_5$	8.00(7.70) (b_1, π)	9.25—9.75 ($b_1 + 2a_2$)	[77]
$C_{14}H_{12}$	*cis*-Stilbene $C_6H_5CH=CHCH_5$	8.20(7.80) (b_1, π)	9.08—9.40 ($b_1 + 2a_2$)	[77]
$C_{14}H_{12}$	α-Phenylstyrene $(C_6H_5)_2C=CH_2$	8.25(8.20) (b_1)	9.05—9.20 ($b_1 + 2a_2$)	[77]
$C_{14}H_{28}$		8.17	—	[76]
C_6N_4	Tetracyanoethylene $(NC)_2C=C(CN)_2$	11.79 ($2b_{3u}, \pi''_{C=C}$)	13.45	[83]
C_3H_3N	Acrylonitrile $H_2C=CHCH$	11.1(10.84)	12.35(12.28)	[83]
C_3H_3N	Allylamine $H_2C=CHCH_2NH_2$	9.44(8.76) (a'', n)	10.04 (a'', π)	[76, 77]
C_4H_5N	$H_2C=C(CH_3)CN$	10.37	—	[46]
C_4H_5N	$H_2C=CCH_2CN$	10.18	—	[48]
C_4H_5N	$H_3CC(H)=C(H)CN$	10.23	—	[46]
C_4H_7N		8.75		[64]
C_5HN	Tricyanoethylene $(NC)_2C=C(H)CN$	11.55	—	[46]
C_5H_9N		8.34	—	[64]
C_5H_9N		8.39	—	[64]
$C_5H_{11}N$	$H_2C=HCCH_2N(CH_3)_2$	8.47(7.84) (n)	(9.37) ($\pi_{C=C}$)	[76]
$C_6H_{11}N$		8.26	—	[64]
$C_6H_{11}N$		8.26	—	[64]

Table 1 (contd.).

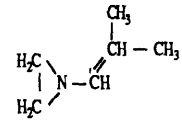
Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
$C_6H_{11}N$		8.2		[64]
$C_6H_{11}N$	$NH(CH_2CH=CH_2)$	8.79 (n, N)	9.82 (π_-)	[76]
$C_9H_{15}N$	$N(CH_2CH=CH_2)_3$	8.30 (n, N)	9.70 (π_+)	[76]
C_4H_2N	*cis*-1.2-Dicyanoethylene *cis*-NCCH=CHCN	11.3(11.15) ($2b_1, \pi''_{CC}$)	(12.77) ($8b_2, \pi''_{CN}$)	[77, 83] [39]
$C_{15}H_{11}N$	C_6H_5—CH=C(CN)C_6H_5	8.22	—	[39]
$C_4H_2N_2$	*trans*-1.2-Dicyanoethylene *trans*-NCCH=CHCN	11.3(11.15) (π_2)	12.9(12.78) ($\pi_{x,y}$)	[77]
$C_4H_2N_2$	1.1-Dicyanoethylene	13.35 ($2b_1, \pi''_{CC}$)	12.90 ($7b_{2g}, \pi''_{CN}$)	[83]
$C_6H_{14}N_2$	$H_2C=C[N(CH_3)_2]_2$	7.5 (π)	8.2 (N_-)	[76]
C_3H_4O	*trans*-Acroleine $H_2C=CHCHO$	10.13(10.13) (a', n)	10.95 ($a'', \pi_{C=C}$)	[77]
C_3H_6O	Allyl alcohol $H_2C=CHCH_2OH$	10.16(9.63) (π)	10.93 (n)	[84]
C_3H_6O	Methyl vinyl ether $H_2C=CHOCH_3$	9.14(8.96) ($3a'', \pi$)	12.10 ($13a', n\sigma$)	[76]
C_4H_6O	Crotonaldehyde $CH_3CH=CHCHO$	9.86(9.77)	10.36(10.21)	[77, 84]
C_4H_6O	$H_2C=C=CHOCH_3$	8.73	—	[77]
C_4H_8O	$H_2C=C(H)OC_2H_5$	9.15	11.68	[76]
C_4H_8O	$H_2C=CHCH_2OCH_3$	9.44	—	[48]
C_5H_8O	2-Methoxybutadiene $H_2C=CHC(OCH_3)=CH_2$	8.62(8.43)	10.1	[77]
C_5H_8O	1-Methoxybutadiene $H_2C=CHCH=CHOCH_3$	8.21(8.03)	10.7	[77]
C_5H_8O	$H_2C=C=CHOC_2H_5$	8.47	—	[11]
$C_5H_{10}O$	$CH_3CH=C(CH_3)OCH_3$	8.25	11.25	[76]
$C_5H_{10}O$	$H_2C=C(H)OCH(CH_3)_2$	8.84	11.34	[76]
$C_6H_{12}O$	$H_2C=C(H)O(CH_2)_3CH_3$	8.77	11.02	[76]
$C_6H_{12}O$	$H_2C=C(OC_2H_5)_2$	8.3	10.3	[76]
$C_7H_{12}O$	$H_2C=C=CH(OC(CH_3)_3)$	8.31		[11]
$C_3H_4O_2$	Acrylic acid $H_2C=CHCOOH$	10.77(10.60) (a', n)	10.91 (a'', π)	[77]
$C_4H_6O_2$	Methyl acrylate $H_2C=CHCOOCH_3$	10.72	11.12	[77]
$C_5H_8O_2$	$H_2C=C(CH_3)COOCH_3$	10.28	11.05	[77]
$C_6H_{10}O_2$	Ethyl *trans*-crotonate *trans*-$CH_3CH=CHOOC_2H_5$	10.11	10.71	[77]
$C_6H_8O_4$	Dimethyl maleate $H_3COOCCH=CHCOOCH_3$	10.47	11.0	[77]
$C_6H_{12}O_4$	Diethyl fumarate $H_5C_2OOCCH=CHCOOC_2H_5$	10.7	11.23	[77]
$C_{11}H_{20}O_4$	$(C_2H_5O)_2C=C=C(OC_2H_5)_2$	8.13	—	[75]
C_2F_4	$F_2C=CF_2$	10.54(10.11) (b_{3u})	15.93	[76,85]
C_3F_4	$F_2C=C=CF_2$	(10.88)	—	[5, 16]

Table 1 (contd.).

Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
C_3F_6	$F_2C=CFCF_3$	11.29	14.57	[76]
C_4F_8	*cis*-$CCF=CFCF_3$	11.49	—	[76]
C_4F_8	*trans*-$F_3CCF=CFCF_3$	11.55	—	[76]
C_6F_{12}	$(CF_3)_2C=C(CF_3)_2$	12.61	—	[76]
C_7F_{12}	$(CF_3)_2C=C=C(CF_3)_2$	12.28	—	[75]
C_2H_3F	$H_2C=CHF$	10.58(10.37) (π)	13.79 (σ)	[77]
C_3H_5F	$H_2C=CHCH_2F$	10.60(10.11) ($\pi_{C=C}$)	12.43	[76]
$C_2H_2F_2$	1,1-Difluoroethylene	10.72(10.31) (π)	14.79(14.06) (σ)	[77]
$C_2H_2F_2$	*cis*-Difluoroethylene	10.43 (π)	13.97 ($\sigma_{C=C}$)	[77]
$C_2H_2F_2$	*trans*-Difluoroethylene	10.38 (π)	13.90 ($\sigma_{C=C}$)	[77]
$C_3H_2F_2$	$H_2C=C=CF_2$	10.1(9.79)	—	[16]
C_2HF_3	$F_2C=CHF$	10.54(10.14) (a'', π)	14.65 (σ)	[76]
$C_3H_3F_3$	$H_2C=CHCF_3$	(10.9)	—	[16]
$C_8H_3F_3$	Pentafluorostyrene $C_6H_5CH=CH_2$	9.36(9.18) (b_1)	9.73 (a_2)	[77]
$C_9H_{10}O_2F_6$	$(CF_3)_2C=C=C(OC_2H_5)_2$	8.93	—	[75]
C_2H_6Si	$H_2C=CHSiH_3$	10.04 (a'', π)	11.5 (a'', σ_1)	[77, 86]
C_3H_8Si	$H_2C=CHCH_2SiH_3$	9.49 ($3a''$, π)	11.72 ($9a'$, σ_{Si-C})	[86]
$C_5H_{12}Si$	Trimethylvinylsilane $H_2C=CHSi(CH_3)3$	9.8 (π_1)	10.3 (σ_1)	[77, 86]
C_6H_{12}	Divinylsilane $(CH_2=CH)_2Si(CH_3)_2$	9.8 (b_1, π)	10.0 (a_2, π_2)	[77, 86]
$C_6H_{14}Si$	Allyltrimethylsilane $H_2C=CHCH_2Si(C_3)_3$	9.0 (π)	10.5 (σ_{Si-C})	[76, 77]
$C_8H_{12}Si$	$(CH_2=CH)_4Si$	9.8 (e, π_1)	10.1 (a_2, π_2)	[76, 77
$C_6H_{12}Si_2$	$(CH_2=CHSiCH_3)_2$	8.63	—	[86]
$C_7H_{18}Si_2$	$H_2C=CHSi_2(CH_3)_5$	8.56	—	[86]
$C_8H_{10}Si_2$	$(CH_3)_3SiHC=CHSi(CH_3)_3$	9.19 ($6a_u$, π_1)	9.45 ($10a_g$, σ_{Si-C})	[86]
$C_5H_{12}O_3Si$	$H_2C=CHSi(OCH_3)_3$	11.0 (π)	11.74	[86]
$C_{18}H_{18}O_3Si$	$H_2C=CHSi(OC_2H_5)_3$	10.16	10.7	[86]
C_3H_6S	$H_2C=CHSCH_3$	8.51(8.44) ($3a''$, π)	11.00 ($17a'$, $n\sigma$)	[76]
C_3H_6S	Allylmercaptan $H_2C=CHCH_2SH$	9.25(9.25) (a'', nS)	10.05 (a'', $\pi_{C=C}$)	[76, 77]
C_4H_6S	$H_2C=C=CHSCH_3$	8.24	—	[11]
C_4H_8S	$H_2C=CCH_2SCH_3$	9.95	—	[48]
C_5H_8S	$H_2C=C=CH(SC_2H_5)$	8.09	—	[11]
$C_6H_{10}S$	Diallyl sulphide $(CH_2=CHCH_2)_2S$	8.60(8.43) (n)	9.82—10.02 (9.5) ($\pi_1+\pi_2$)	[77]

Table 1 (contd.).

Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
$C_7H_{12}S$	$H_2C=C=C(H)SC(CH_3)_3$	8.26	—	[11]
C_8H_8S	$H_2C=CHSC_6H_5$	10.5	—	[48]
$C_9H_{10}S$	Methyl styryl sulphide $C_6H_5CH=CHSCH_3$	7.75 (π_5)	9.13 (π_4)	[77]
$C_4H_8S_2$	$H_2C=C(SCH_3)_2$	8.12 (π)	8.74 (nS)	[76]
$C_4H_8S_2$	*cis*-$CH_3SCH=CHSCH_3$	7.80	9.15	[76]
$C_4H_8S_2$	*trans*-$CH_3SCH=CHSCH_3$	7.85 (π_u)	8.67 (nS)	[76]
$C_6H_{12}S_4$	$(CH_3S)_2C=C(SCH_3)_2$	7.75	8.58	[76]
$C_5H_{11}NS$	$H_2C=C(SCH_3)N(CH_3)_2$	7.8	8.6	[76]
C_2Cl_4	$Cl_2C=CCl_2$	9.5(9.34) ($2b_{3u}$, π)	11.4 ($3b_{3g}$, nCl)	[76]
C_2H_3Cl	$H_2C=CHCl$	10.2(10.0) ($2a''$, π)	11.7 ($7a'$, nCl)	[87]
C_3H_5Cl	Allyl chloride $H_2C=CHCH_2Cl$	10.34 ($\pi_{C=C}$)	11.3 (nCl)	[48, 83]
C_4H_7Cl	$ClCH=CHC_2H_5$	10.00	—	[48]
$C_2H_2Cl_2$	$H_2C=CCl_2$	10.0(9.83) ($2b_1$, π)	11.7 ($4b_2$, nCl)	[87]
$C_2H_2Cl_2$	*cis*-$ClHC=CHCl$	9.8(9.65) ($2b_1$, π)	11.9 ($4b_2$, nCl)	[87]
$C_2H_2Cl_2$	*trans*-$ClHC=CHCl$	9.8(9.64) ($2a_u$, π)	11.9 ($5a_g$, nCl)	[87]
$C_8H_6Cl_2$	*o,o*-Dichlorostyrene $C_6H_3Cl_2CH=CH_2$	9.05(8.70) (b_1)	9.30 (a_2)	[77]
C_2HCl_3	$Cl_2C=CHCl$	9.6(9.48) ($4a''$)	11.7 ($11a'$)	[87]
C_2F_3Cl	$F_2C=CFCl$	10.24	13.01	[76]
C_2HF_2Cl	$F_2C=CHCl$	10.04	12.15	[76]
C_2H_2FCl	$H_2C=CFCl$	10.21	—	[17]
$C_2F_2Cl_2$	$F_2C=CCl_2$	9.82	12.13	[76]
$C_4F_6Cl_2$	*trans*-$F_3CClC=CClCF_3$	10.55	12.05	[76]
$C_4H_6SiCl_2$	$(CH_2=CH)_2SiCl_2$	10.8	—	[86]
$C_8H_{18}Si_2Cl_2$	$(CH_3)_3SiClC=CClSi(CH_3)_3$	8.96 ($7a_u$)	9.75 (12_{ag})	[86]
$C_2H_3SiCl_3$	$H_2C=CHSiCl_3$	10.7	11.3	[86]
C_2Br_4	$Br_2C=CBr_2$	9.264(9.105) ($2b_{3u}$)	—	[88]
C_2H_3Br	$H_2C=CHBr$	9.83(9.83) (a'', π)	10.93(10.93) (a', nBr)	[76]
C_3H_5Br	$H_2C=CHCH_2Br$	10.01 ($\pi_{C=C}$)	10.20	[76]
C_3H_5Br	$H_2C=C(Br)CH_3$	9.58 ($\pi_{C=C}$)	10.63(10.51) (nBr)	[76]
C_4H_7Br	$BrHC=CHC_2H_5$	9.82	—	[48]
C_2F_3Br	$F_2C=CFBr$	10.11	11.94	[76]
C_2H_2FBr	*cis*-$FCH=CHBr$	9.75	11.05	[76]
$C_2H_2Br_2$	$Br_2C=CH_2$	9.78 (π)	10.73 (nBr)	[76]
C_2H_2Br	*cis*-$CHBr=CHBr$	9.44(9.32) (b_1, π)	10.74 (b_2, nBr)	[76]
$C_2H_2Br_2$	*trans*-$CHBr=CHBr$	9.44(9.30) (a_u, π)	11.05 (a_g, b_g, nBr)	[76]

Table 1 (contd.).

Empirical formula	Name, structural formula	IE(IE$_{adi}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
$C_6H_{14}Sn$	Allyltrimethyltin $(CH_3)_3SnCH_2CH=CH_2$	8.70 (σ/π)	—	[89]
$C_{15}H_{32}Sn$	Allyltributyltin $(C_4H_9)_3SnCH_2CH=CH_2$	8.40 (σ/π)	—	[89]
$C_{21}H_{20}Sn$	Allyltriphenyltin $(C_6H_5)_3SnCH_2CH=CH_2$	8.33 (σ/π)	—	[89]
			—	[89]
$C_5H_{11}ClSn$	Allyldimethyltin chloride $(CH_3)_2ClSnCH_2CH=CH_2$	8.95 (σ/π)	—	[89]
$C_{11}H_{23}ClSn$	Allyldibutyltin chloride $(C_4H_9)_2ClSnCH_2CH=CH_2$	8.63 (σ/π)	—	[89]
$C_4H_8Cl_2Sn$	Allylmethyltin dichloride $CH_3Cl_2SnCH_2=CH_2$	9.33 (σ/π)	—	[89]
$C_7H_{14}Cl_2Sn$	Allylbutyltin dichloride $C_4H_9Cl_2SnCH_2CH=CH_2$	9.24 (σ/π)	—	[89]
C_2H_3I	$H_2C=CHI$	9.33(9.33) (a', π)	10.10(10.10) (a'', n)	[76]
C_3H_5I	$H_2C=CHCH_2I$	9.75	—	[48]
$C_2H_2I_2$	*cis*-IHC=CIH	8.92 (n)	9.86 (π_1)	[76]
C_2H_2I	*trans*-IHC=CHI	8.94 (n)	9.60 (π_1)	[76]
$C_3H_2I_3$	$I_2C=ClCH_2I$	9.30 (n)	9.75 (n)	[76]

References

1. K E Ballard *Photoelectron Spectroscopy and Molecular Orbital Theory*, Wiley, New York, 1978
2. J H D Eland *Photoelectron Spectroscopy, 2nd Edition*, Butterworth, London, 1984
3. R M Hochstrasser *Molecular Aspects of Symmetry* (Translated into Russian), Mir, Moscow, 1968
4. K Fukui *Angew. Chem. Int. Ed. Engl.*, 1982, **21** 801
5. D A Dixon, B E Smart *J. Phys. Chem.*, 1989, **93**(23) 7772
6. P Bischof, R Gleiter, H Hopf, F T Lenich *J. Am. Chem. Soc.*, 1975, **97**(19) 5467
7. D C Frost, J S Sandhu *Indian J. Chem.*, 1971, **9** 1105
8. E Honegger, J Zhong-zhi, E Heilbronne, et al. *Helv. Chim. Acta*, 1984, **67**(3) 640
9. M J S Dewar, R C Dougherty *The PMO Theory of Organic Chemistry* (Translated into Russian), Mir, Moscow, 1977
10. H Basch, G Bieri, E Heilbronne, T B Jones *Helv. Chim. Acta*, 1978, **61** 46
11. J Kamphuis, H J T Bos, C W Woryell, W Runge *J. Chem. Soc., Perkin Trans. 2*, 1986, 1509
12. T B Jones, J P Maier *Int. J. Mass Spectr.*, 1979, **31**(3) 287
13. F Brogli, J K Grandall, E Kloster-Jensen, et al. *J. Electron. Spectrosc. Relat. Phenom.*, 1973, **2** 455
14. F Bernardi, A Mangini, N D Epiotis, et al. *J. Am. Chem. Soc.*, 1977, **99**(23) 7465
15. G Bieri, J D Dill, E Heilbronner, et al. *Helv. Chim. Acta*, 1977, **60** 629
16. L N Dommelsmith, K N Houk, C Piedrahita, W J Dolbier *J. Am. Chem. Soc.*, 1978, **100**(22) 6908
17. A W Potts, J M Benson, I Novak, W A Svensson *Chem. Phys.*, 1987, **115** 253
18. S Mezz, U Wahlgren *Theor. Chim. Acta*, 1971, **21** 323
19. I Fischer-Hjalmars, S Meza *Acta Chem. Scand.*, 1972, **26** 2991
20. C R Brundle, M B Robin, N A Kuebler, H Basch *J. Am. Chem. Soc.*, 1972, **94** 1451
21. M M Heaton, M R El-Talbi *J. Chem. Phys.*, 1986, **85**(12) 7198
22. G L Gutsev, A I Boldyrev, A A Ovchinnikov *Zh. Strukt. Khim.*, 1986, **60**(11) 2756
23. W Niessen, G H F Dierksen, L S Cederbaum, W Domcke *Chem. Phys.*, 1976, **18** 469
24. J A Pople, D L Beveridge *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970
25. L Asbrink, C Fridh, E Lindholm *J. Am. Chem. Soc.*, 1972, **94**(15) 5501
26. M J S Dewar *The Molecular Orbital Theory of Organic Chemistry* (Translated into Russian), Mir, Moscow, 1972
27. M J S Dewar, W Thiel *J. Am. Chem. Soc.*, 1977, **99** 4899
28. M J S Dewar, E G Zoebisch, E F Healy, J J P Stewart *J. Am. Chem. Soc.*, 1987, **107** 3902
29. R Hoffmann *J. Chem. Phys.*, 1963, **39** 1397
30. P G Parr *The Quantum Theory of Molecular Electronic Structure*, Benjamin, New York, 1964
31. W Thiel *J. Am. Chem. Soc.*, 1981, **103** 1413
32. N H Werstiuk, G Timmins *Can. J. Chem.*, 1988, **66**(11) 2954
33. S Millefiori, G Scarlata, A Millefiori, D Carbone *Z. Phys. Chem.*, 1981, **128**(1) 63
34. T Koopmans *Physica*, 1933, **1** 104
35. J Del Bene, H H Jaffe *J. Chem. Phys.*, 1968, **48** 1807
36. G Lauer, K W Schulte, A Schweig *J. Am. Chem. Soc.*, 1978, **100** 4925
37. D W Smith, O W Day *J. Chem. Phys.*, 1975, **62**(1) 113
38. D W Smith, O W Day *J. Chem. Phys.*, 1975, **62**(1) 115
39. B T Bickup, J G Snijders *Chem. Phys. Lett.*, 1988, **153**(1) 69
40. N F Stepanov, A A Ustenko, A I Dement'ev *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1973, (1) 102
41. H Köppel, L S Gerderbaum, W Domcke *Chem. Phys. Lett.*, 1984, **110** 469
42. W Runge, H F Baumann, A M F Hezemans, et al. *J. Am. Chem. Soc.*, 1985, **105** 2537
43. H Köppel, L S Gederbaum, W Domcke, S S Skaik *Angew. Chem.*, 1983, **95** 221
44. C J Elsevier, O Vermeer, A Gedanken, W Runge *J. Am Chem. Soc.*, 1985, **105** 2537
45. G A Segal (Editor) *Approximate Methods for Molecular Structure Calculations* (Translated into Russian), Mir, Moscow, 1980
46. K N Houk, L L Munhausen *J. Am. Chem. Soc.*, 1976, **98**(4) 937
47. J Delwiche, M-Th Praet, G Caparace, et al. *J. Electron. Spectrosc. Relat. Phenom.*, 1979, **16** 35
48. D J Nelson, P J Cooper, R Soundararajan *J. Am. Chem. Soc.*, 1989, **111**(4) 1414
49. C B Duke, K L Yip, G P Ceasar, et al. *J. Chem. Phys.*, 1977, **66** 256

50. H Nakatzuji *J. Chem. Phys.*, 1984, **80**(8) 3703
51. G G Furin, A V Zibarev, L N Mazalov, V D Yumatov *Elektronnaya Struktura Ftororganicheskikh Soedinenii* (The Electronic Structures of Organofluorine Compounds), Nauka, Novosibirsk, 1988
52. A K Fokin, M A Landau *Ftoridy Fosfora i Ftorolefiny* (Phosphorus Fluorides and Fluoroolefins), Nauka, Moscow, 1989
53. M E Akopyan, A V Golovin, A A Rodin, Yu L Sergeev *Usp. Khim.*, 1988, **57**(8) 1297 [English translation in *Russ. Chem. Rev.*, 1988(8)]
54. J A Pappas *J. Mol. Struct.*, 1974, **22** 69
55. M A Landau, A V Fokin, A S Kabankin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, (10) 2199
56. A V Fokin, M A Landau, A S Kabankin *Zh. Fiz. Khim.*, 1973, **47**(10) 2679 [English translation in *Russ. J. Phys. Chem.*, 1973(10)]
57. J A Cell, A Kupperman *J. Chem. Phys.*, 1979, **71**(11) 4703
58. R S Prasad, R Sharma *Ind. J. Phys.*, 1987, **61**(2) 87
59. V A Koptyug, N F Salakhutdinov *Zh. Org. Khim.*, 1987, **23**(7) 1396
60. B G Zykov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, (10) 2230
61. D Ajo, E Tondello, F Marcuzzi, G Modena *J. Crystallogr. Spectrosc. Res.*, 1989, **19**(4) 683
62. M Mintas, K Jakopeic, L Klasinc *Croat. Chim. Acta*, 1983, **56**(2) 263
63. V V Plemenkov, O Ju Butenko, V V Zverev, et al. *J. Mol. Struct.*, 1990, **218** 195
64. K Muller, F Privaldi *Helv. Chim. Acta*, 1981, **64** 2508
65. R P Hosteny, T H Dunning, R P Gilman, A Pipano *J. Chem. Phys.*, 1975, **62**(12) 4764
66. M A C Nasamento, W A Goddard *Chem. Phys.*, 1979, **36**(2) 147
67. M Beez, G Bieri, H Bock, E Heilbronner *Helv. Chim. Acta*, 1973, **56**(3) 1028
68. G L Gutsev, A I Boldyrev, A A Ovchinnikov *Zh. Fiz. Khim.*, 1987, **61**(5) 1235 [English translation in *Russ. J. Phys. Chem.*, 1987(5)]
69. G L Gutsev, A I Boldyrev, A A Ovtchinnikov *Int. J. Quantum Chem.*, 1986, **30**(5) 625, 647
70. F Brogli, E Heilbronner, E Kloster-Jensen, et al. *Chem. Phys.*, 1974, **4** 107
71. A M Taber, E A Mushina, V A Krenchel' *Allenovye Uglevodorody* (Allene Hydrocarbons), Nauka, Moscow, 1987
72. E Haselbach *Chem. Phys. Lett.*, 1970, **7** 428
73. L S Cederbaum, W Domcke, H Köppel, W Niessen *Chem. Phys.*, 1977, **26**(2) 169
74. L M Sinegovskaya, S V Eroshenko, O A Tarasova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, (1) 81
75. R Gleiter, R W Saalfrank, W Paul, et al. *Chem. Ber.*, 1983, **116**(8) 2888
76. C N R Rao, P K Basu, M S Hedge *Applied Spectroscopy Reviews*, 1979, **15**(1) 1
77. V I Vovna, F I Vilesov *Uspekhi Fotoniki* (Advances in Photonics), Izd. Leningrad. Gos. Univ., Leningrad, 1975, No. 5, p. 3
78. G Bieri, F Burger, E Heilbronner, J P Maier *Helv. Chim. Acta*, 1977, **60** 2213
79. G Bieri, L Asbrink *J. Electron. Spectrosc. Relat. Phenom.*, 1980, **20** 149
80. F Brogli, E Heilbronner, J Wirz, et al. *Helv. Chim. Acta*, 1975, **58** 2620
81. W E Hill, C H Ward, T R Webb, S D Worley *Inorg. Chem.*, 1979, **18**(7) 2029
82. T Kobayashi, T Arai, H Sakuragi, et al. *Bull. Chem. Soc. Jpn.*, 1981, **54**(6) 1658
83. G Bieri, L Asbrink *J. Electron. Spectrosc. Relat. Phenom.*, 1982, **27** 129
84. B Yu Khel'mer, O I Mazalov, A T Shuvaev, O E Shelepin *Zh. Strukt. Khim.*, 1981, **22**(2) 135
85. J A Sell, D M Mintz, A Kuppermann *Chem. Phys. Lett.*, 1978, **58**(4) 601
86. A I Ermakov, E I Kirichenko, N A Makrushin *Tablitsa Potentsialov Ionizatsii Kremniisoderzhashchikh Soedinenii* (Table of Ionisation Potentials of Organosilicon Compounds), Moscow Institute of Chemical Engineering, 43 pp—Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 29.03.83, No. 1574-83, 1983, Moscow

Received 20th February 1992

Translated from *Uspekhi Khimii* **61** 1303–1331 U.D.C. 547.596/599

Ozonolytic transformations of labdane diterpenoids

P F Vlad, A N Aryku
Institute of Chemistry, Academy of Sciences of the Moldavian Republic, Kishinev

ABSTRACT. Information on the products of ozonolysis of labdane and *ent*-labdane diterpenoids is correlated. The effects of the ozonolysis conditions, the procedure for treating the products and the location of double bonds and other functional groups on the character of the resulting ozonolysis products are considered.

The bibliography contains 91 references.

Contents

I. Introduction 716
II. Ozonolysis of labd-8-enoids without functional groups at C(3) and labda-8(17),13-dienoids 716
III. Ozonolysis of labdenoids and norlabdanoids containing a functional group at C(8) and a double bond at C(9)–C(11), C(11) or C(12) 719
IV. Ozonolysis of labdanoids with oxygen-containing functional groups at C(8) and C(13) and a double bond at C(14) or with a hydroxyl group at C(8) and a double bond at C(13)–C(14) 721
V. Products of the ozonolysis of 8α,13-epoxy-14,15-di-norlabd-12-ene and its derivatives 723
VI. Products of the ozonolysis of labda-8(17),14-dien-13-ol (manool) and compounds related to it 723
VII. Ozonolysis of labda-13(16),14-diene compounds, furanolabdanoids and labd-13(14)-enoids with oxygen-containing functional groups at C(15) and C(16) 727

I. Introduction

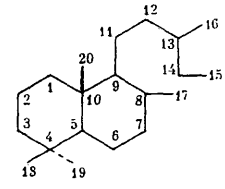
The labdane diterpenoids are bicyclic compounds based on the carbon skeleton (**1**).[1] A characteristic feature of many of them is their availability and practical value. Well known diterpenoids produced on an industrial scale (manool, sclareol, larixol, etc.) belong to this group. Raw materials for obtaining them are fairly accessible. For example, sclareol is isolated from the waste products of sage essential oil manufacture and the majority of the other compounds from the oleoresin of various coniferous plants.[2] Some of these diterpenoids display a high biological activity. For example forskolin proved to be an effective agent for the treatment of glaucoma, cardiac and other diseases[3] and sclareol displays antifungal activity.[4] However the chief practical value of the majority of the available labdanoids is that their transformation products are used in perfume manufacture as rich substitutes for the extremely precious, but unavailable at present, grey amber and in the tobacco industry for the aromatisation of tobacco products.[2]

Labdanoids are subjected to oxidative fission to obtain the indicated products. Compounds of hexavalent chromium or potassium permanganate serve as oxidising agents.[2] However these oxidising processes generally occur non-selectively and lead to a complex mixture of compounds from which the desired compounds are isolated with difficulty and in relatively low yield. Toxic aqueous effluents are formed which are difficult to purify. In addition potassium permanganate is not a readily available reagent. Consequently the development of alternative methods of obtaining the fission products of the available labdanoids using other inexpensive, more selective and ecologically clean oxidising agents is a pressing problem of both theoretical and practical interest.

Ozone is just such an oxidising agent. As is known, it is a powerful and at the same time selective oxidising agent, reacting with unsaturated compounds under mild conditions.[5–7] Thanks to this property ozone proved to be a convenient reagent to effect oxidative conversions of natural compounds in the clarification of their structures. It is perhaps used most frequently and successfully for these purposes in the terpenoid field,[8] the labdanoid diterpenoids amongst them.[1,2]

There are double bonds in the structure of the numerous known representatives of the labdanoid diterpenoid group, which most frequently occupy positions C(7), C(8)–C(9), C(8)–C(17), C(13)–C(14), C(13)–C(16) and C(14)–C(15) and only they react with ozone.[1,9] However the character of the resulting labdanoid ozonolysis products depends not only on the presence and position of the double bonds but also on such functional groups as hydroxyl and carbonyl groups.

In the present review, data on the ozonolysis of labdanoids are correlated according to the number, character and mutual disposition of functional groups in the molecule. Studies published up to 1991 are discussed. The numbering system used for the labdane carbon atoms (1) is taken from the IUPAC rules.[10]



(I)

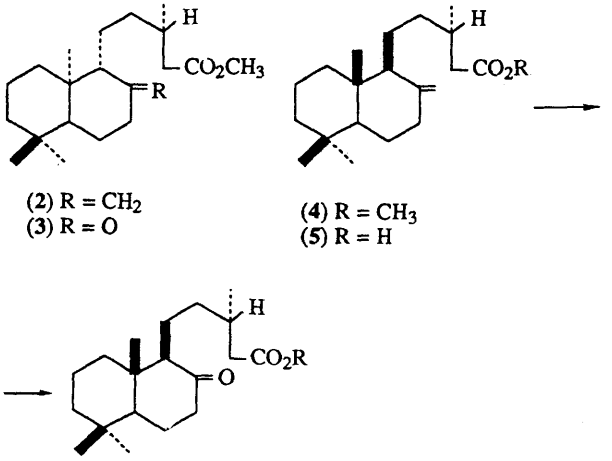
II. Ozonolysis of labd-8-enoids without functional groups at C(13) and labda-8(17),13-dienoids

Ozone proved to be the preferred reagent for the oxidation of labdane diterpenoids with an exocyclic double bond at C(8)–C(17) to the corresponding ketones. This bond is fairly stable, for

example, to such widely used oxidising agents as potassium permanganate or compounds of hexavalent chromium. Satisfactory yields of ketones were obtained only in the two-step oxidation of labd-8(17)-enoids in which osmic acid was used in the first step,[1,2] however this reagent is expensive and available with difficulty. Ozone also oxidises these compounds efficiently. It is convenient both preparatively and for the qualitative detection of this bond. In reality the formation of formaldehyde during the process in conjunction with IR spectroscopy serves as a strict confirmation of the presence of an exocyclic double bond in labdanoids at position C(8)–C(17).

King and Jones[11] effected the ozonolysis of eperuic acid (*2*) in dichloromethane by oxidative fission of the ozonide with hydrogen peroxide and obtained the ketoester (3) in 71% yield (Scheme 1). A good yield (91%) of a mixture of ketoester (**3**) with its epimer at C(13) was also achieved on ozonolysis of a mixture of the ester (**2**) and its epimer at C(13) in ethyl acetate and reduction of the ozonolysis product with zinc in acetic acid.[12] Ozonolysis of the methyl ester of labd-8(17)-en-15-oic acid (**4**) [13] and of labdenoic acid (5) itself,[14] which are structurally close but belong to the enantiomeric series, under analogous conditions led to the keto compounds (**6**) and (**7**) respectively but in poor yield. Replacement of ethyl acetate by dichloromethane affects significantly the result of ozonolysis of methyl labdenoate (**4**) [the yield of ketoacid (**7**) after saponification of the reaction product was 46%].[15] The one-step ozonolysis of methyl labdenoate (**4**) in the presence of pyridine proceeds more smoothly [yield of ketoester (6) was 60%].[16]

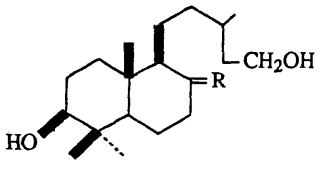
Scheme 1



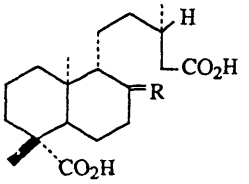
(**2**) R = CH_2
(**3**) R = O

(**4**) R = CH_3
(**5**) R = H

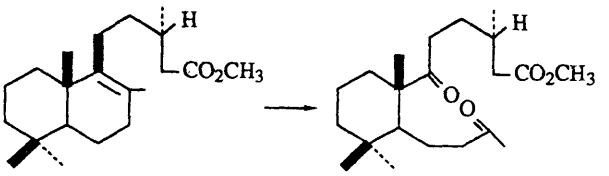
(**6**) R = CH_3
(**7**) R = H



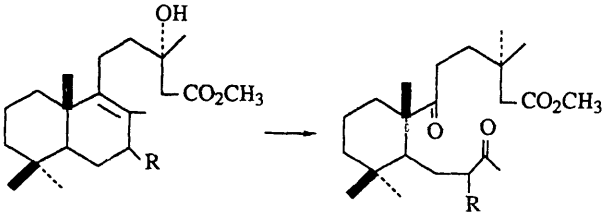
(**8**) R = CH_2
(**9**) R = O



(**10**) R = CH_2
(**11**) R = O

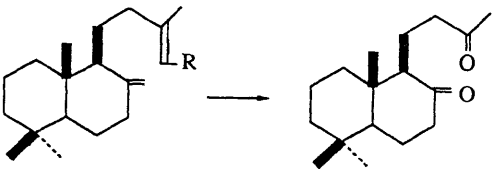


(**12**) (**13**)



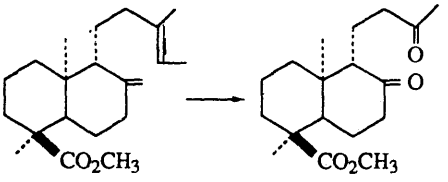
(**14**) R = H
(**16**) R = OAc

(**15**) R = H
(**17**) R = OAc

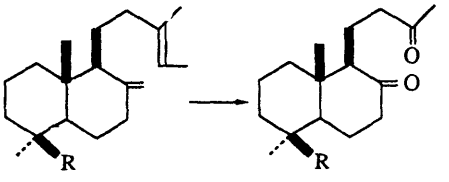


(**18**) R = CH_3
(**26**) R = CH_2OAc
(**27**) R = CO_2H

(**19**)



(**20**) (**22**)



(**21**) R = CO_2CH_3
(**24**) R = CH_2OAc

(**23**) R = CO_2CH_3
(**25**) R = CH_2OAc

Chandra and collaborators[17] ozonolysed labd-8(17)-ene-3,15-diol (**8**) in chloroform and reduced the ozonide with zinc in acetic acid. The reaction product proved to be the ketodiol (**9**). The ozonolysis of oliveric acid (**10**) in dichloromethane in the presence of pyridine gave formaldehyde and the ketoacid (**11**).[18] Thus the functional groups removed from C(8) [the hydroxyl group at C(3) and the axial carboxyl group at C(4)] have no effect on the course of ozonolysis.

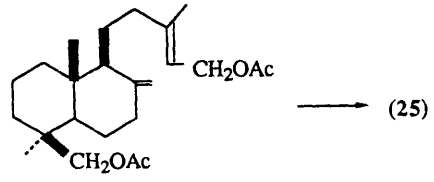
The ozonolysis of the methyl ester of labd-8(9)-en-15-oic acid (**12**) proceeds smoothly when carrying out the reaction in ethyl acetate with hydrogenation of the ozonide over palladium on calcium carbonate.[16] The yield of the diketoester (**13**) was 94%. The position of the double bond, the presence of a hydroxl group at C(13) or a hydroxyl group at C(13) and an acetoxy group at C(7) does not

affect the ozonation reaction. In fact on carrying it out in a mixture of dichloromethane and methanol (1:1) and treating the reaction product with triethyl or trimethyl phosphite, the hydroxyester (**14**) gave the hydroxydiketoester (**15**) in 76% yield[19] and the related diterpenoid (**16**) gave the polyfunctional compound (**17**) in 77% yield (see Scheme 1).[20] It should be noted that oxidation of $\Delta^{8(9)}$-labdanoids with other reagents frequently does not occur at the double bond but at position C(7),[1,2] i.e. ozonolysis is a selective process.

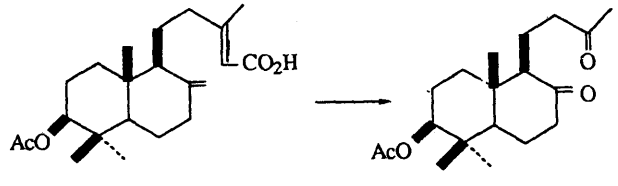
Ozonolysis also proved to be an efficient process for the oxidation of labdenoids with double bonds at C(8)–C(17) and C(13)–C(14). For example, the diketone (**19**) proved to be the sole product (74% yield) of the ozonolysis of labda-8(17),13-diene (18) in dichloromethane in the presence of pyridine.[21] Although the esters (**20**)[22] and (**21**)[23] were also ozonolysed in an aprotic solvent (ethyl acetate) the reduction of the ozonides with zinc in acetic acid led to the diketoesters (**22**) and (**23**) respectively in relatively low yield (~40%). However, the diketoacetate (**25**) was isolated in 78% yield on reduction of the ozonide obtained from 19-acetoxylabda-8(17),13-diene (**24**) in dichloromethane by the same method.[24]

The functionalisation of the carbon atom C(15) in labda-8(17),13-dienes apparently does not ease the fission of the double bond at C(13)–C(14). 15-Acetoxylabda-8(17),13-diene (**26**) is oxidised by ozone (dichloromethane solvent, reducing agent zinc in acetic acid) to the diketone (**19**) in 84% yield.[25] The latter is also formed, though in far poorer yeild (42%), on ozonolysis of labda-8(17),13-diene-15-oic acid (**27**) in ethyl acetate and reduction of the ozonide with the same reagent.[26] Additional functional groups in ring A have no effect on the ozonolysis which is evident in the example of the oxidation of the acetoxydienes (**28**)[24] and (**29**)[27] giving the corresponding acetoxydiketones (**25**) and (**30**) in identical yield (89%) (Scheme 2). In the first case the reaction was carried out in dichloromethane and the ozonide was reduced with zinc and acetic acid and in the second in ethyl acetate and the ozonide was hydrogenated over palladium on carbon.

Scheme 2



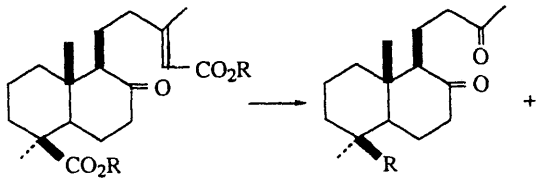
(**28**)



(**29**) (**30**)

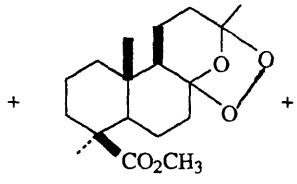
These data show that the result of the ozonolysis of the labdanones depends significantly on the conditions, especially on the solvent. In particular ozonolysis in ethyl acetate with subsequent reduction of the ozonides with zinc in acetic acid leads to a low yield of ozonation product (Scheme 3).

Scheme 3

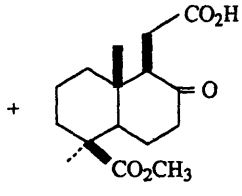


(**31**) R = CH_3
(**32**) R = H

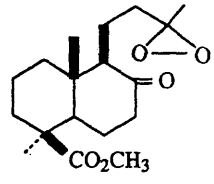
(**23**) R = CO_2CH_3
(**36**) R = CO_2H



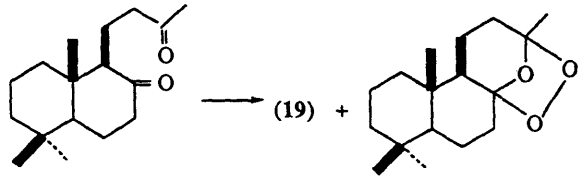
(**34**)



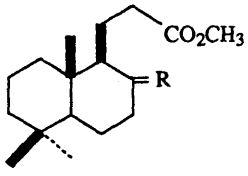
(**35**)



(**33**)



(**37**) (**38**)



(**39**) R = CH_2
(**40**) R = O

Ruzicka and collaborators[28] carried out the ozonolysis of the dimethyl ester (**31**) of agathic acid (**32**) under forcing conditions in acetic acid and, after reduction of the product by boiling in water with zinc dust, obtained a complex mixture of compounds of which the main was the labile diketoester (**23**) (20% yield). In addition an intramolecular peroxide (10%) was isolated to which the authors assigned the structure (**33**). In reality it has the structure (**34**),[5] and a ketoesteracid (**35**) was isolated from the acid fraction. Compound (**34**) is fairly stable and is not reduced by zinc dust in water. The ozonolysis of the same agathic acid (**32**) occurs less ambiguously under milder conditions. In an aprotic solvent (dichloromethane) in

the presence of pyridine it leads mainly to the diketoacid (**36**) 61% yield.[29]

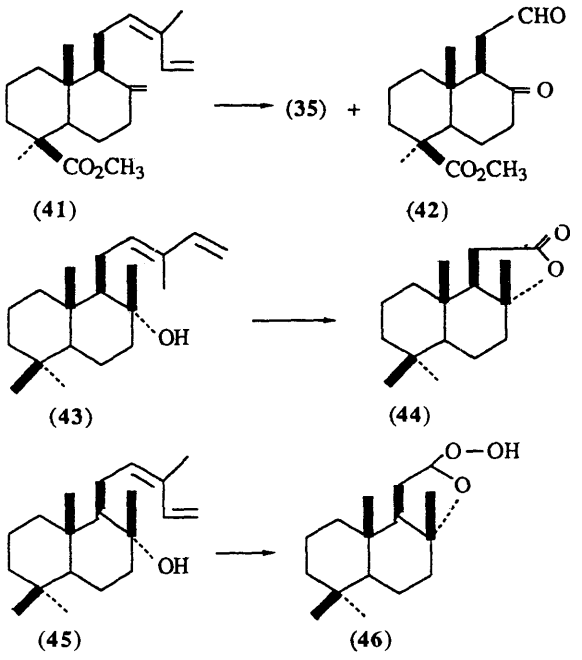
The double bond at C(8)–C(17) is norlabdanoids also reacts smoothly with ozone. Thus 14,15-bisnorlabd-8(17)-en-13-one (**37**) gives the diketone (**19**) (84%) on ozonolysis in dichloromethane in the presence of pyridine.[30] The indicated yield of diketone (**19**) was however achieved after additional treatment of the ozonolysis product with sodium iodide solution. Evidently this treatment was carried out to decompose stable peroxide compounds which were still present since it was later[31] shown from example that one of the ozonolysis products of the unsaturated ketone (**37**) was the oxonide (**38**), an analogue of compound (**34**). Its yield reached 33% if the ozonolysis product was subjected to oxidative fission with hydrogen peroxide.

The tetranorlabdene ester (**39**) is also ozonised smoothly (solvent is chloroform, reducing agent zinc in acetic acid). The sole ozonolysis product was the expected ketoester (**40**).[32]

III. Ozonolysis of labdanoids and norlabdanoids containing a functional group at C(8) and a double bond at C(9)–C(11), C(11) or C(12)

Few labdanoids with the functionalisation indicated are known. Of the compounds with a double bond at C(12) the first investigations were of the ozonolysis of the methyl ester of *cis*-communic acid (**41**) (Scheme 4).[24] The reaction was carried out in dichloromethane and the ozonide was decomposed by boiling with water or with aqueous methanol. A mixture of compounds (**35**) and (**42**) was formed in both cases. In the first case the aldehyde (**42**) predominated in the product [yields of (**35**) and (**42**) were 9 and 59% respectively] and in the second the ketoacid (69.5%) predominated [yield of ketoaldehyde (**42**) was 22.6%]. The conditions therefore affected significantly both the product ratio (6.5 : 1 and 1 : 3) and their overall yield.

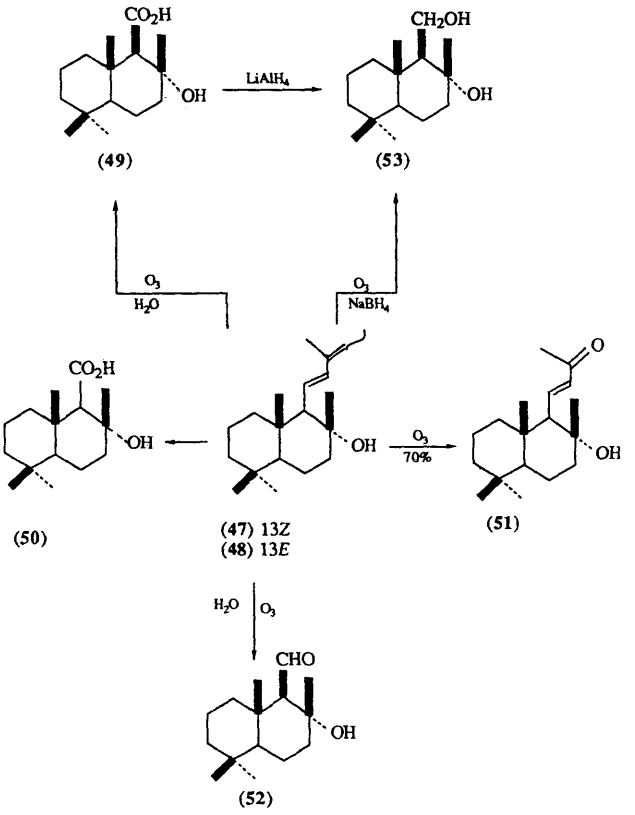
Scheme 4



Chirkova and collaborators[33] have carried out the ozonolysis of *trans*-abienol (**43**) which was isolated by them from Siberian fir and was erroneously mistaken for isoabienol.[34] Ozonolysis was effected in dichloromethane, the ozonide was decomposed by boiling with water, the product was oxidised again with potassium permanganate in acetic acid and norambreinolide (**44**) (70%) was obtained.

A compound of an altogether different nature was obtained in fairly good yield (50–70%) on ozonolysis of *cis*-abienol (**45**), which is distributed in the oleoresin of conifers, in ethyl acetate with oxidative fission of the ozonolysis product with hydrogen peroxide in acetic acid.[35] It turned out to be the epoxyhydroperoxide (**46**) which is formed by intramolecular attack of the Criegee zwitterion by the hydroxy group at C(8).[5,6] This was the first recorded case of the formation of an intramolecular alkoxyhydroperoxide in an aprotic solvent, analogous to the preparation of acyclic alkoxyhydroperoxides on ozonolysis of unsaturated compounds in alcoholic solvents.[6]

Scheme 5

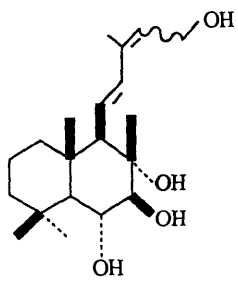


A detailed investigation has been made of the ozonolysis of *cis*- and *trans*-neoabienols (**47**) and (**48**), the stereoisomeric labdanoids with a double bond at C(11) and a hydroxyl group at C(8) which are artefacts formed from *cis*-abienol (**45**) on distillation of oleoresins containing it.[36–39] The authors[36] isolated a hydroxyacid which was assigned the structure (**49**) on ozonolysis of *cis*-neoabienol (**47**) under the conditions indicated above for *trans*-abienol (**43**) (Scheme 5). However its constants differed from those described.[41] Seemingly it is an epimer of compound (**50**). The ozonolysis of a mixture of *cis*- and *trans*-neoabienols (**47**) and (**48**) has been investigated in detail.[42]

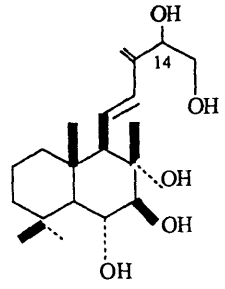
It was shown that the character of the ozonolysis products depends significantly on the quantity of oxidising agent and the method of decomposing the ozonide or peroxide. Thus on using one mole equivalent of ozone and carrying out the reaction at −60 to −70 °C in ethyl acetate in the presence of pyridine or in methanol with subsequent decomposition of the peroxide reaction products with dimethyl sulphide, the selective formation occurs of the conjugated hydroxyketone (**51**) (yield 70%), which is a component of the oleoresin of Siberian fir together with neoabienols (**47**) and (**48**).[40] On increasing the temperature the yield of the hydroxyketone (**51**) is reduced and is 55% at 0 °C. Exhaustive ozonolysis of a mixture of neoabienol in hexane with subsequent heating of the ozonide with water leads to a mixture of driman-8α-ol-11-al (**52**) (60%) and the hydroxyacid (**49**) (25%),[42] the structure of which was demonstrated unequivocally by reduction with lithium aluminium hydride to the known drimane-8α-11-diol (**53**). A mixture of the same compounds is formed on ozonolysis of a mixture neoabienols in ethyl acetate or dichloromethane in the presence of pyridine or in methanol and reduction of the peroxides with dimethyl sulphide. The acid (**49**) is the chief reaction product (yield 71%) on ozonolysis in hexane with oxidative fission of the ozonide with hydrogen peroxide. If the reaction is carried out in methanol at −75 to −78 °C and peroxides are reduced with sodium borohydride, the main reaction product is the diol (**53**) (74%) which is an important starting material for the synthesis of the natural drimane sesquiterpenoids.[43] The yield of the diol (**53**) falls with increasing temperature. The ozonolysis of the hydroxyketone (**51**) has also been investigated in detail and it was shown that there is a definite parallel between the yields of the individual products on ozonolysis under the same conditions of a mixture of neoabienols (**47**) and (**48**) and the hydroxyketone (**51**).

Japanese chemists[44] have ozonolysed sterebins E (**54**), F (**55**), G (**56**) and H (**57**) and 14,15-dinorsterebin (**58**), isolated from the leaves of *Stevia rebaudiana*, in methanol and the ozonolysis products were reduced with sodium borohydride. The tetrol (**59**) was isolated in 60–65% yield in all cases (Scheme 6).

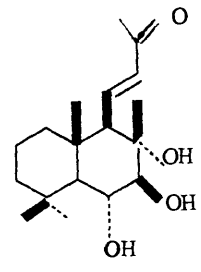
Scheme 6



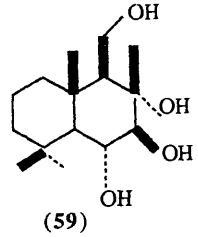
(**54**) 13*E*
(**55**) 13*Z*



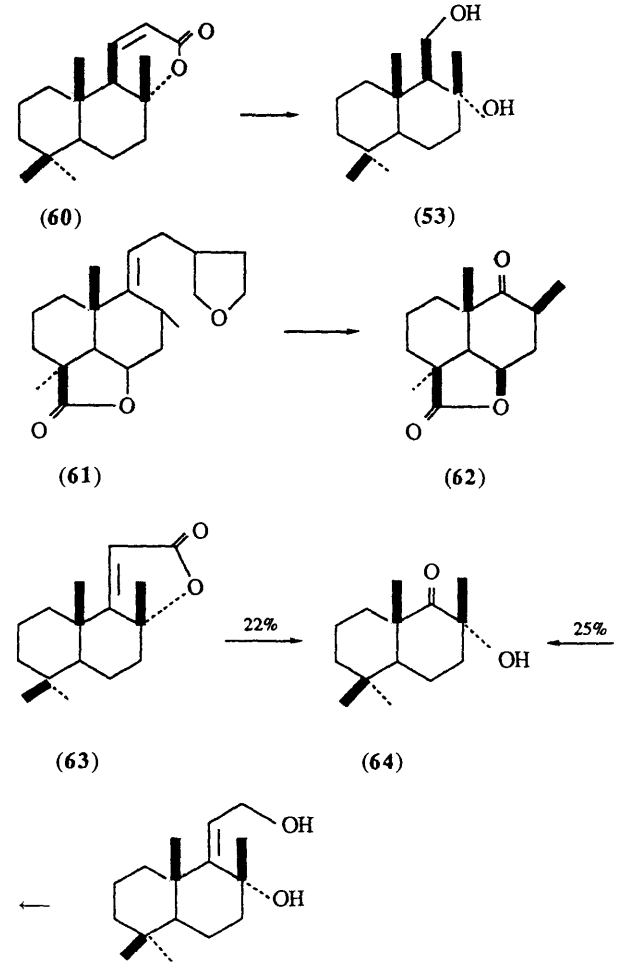
(**56**) 14*R*
(**57**) 14*S*



(**58**)



(**59**)



(**60**) (**53**) (**61**) (**62**) (**63**) (**64**) (**65**)

The tetranorlabdanoid Δ^{11}-dehydroabreinolide (**60**) is also smoothly ozonolysed giving driman-8α,11-diol (**53**) in 70% yield on carrying out the reaction in dichloromethane with reduction of the ozonide with sodium bis(2-methoxyethyl)aluminium hydride in benzene.[45] If the ozonide is reduced with lithium aluminium hydride in ether the yield of diol (**53**) was greater (92%).[21]

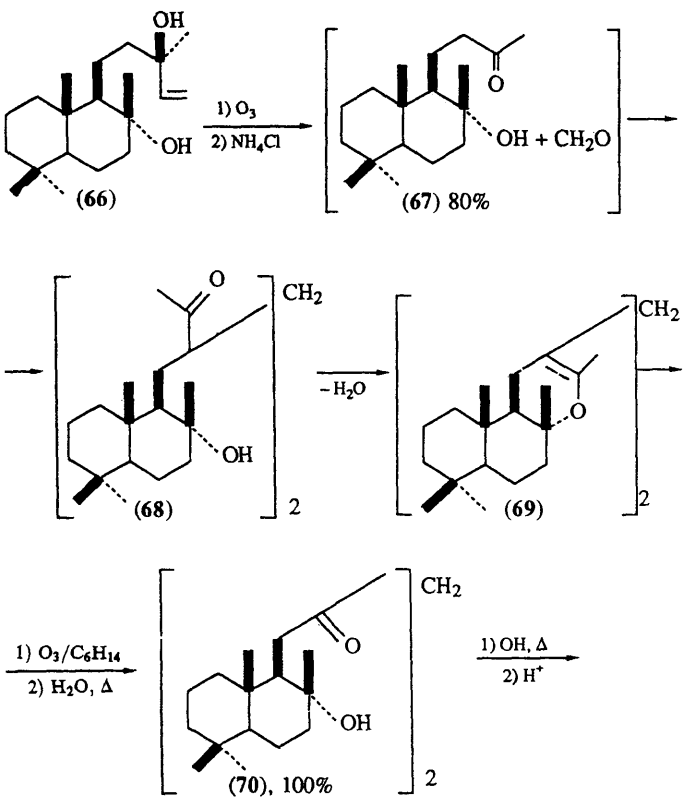
The 9,11-double bond in labdanoids and norlabdanoids is sterically hindered and reacts with ozone with difficulty. It has not as yet been detected in such compounds from natural sources.

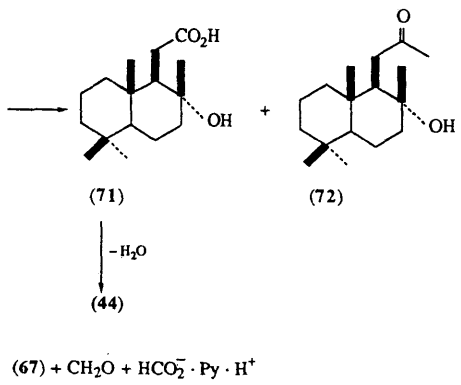
The ozonolysis of anhydrotetrahydromarrubiin (**61**) in ethyl acetate at a relatively high temperature (−5 °C) and hydrogenation of the ozonide over palladium on carbon gave the ketolactone (**62**) in only 18.5% yield.[46] $\Delta^{9(11)}$-Dehydronorambreinolide (**63**) proved to be very inert towards the action of ozone. On ozonolysis in a mixture of ethyl acetate and methanol, hydrogenation of the ozonolysis products over Lindlar catalyst and subsequent saponification with alkali, only a small quantity (22%) of the hydroxyketone (**64**) is formed, a large portion of the initial compound is recovered unchanged in spite of the use of an excess of ozone and forcing conditions.[47] An analogous result was also obtained on ozonation (methanol, hydrogenation of the peroxide over Pd/C) of the product of reduction of this lactone, viz. the diol (**65**) (see Scheme 6).[48]

IV. Ozonolysis of labdanoids with oxygen-containing functional groups at C(8) and C(13) and a double bond at C(14) or with a hydroxy group at C(8) and a double bond at C(13)–C(14)

Sclareol (**66**) was one of the first labdanoids of this type to be subjected to ozonolysis (CCl_4, fission of the ozonide by boiling with water).[49] However the product was not identified exactly. It was only recorded that is has the composition $C_{18}H_{30}O$ and was an oxide in character. On carrying out the reaction under the conditions indicated we obtained a complex mixture of products.[50] Subsequently sclareol was treated with ozone in a polar solvent (methanol) and the ozonolysis product was decomposed with ammonium chloride.[51] The epoxide (**69**) was readily isolated by crystallisation in high yield (80%) in this way. It is formed by the condensation of the primary ozonolysis products, formaldehyde and the hydroxyketone (**67**), and subsequent dehydration of the dihydroxydiketone (**68**) (Scheme 7). Compound (**69**) is either not formed or its yield is reduced significantly on using other compounds (common acids, Lewis acids, acid salts, etc.) for the decomposition of the peroxide oxidation products. Ozonation of compound (**69**) in hexane with subsequent heating of the ozonide with water leads quantitatively to the 1,3-diketone (**70**). This was decomposed with alkali to the hydroxyacid (**71**), which lactonises to norambreinolide (**44**) and to 14,15,16-trinorlabd-8α-ol-12-one (**72**),[52,53] important compounds in practice for the synthesis of perfumes. In particular, a mixture of them may be converted readily into an analogue of the known perfume ambroxide.[52]

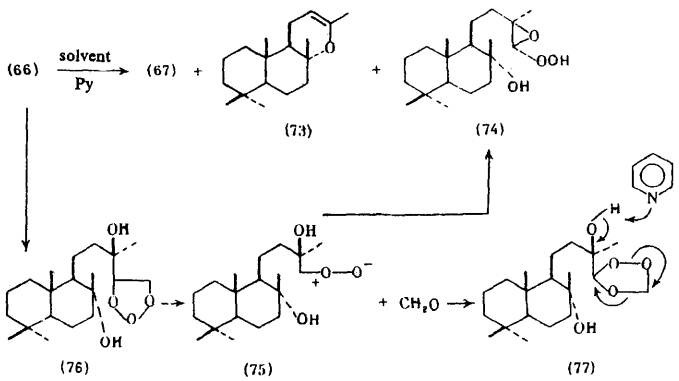
Scheme 7





(67) + CH_2O + HCO_2^- · Py · H^+

Scheme 8

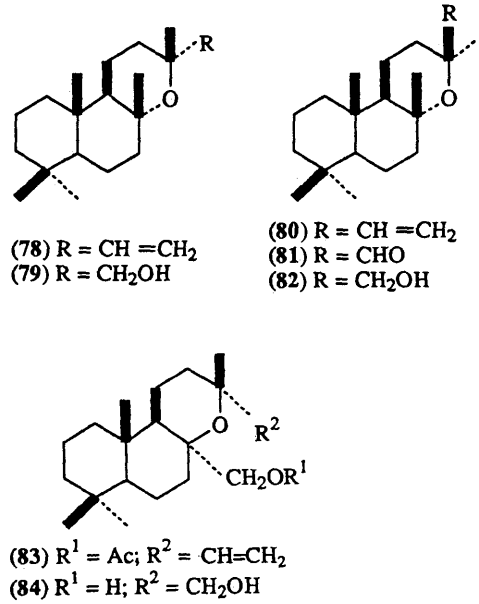


The ozonolysis of sclareol (**66**) has been investigated by other authors.[50] It was shown that on carrying it out in methanol and treating the product with dimethyl sulphide a mixture of at least six compounds is formed. Ozonolysis in dichloromethane, carbon tetrachloride, methanol or ethyl acetate in the presence of pyridine or in ethyl acetate with subsequent heating of the ozonide with water gives a mixture of the hydroxyketone (**67**), the epoxide (**73**) and the α-epoxyhydroperoxide (**74**) (Scheme 8). The latter is unstable and was characterised by spectral data and chemical conversions. Its formation is in agreement with and confirms the ozonation mechanism of allyl alcohols proposed by Everest and collaborators,[54] according to which the zwitterion (**75**), generated from the initial ozonide (**76**) of sclareol, is stabilised as the epoxyhydroperoxide (**74**). The nature of the solvent therefore has little effect on the composition of the reaction products in the ozonolysis of sclareol in the presence of pyridine. It was shown that pyridine does not react with hydroperoxide (**74**). Consequently if the ozonolysis of sclareol (**66**) occurs only by the mechanism proposed by Everest and collaborators,[54] then the presence of pyridine in the reaction mixture must have no effect on the yield and ratio of the compounds (**67**), (**73**), and (**74**). However, experimentally this is not so. This may be explained by the ozonolysis of sclareol proceeding partially according to the mechanism of Criegee[5,6] with the formation of the normal ozonide of sclareol (**77**) and its decomposition involving pyridine evidently as indicated in Scheme 8. The course of the reaction according to the latter mechanism depends to a definite extent on the solvent used.

The oxidation with ozone of those labdanoids in which the carbon atoms C(8) and C(13) are linked by an oxygen bridge, i.e. the manoyl oxides, proceeds in a different way.

The ozonolysis of manoyl oxide (**78**) (CCl_4, the ozonide was decomposed by boiling with water) was carried out for the first time by Hosking and Brandt.[55] However the nonvolatile products were not investigated by them. Later Cambie and collaborators[56] ozonised manoyl oxide (**78**) in dichloromethane in the presence of pyridine and the product was reduced with sodium borohydride giving 15-nor-8-α,13-epoxy-14-hydroxylabdane (**79**) (80%) (Scheme 9).

Scheme 9

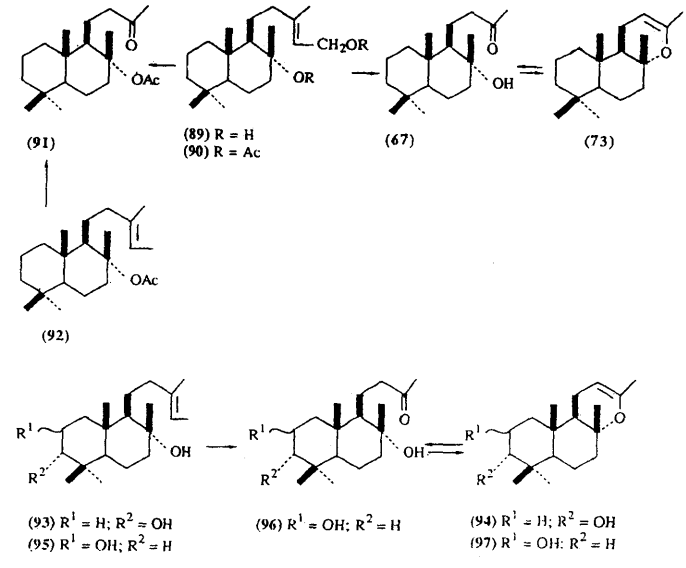


13-Epimanoyl oxide (**80**) was ozonised in carbon tetrachloride with subsequent heating of the ozonide with water. The reaction product proved to be the aldehyde (**81**) (70%).[57] On ozonising the epoxide (**80**) in dichloromethane in the presence of pyridine and reducing the product with sodium borohydride, the alcoholic epoxide (**82**), an epimer of compound (**79**), was isolated in 78% yield.[58] The ozonolysis of 8-epi-20-acetoxymanoyl oxide (**83**) to the dihydroxyepoxide (**84**) (75%) was effected fairly smoothly under the conditions indicated above.[56]

The appearance of a functional group at C(12) in manoyl oxides leads to the fission of the C(12)–C(13) bond on ozonolysis. Norambreinolide (**44**) (40%) and the acetoxyacid (**86**) (15%) were formed on ozonation of 12α-hydroxy-13-epimanoyl oxide (**85**) in chloroform followed by oxidative fission of the ozonide with hydrogen peroxide.[59]

The first of the labdanoids with a hydroxyl group at C(8) and a double bond at C(13) to be subjected to ozonation was (13*E*)-*ent*-8β,15-dihydroxylabd-13-ene (afanamixol) (**87**). The reaction was carried out in acetic acid and the ozonolysis product was reduced with metallic magnesium in hydrochloric acid. The hydroxyketone (**88**) was obtained in 88% yield.[60] The unsaturated epoxide (**73**) (75%) was isolated on ozonolysis of the antipode (**89**) of afanamixol (**87**) in a mixture of methanol and dichloromethane and reduction of the peroxide compounds with dimethyl sulphide.[61] In this case also the first reaction product is the hydroxyketone (**67**), which, as is known,[62] on heating or by the action of acid is transformed into the epoxide (**73**) with which it is in equilibrium. The equilibrium transition (**67**) ⇆ (**73**) is impossible if the hydroxy group of the starting material (**89**) is esterified. In fact the ozonation of the diacetate (**90**) [$CH_3OH-CH_2Cl_2$; $(CH_3)_2S$] leads to ketoacetate (**91**) (90%).[61] This same compound is also formed in almost quantitative yield (98%) on ozonation of the unsaturated acetate (**92**) in dichloromethane in the presence of pyridine.[21] Under the same conditions (13*E*)-3α,8α-dihydroxylabd-13-ene (**93**) gave 3α-hydroxy-8α,13-epoxy-14,15-dinorlabd-12-ene (**94**) (90%),[63] and a mixture of (13*E*)-2α- and 2β,8α-dihydroxylabd-13-enes (**95**) gave an equilibrium mixture of the 2α- and 2β,8α-dihydroxyketones (**96**) and the epoxides (**97**) (91%) (Scheme 10).[64]

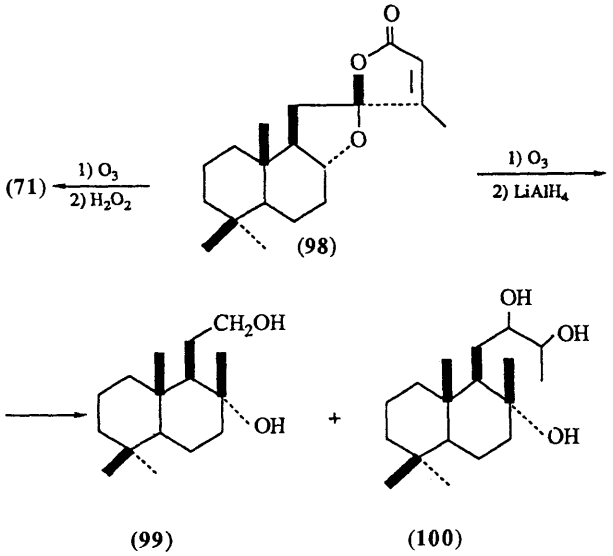
Scheme 10



If an oxygen-containing group is present at C(12) in addition to the hydroxyl group at C(8) and a double bond at C(13) in a labdanoid then depending on the conditions fission of the single

bond at C(12)–C(13) may result. The diol (**99**) (55% yield) and the triol (**100**) (~45%) were isolated on ozonolysis of α-levantenolide (**98**) in ethyl acetate and reduction of the ozonide with lithium aluminium hydride (Scheme 11). On oxidative fission of the ozonide with hydrogen peroxide the sole reaction product is norambreinolide (**44**) (78.5%).[65]

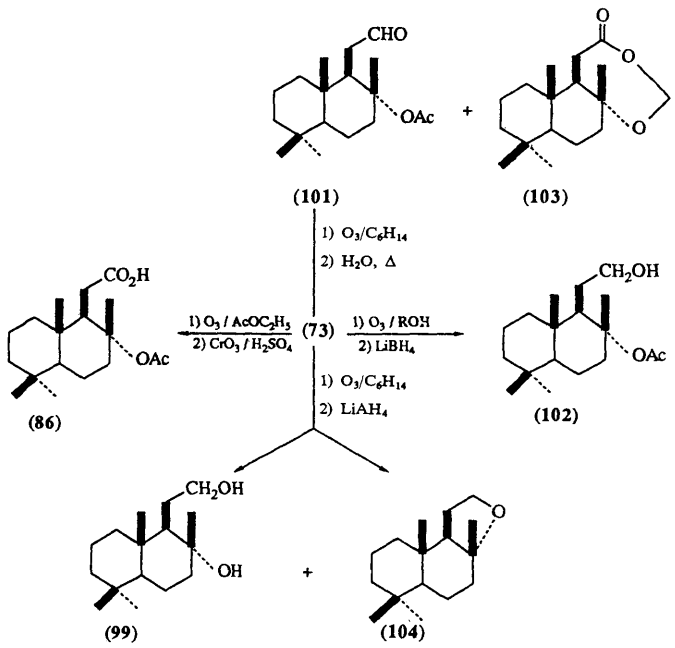
Scheme 11

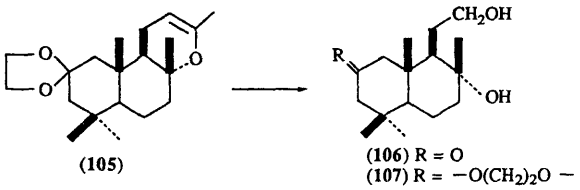


V. Products of the ozonolysis of 8α,13-epoxy-14,15-dinorlabd-12-ene and its derivatives

8α,13-Epoxy-14,15-dinorlabd-12-ene (**73**) and its derivatives are important intermediates on the route from the labdanoids to valuable perfumes,[2] consequently its ozonolysis is not solely of theoretical interest and has been investigated in detail (Scheme 12).

Scheme 12





The ozonolysis of the epoxide (**73**) was effected for the first time in hexane with subsequent treatment of the ozonide with water.[62] The acetoxyacid (**86**) was isolated in 24% yield. Later Stoll and Hinder[66] showed that if the reaction is carried out in ethyl acetate and the ozonide is decomposed with an excess of Raney nickel, then the main reaction product is the acetoxyaldehyde (**101**) (~48%), minor products being the acetoxyacid (**86**) (~3%) and the hydroxyacetate (**102**) (traces). On decomposing the ozonide by boiling with water yield of the acetoxyaldehyde was increased to 61–67% and that of the acetoxyacid (**86**) remained unchanged. A small quantity of the lactone acetal (**103**) was also isolated.[66,67] The same authors[68] ozonolysed the epoxide (**73**) in hexane and reduced the ozonide with lithium aluminium hydride. As a result the glycol (**99**) (57 to 73%) and the epoxide (**104**) (14 to 1.2%) were obtained the ratio of which depended on the conditions. Ozonolysis of the epoxide (**73**) has been repeated[58,61,69] in hexane with reduction of the ozonide with lithium aluminium hydride. The diol (**99**) was obtained in 67, 68, and 76% yield respectively but no formation of the epoxide (**104**) was observed.

A study[69] has been devoted to the search for conditions for a purpose-directed synthesis of bicyclohomofarnesane compounds from sclareol oxide. It was shown that the most convenient route to the acetoxyaldehyde (**101**) was the ozonolysis of the epoxide (**73**) in dichloromethane or ethyl acetate in the presence of pyridine or in hexane with decomposition of the ozonide by heating with water. A small quantity (13–19%) of the acetoxyacid (**86**) was formed in addition to the acetoxyaldehyde (80% yield). If the ozonide obtained in hexane was decomposed by heating with hydrogen peroxide then the reaction product was a 3:2 mixture of the compounds (**86**) and (**101**). The acetoxyacid (**86**) is the predominant product on oxidative fission of the ozonide with Jones reagent (65% yield) or on ozonolysis in cyclohexane in the presence of acetic acid and silica gel (74% yield under optimal conditions). The hydroxyacetate (**102**) (62–64% yield) was obtained on ozonolysis of sclareol oxide (**73**) in isopropanol or methanol and reduction of the peroxide products with lithium borohydride.

The ozonolysis products of the ethyleneketal of 2-ketomanoyl oxide (**105**) have also been investigated. A mixture of the dihydroxyketone (**106**) (39%) and the dihyroxyketal (**107**) (40%) was formed on carrying out the ozonolysis then reducing the ozonide with lithium aluminium hydride.[70]

VI. Products of the ozonolysis of labda-8(17),14-dien-13-ol (manool) and compounds related to it

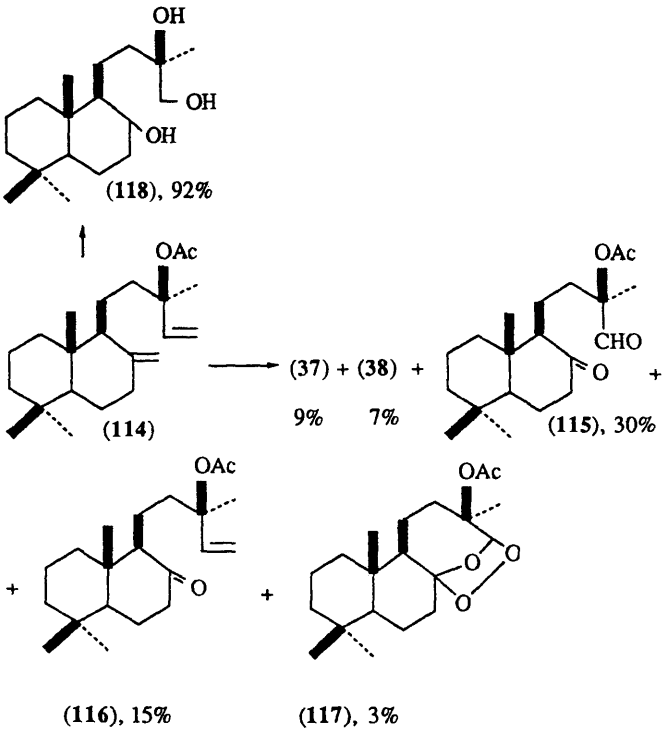
The ozonolysis of manool (**108**), one of the most important labdanoids in practice, has been investigated fairly thoroughly. It was first carried out by Hocking (CCl_4, 0 °C, decomposition of the ozonide by heating with water)[71] who identified the diketone (**19**) (34% yield). 14,15-Dinorlabd-8(17)-en-13-one (**37**) (13%) and the unsaturated epoxide (**109**) (9%) were obtained by the same

procedure for decomposing the reaction products but carrying it out under more forcing conditions in acetic acid.[72] Barltrop and collaborators[73] ozonolysed manool (**108**) in ethyl acetate, decomposed the ozonide with zinc dust in boiling water and isolated the diketone (**19**) (36%) and a product of its further transformation (**110**) (6%). A far more complex mixture of neutral products (**37**), (**38**), (**111**)–(**113**) is formed on ozonation of manool (**108**) in dichloromethane with oxidative fission of the ozonolysis products with hydrogen peroxide.[31] Compounds (**37**) and (**113**) are formed in trace amounts. The yields of the remaining product are shown in Scheme 13 under the formulae. Products of an acid character were not investigated by these authors.

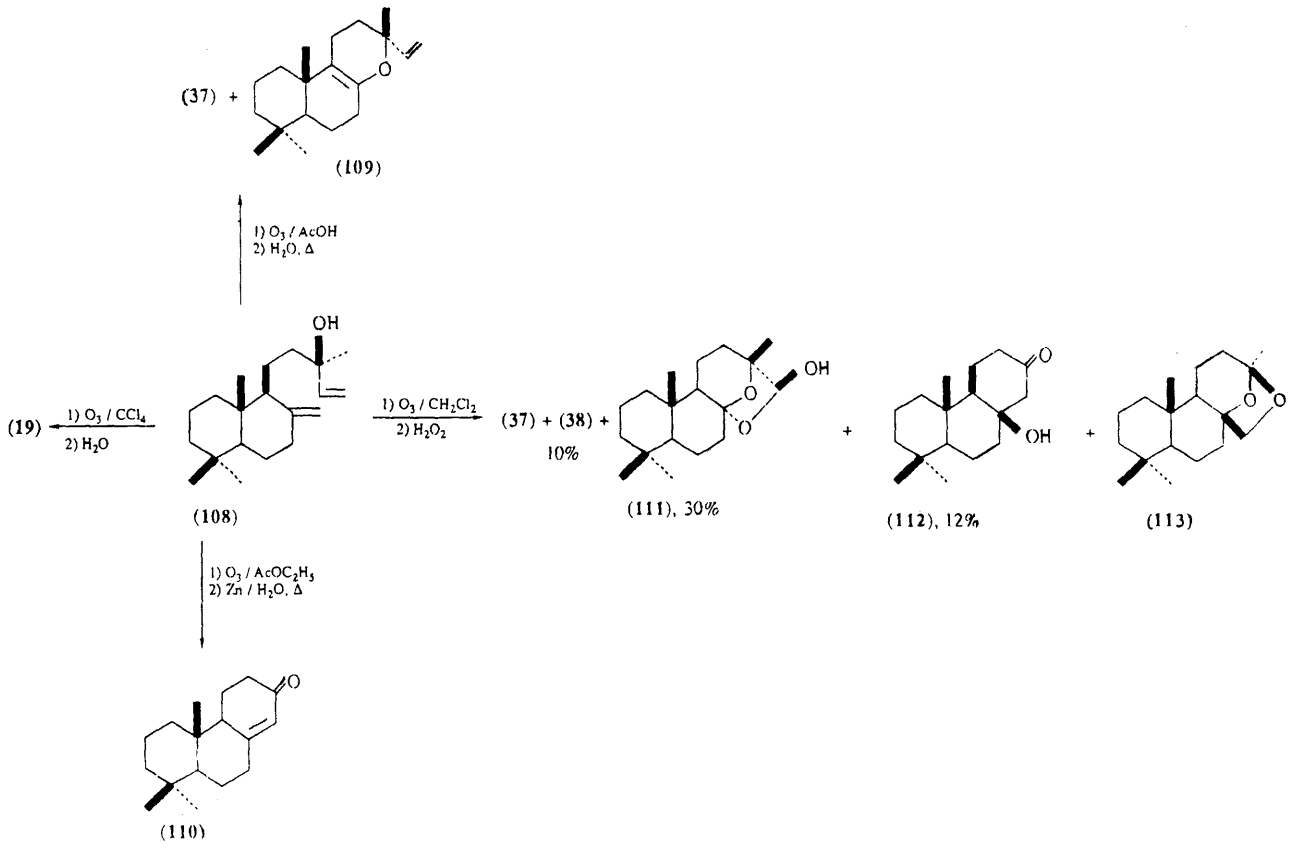
These authors[31] also investigated the ozonolysis products of manool acetate (**114**) under the same conditions. In this case also a complex mixture of products was obtained which are shown in Scheme 14 (with an indication of the yield). The cyclic products (**38**) and (**117**), called oxonides by the authors, were the unusual products of the ozonation and are unstable compounds. The ozonolysis of manool acetate (**114**) in dichloromethane in the presence of pyridine occurs in an altogether different way.[58] The triol (**118**) is isolated in 92% yield after reduction of the ozonolysis products with lithium aluminium hydride, i.e. only the double bond is broken under these conditions.

In view of the data given above it may be concluded that the ozonolysis of manool (**108**) does not as yet have any practical value.

Scheme 14

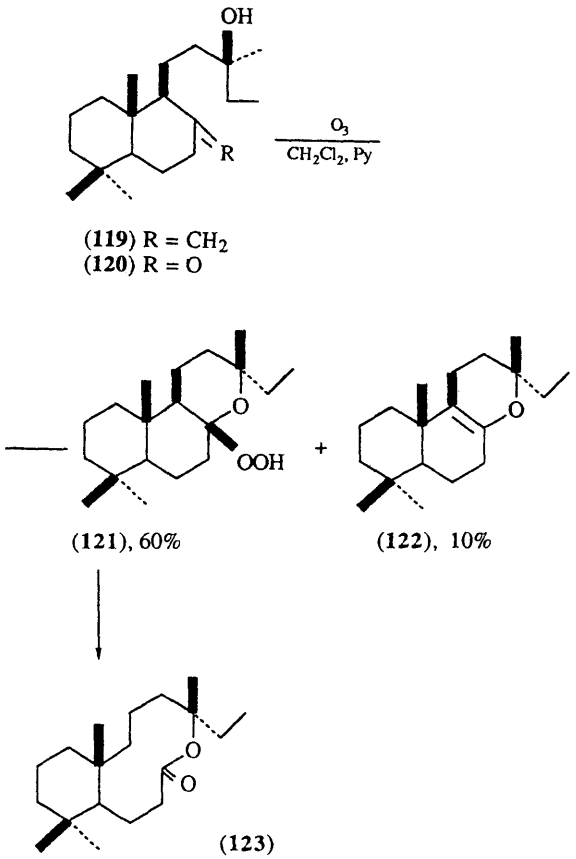


Scheme 13



The ozonolysis of dihydromanool (**119**) has also been investigated. Conducting the reaction in methanol and reducing the peroxide compounds with dimethyl sulphide leads smoothly to the hydroxyketone (**120**) (81%).[74] A mixture (6:1) of compounds (**121**) and (**122**) is formed in dichloromethane in the presence of pyridine (Scheme 15).[75] This result indicates that pyridine is ineffective as a reducing agent when hydroperoxides and not ozonides are formed as a result of the ozonolysis. The hydroperoxide (**121**) is unstable and on storage is converted into the epoxide (**122**). This hydroperoxide undergoes an interesting conversion under the action of mesyl chloride into the lactone (**123**) containing a ten-membered lactone ring. This reaction is of a general nature.

Scheme 15



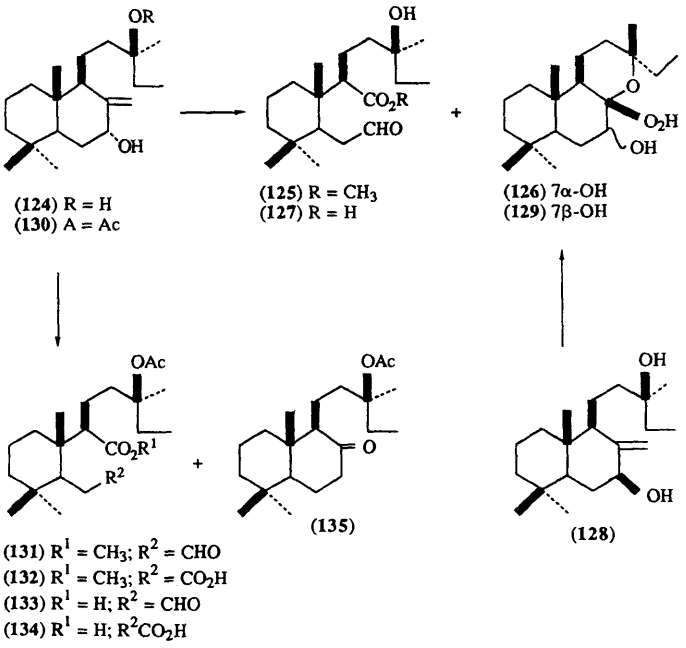
(**119**) R = CH_2
(**120**) R = O

(**121**), 60% (**122**), 10%

(**123**)

Interesting results were obtained by Everest and collaborators on ozonolysis of a series of allyl derivatives of dihydromanool.[54] They found that the character of the products formed depends on the solvent used and the conditions. Anomalous ozonolysis products were formed on simple evaporation of the solvent at low temperature, and differed depending on whether an aprotic solvent or an alcohol was used. On reduction of the ozonation product either a normal or a mixture of normal and anomalous reaction products was formed. The stronger the reducing agent the greater was the quantity of the normal product. For example, ozonolysis of 7α-hydroxydihydromanool (**124**) in methanol and evaporation of the solvent gave compounds (**125**) (40%) and (**126**) (34%) but with the same treatment and in dichloromethane compounds (**126**) (26%) and (**127**) (14%) were formed. The configuration of the hydroxyl group at position C(7) is important. 7β-Hydroxydihydromanool (**128**) gave a mixture of compounds (**125**) (8%) and (**129**) (30%) on ozonolysis in methanol (Scheme 16).

Scheme 16



(**124**) R = H
(**130**) A = Ac

(**125**) R = CH_3
(**127**) R = H

(**126**) 7α-OH
(**129**) 7β-OH

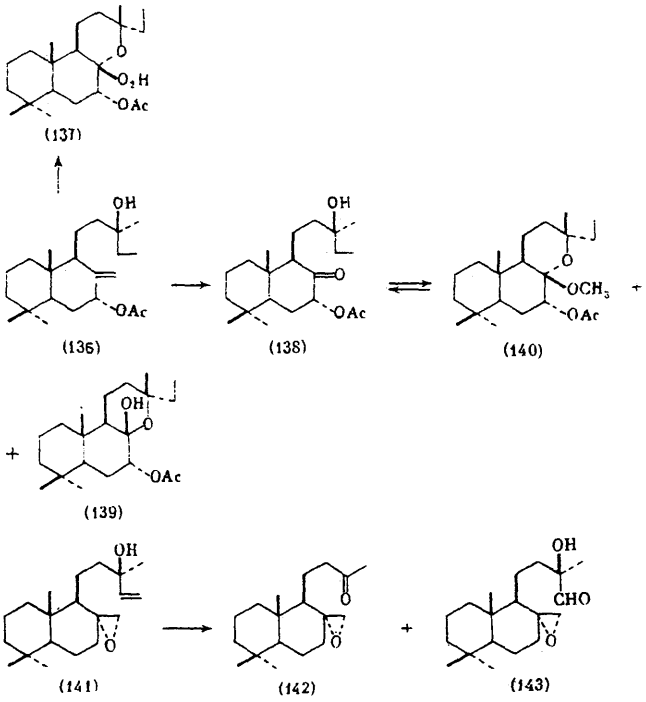
(**135**)

(**128**)

(**131**) R^1 = CH_3; R^2 = CHO
(**132**) R^1 = CH_3; R^2 = CO_2H
(**133**) R^1 = H; R^2 = CHO
(**134**) R^1 = H; R^2CO_2H

7α-Hydroxydihydromanool 13-monoacetate (**130**) is converted on ozonolysis in methanol into a mixture of the products (**131**) (37%) and (**132**) (46%), in dichloromethane into a mixture of compounds (**133**) (40%) and (**134**) (41%) and in methanol and reduction with dimethyl sulphide into the acetoxyketone (**135**) (88%). As might have been expected only the normal product, the unstable acetoxyhydroperoxide (**137**) (67%), is formed on ozonolysis of 7α-hydroxydihydromanool 7-monoacetate (**136**) (with a protected allylic hydroxyl group) in methanol with subsequent distillation of the methanol. An equilibrium mixture of substances (**138**) and (**139**) was isolated in 60% yield on reducing the ozonolysis product of the same compound with triethyl phosphite. If dimethyl sulphide is used as the reducing agent then a small quantity (17%) of the methoxyacetate (**140**) is formed in addition to compounds (**138**) and (**139**) (58%) (Scheme 17).[74]

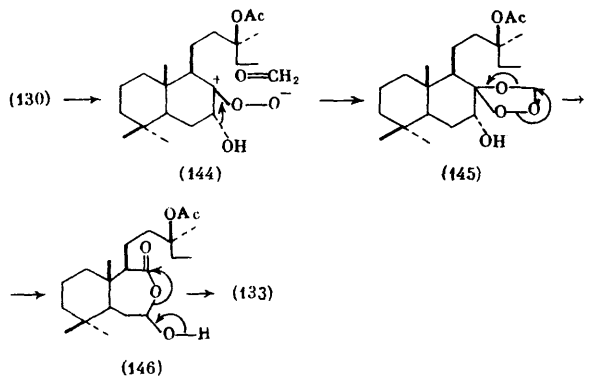
Scheme 17



The ozonolysis of 8(17)α-epoxymanool (**141**) has also been investigated.[54] The epoxyketone (**142**) (32%) was isolated on ozonolysis in methanol and evaporation of the solvent, but on reduction of the ozonolysis product with dimethyl sulphide a mixture of the epoxyketone (**142**) (15%) and aldehyde (**143**) (30%) was formed. If the same reduction is carried out with triethyl phosphite then the yields of compounds (**142**) and (**143**) are 6 and 36% respectively. Demole[76] effected the ozonolysis of the epoxymanool (**141**) in carbon tetrachloride and decomposed the ozonide with an aqueous solution of sodium bicarbonate. The ozonolysis product was subjected to further conversions without isolation, but judging by the results the yield of the epoxyketone (**142**) did not exceed 25–30%.

When analysing the above data it was concluded[54] that the mechanism proposed by Criegee for the ozonolysis of allylic alcohols[5,6] does not provide an adequate explanation. According to Criegee's mechanism the ozonolysis of compound (**130**) must proceed as in Scheme 18.

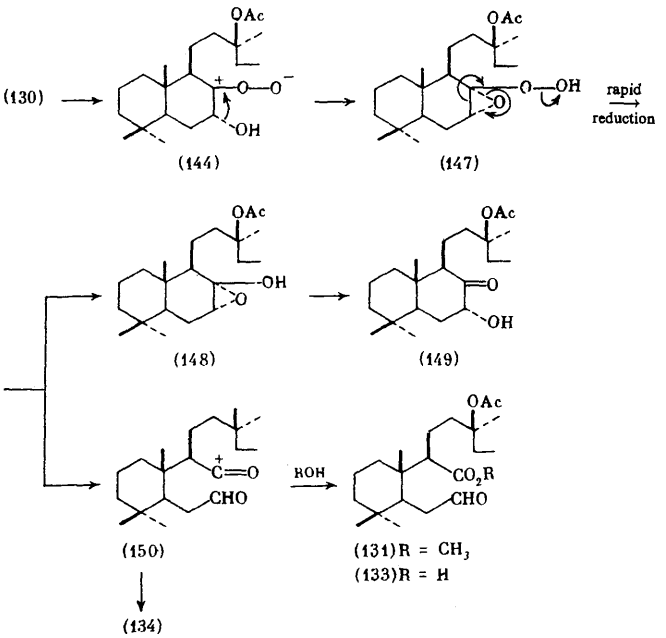
Scheme 18



If the reaction goes by this mechanism then: 1) the zwitterion (**144**) must react with methanol and give the corresponding methoxyhydroperoxide, 2) the C(9) atom, which is more electrophilic than C(7), should migrate preferentially to oxygen in the ozonide (**145**) and 3) the aldehydoacid (**133**) should be the reaction product and not its methyl ester which was in fact obtained.

Another mechanism has been proposed[54] for the ozonolysis of allylic alcohols [this is illustrated in Scheme 19 for compound (**130**) as an example] which explains all the facts mentioned above. In particular: 1) the rapid reduction of the ozonolysis product suppresses the formation of anomalous compounds, 2) carbon monoxide is evolved on ozonolysis of compounds in which there is a proton on the carbon atom bound to the carbonyl carbon atom and 3) specifically, the acids (**133**) and (**134**) are formed on ozonolysis of the unsaturated compound (**130**) in an aprotic slvent

Scheme 19

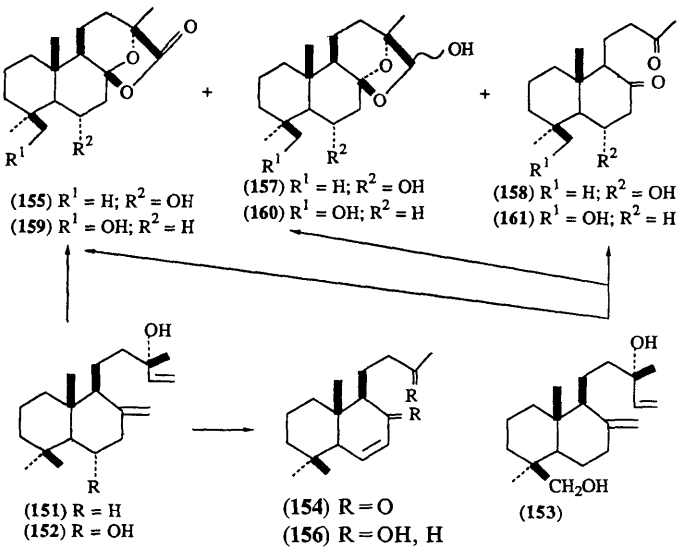


The very strained α-epoxyhydroperoxide (**147**) is spontaneously converted into the carbocation (**150**) which is neutralised by the solvent. When the grouping $-CH_2=CH-C-OH$ is present in the molecule, expulsion of proton occurs and carbon monoxide is evolved.

The ozonolysis of two derivatives of 13-epimanool (**151**) has also been investigated. These were larixol, labda-8(17),14-diene-6α,13(*S*)-diol, (**152**) and 13-epitorulosol, labda-8(17),14-diene-19,13(*S*)-diol (**153**).

The formation of a peroxide of composition $C_{19}H_{32}O_7$ of unestablished structure was recorded on ozonolysis of larixol (**152**), however, its decomposition was not carried out.[77] On carrying out the reaction in absolute methanol and treating the product with ammonium chloride a mixture was formed of no less than seven compounds among which the unsaturated diketone (**154**) and the hydroxylactone acetal (**155**) predominated (Scheme 20).[78] Other authors[79] have also ozonolysed larixol in methanol but the product was reduced with di-isobutylaluminium hydride. The diol (**156**) was isolated in low yield from the reaction products. Its structure was confirmed by X-ray structural analysis.

Scheme 20



The ozonolysis of larixol in methanol and reduction of the peroxide products with dimethyl sulphide or in dichloromethane in the presence of pyridine leads to a mixture of five compounds, identical in qualitative composition, the predominating components of which, compounds (**157**) and (**158**), were isolated and identified.[78]

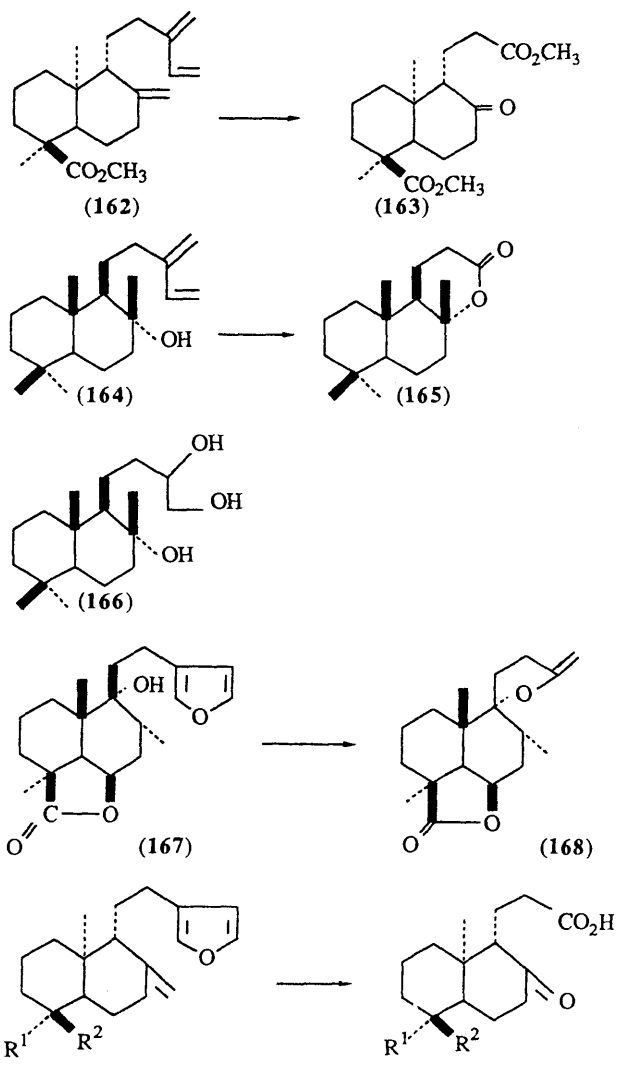
The ozonolysis of 13-epitorulosol (**153**) has been carried out under a variety of conditions: in methanol with subsequent treatment of the ozonation product with dimethyl sulphide, in a mixture of dichloromethane and pyridine and in hexane with decomposition of the ozonide by heating with water.[80] In all cases the reaction product was a mixture of three compounds (**159**)–(**161**). In the first case the hydroxylactone (**159**) predominates and in the latter the two compounds (**160**) and (**161**) predominate (Scheme 20).

The data given above indicate that the main products of the ozonolysis of larixol (**152**) and 13-epitorulosol (**153**) are formed by fission of their double bonds and the single bond at C(13)–C(14) and by the reaction of the keto group at C(8) with the hydroxyl group at C(13) and the functional group generated at C(14).

VII. Ozonolysis of labda-13(16),14-diene compounds, furanolabdanoids and labd-13(14)-enoids with oxygen-containing functional groups at C(15) and C(16)

On treating representatives of this structural group of labdanoid diterpenes with ozone the side chain is, as a rule, shortened by three carbon atoms. On ozonolysis of the methyl ester of *ent*-labda-8(17),13(16),14-trien-18-oic acid (**162**) in a mixture of acetic acid and ethyl acetate at 0 °C followed by oxidative fission of the ozonation products with alkaline hydrogen peroxide, Ourisson and collaborators[81] isolated, after methylation and diazomethane, the ketodiester (**163**) (25%) (Scheme 21). In contrast to compound (**162**) the ozonolysis of isoabienol (**164**) in absolute methanol with subsequent hydrogenation of the product over Lindlar catalyst leads to ambreinolide (**165**) (93%). The yield of ambreinolide was less (85%) on using dimethyl sulphide as reducing agent.[82] It is more convenient to carry out the ozonolysis of isoabienol (**164**) in ethyl acetate in the presence of pyridine (72% ambreinolide yield).[83] If the ozonolysis of isoabienol is carried out in methanol and the peroxide products are reduced with lithium borohydride then the triol (**166**) is the main reaction product (72%). These data show that on using dimethyl sulphide for the reduction of the peroxide ozonolysis products of isoabienol, there is an initial rearrangement with fission of the single carbon–carbon bond at C(13)–C(14) and then reduction occurs. Potassium borohydride only reduces the peroxide compounds. In view of the value of the ambreinolide for perfume manufacture[2] and the cheapness of isoabienol (it is contained in large amounts in the needles of the Scots pine[84]), the ozonolysis of the latter may be of practical interest.

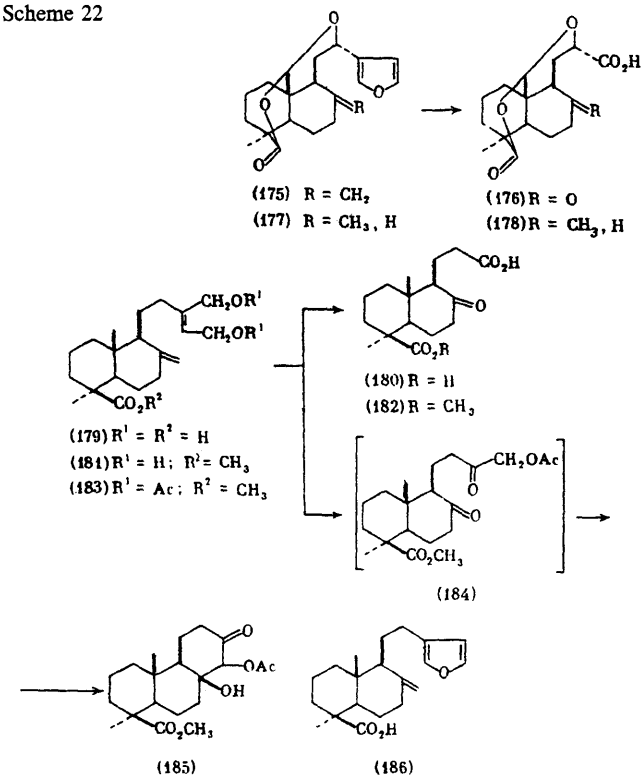
Scheme 21



Marrubiin (**167**) was one of the first of the furanolabdanoids to be subjected to ozonolysis (see Scheme 21).[85] The reaction was carried out in acetic acid and the reaction product proved to be the dilactone (**168**) (20%). Polyalthic acid (**169**) was ozonolysed in the same solvent. The ketodiacid (**170**) (17%) was isolated after treatment of the reaction product with hydrogen peroxide in alkali.[86] On ozonolysis of polyalthic acid methyl ester (**171**) in chloroform and fission of the ozonide with hydrogen peroxide, the reaction product was the monoester (**172**) (25%) of the ketodiacid (**170**). An epimer of polyalthic acid, daniellic acid (**173**), was oxidised with ozone in dichloromethane in the presence of pyridine and the product oxidised further with hydrogen peroxide in alkali. These conditions are appropriate since the yield of the ketodiacid (**174**) proved to be fairly high (66.5%).[29] Sciadin (**175**), which is more complex in structure, gave a product (**176**) on ozonolysis in chloroform in only 8.7% yield.[87] The ozonation of dihydrosciadin (**177**) to compound (**178**) proceeded with a better yield (17.4%) but in this case the products of ozonolysis were boiled with water.

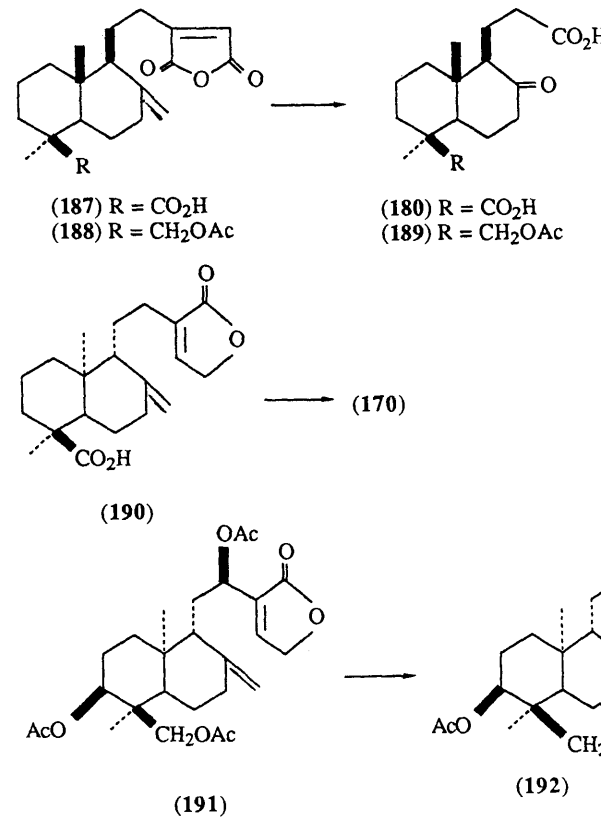
Sciadopic acid (**179**) is an example of a compound with a double bond at C(13)–C(14) and functional groups at C(15) and C(16) (Scheme 22).[84] The ketodiacid (**180**) (27%) was isolated on treating it with ozone in dichloromethane with oxidative fission of the product with hydrogen peroxide in alkali. Fission of the ozonolysis product by heating with water proved to be less effective. In such cases methyl sciadopate (**181**) was converted into compound (**182**) in only 10% yield (after alkaline saponification). The ozonolysis of the diacetoxyester (**183**) occurs in an altogether different way. The ozonolysis was carried out in dichloromethane and the product was reduced with zinc in acetic acid. The tricyclic compound (**185**) was obtained in this case in 77% yield, evidently formed by aldol cyclisation of the ozonation product, via. the diketoester (**184**) (Scheme 22).

Scheme 22



The transformation products of lambertianic acid (**186**) and the anhydrides (**187**) and (**188**) belong to the same group of labdanoids. On ozonolysis in a mixture of ethyl acetate and acetic acid with oxidative fission of the products with hydrogen peroxide the ketodiacid (**180**) (56%) and the ketoacid ester (**180**) (56%) and the ketoacid ester (**189**) (44%) respectively were obtained (Scheme 23).[89]

Scheme 23



The ozonolysis labdanoids containing an unsaturated γ-lactone grouping in the side chain, such as nivenolide (**190**), occurs in a similar manner.[90] On ozonolysis in methanol and treatment of the product with hydrogen peroxide in alkali the ketodiacid (**170**) (49%) was isolated (Scheme 23).

If there is an oxygen-containing functional group at position C(12) in a labdanoid with an unsaturated γ-lactone grouping then fission of the single bond at C(12)–C(13) occurs on ozonolysis. For example, the derivative andrographolide (**191**) gave the ketoacid (**192**) on ozonolysis in ethyl acetate and treatment of the product with hydrogen peroxide.[91]

* * *

The data accumulated show that ozonolytic transformations of labdanoids affect the carbon side chain and ring A. If there are isolated double bonds and no functional groups in the positions 4 and 5 relative to them in this structural fragment then the ozonolysis proceeds fairly unequivocally. If there are functional groups in the labdanoids at positions C(8) and C(12)–C(16) then ozonolysis leads to a complex mixture of compounds. This is a particular feature of labdanoids with an allyl structural fragment, a furan ring and an

unsaturated γ-lactone grouping. The latter two types of compound give α-dicarbonyl compounds as primary ozonolysis products.

The investigation of the ozonolysis products of the available labdanoids (sclareol, manool, abienols, etc.) and the effect of the reaction conditions on the route of the process, the clarification of the mechanism and principles of the ozonolysis reaction and the development of industrial ozonolytic processes are all problems of both theoretical and practical interest.

References

1. P F Vlad, G V Lazur'evskii *Bitsiklicheskie Diterpenoidy* (Bicyclic Diterpenoids), RIO, AN Moldavian SSR, Kishinev, 1967, 138 pp
2. P F Vlad, M N Koltsa *Sintez i Primenenie Dushistykh Veshchestv iz Labdanovykh Diterpenoidov* (Synthesis and Application of Aromatic Principles from Labdanoid Diterpenes), Shtiintsa, Kishinev, 1988, 182 pp
3. P F Vlad *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1991, (4) 428–434
4. Japanese Appl. 62-252703; *Ref. Zh. Khim.*, 1989, 50390P
5. P S Bailey *Chem. Rev.*, 1958, **59**(5) 925–1010
6. P S Bailey *Ozonation in Organic Chemistry. Olefinic Compounds*, Acad. Press., New York, 1978, Vol. 1, 272 pp
7. S D Razumovskii, G E Zaikov *Ozon i Ego Reaktsii s Organicheskimi Soedineniyami (Kinetika i Mekhanizm)* [Ozone and its Reactions with Organic Compounds (Kinetics and Mechanism)], Nauka, Moscow, 1974, 322 pp
8. P De Mayo *Terpenoids* (Translated into Russian), Izd. Inostr. Lit., Moscow, 1963, 494 pp
9. J S Glasby *Encyclopedia of the Terpenoids*, John Wiley and Sons, Chichester–New York, 1982, Vol. 1, 2646 pp
10. *Nomenklaturnie Pravila IYuPAK po Khimii. T. 3. Organicheskaya Khimiya: Vysokomolekulyarnye Soedineniya* IUPAC Nomenclature Rules in Chemistry, Vol. 3, Organic Chemistry: High Molecular Compounds), Izd. VINITI, Moscow, 1983, 403 pp
11. F E King, G Jones *J. Chem. Soc.*, 1955, (3) 658–665
12. T Nakano, C Djerassi *J. Org. Chem.*, 1961, **26**(1) 167–173
13. J D Cocker, T G Halsall *J. Chem. Soc.*, 1956, (11) 4262–4271
14. J D Cocker, T G Halsall *J. Chem. Soc.*, 1957, (10) 4401–4403
15. C Enzell, O Theander *Acta Chem. Scand.*, 1962, **16**(10) 607–614
16. P F Vlad, G V Lazur'evskii *Zh. Obshch. Khim.*, 1965, **35** 80–85
17. G Chandra, J Clark, J Mc Lean, et al. *J. Chem. Soc.*, 1964, (10) 3648–3655
18. J Haeuser, S F Hall, A C Oehlschlager, et al. *Tetrahedron*, 1970, **26**(14) 3461–3465
19. M Gonzalez-Sierra, A C Olivieri, M I Colombo, et al. *J. Chem. Soc., Perkin Trans. 1*, 1989, (8) 1393–1399
20. A C Olivieri, M Gonzalez-Sierra, E A Ruveda *J. Org. Chem.*, 1986, **51**(14) 2824–2826
21. R C Cambie, B D Palmer *Aust. J. Chem.*, 1981, **34**(6) 1265–1284
22. C W L Bevan, D E U Ekong, J I Okogun *J. Chem. Soc.*, 1968, (9) 1063–1066
23. R M Carman, H C Deeth *Aust. J. Chem.*, 1971, **24**(2) 353–359
24. V P Arya, H Erdman, T Kubota *Tetrahedron*, 1961, **16**(3) 255–263
25. R C Cambie, K N Joblin, A F Preston *Aust. J. Chem.*, 1971, **24**(11) 2365–2377
26. C W L Bevan, D E U Ekong, J I Okogun *J. Chem. Soc. C*, 1968, (9) 1067–1070
27. S Braun, H Breitenbach *Tetrahedron*, 1977, **33**(1) 145–150
28. L Ruzicka, E Bernold, A Tallichet *Helv. Chim. Acta*, 1941, **24**(2) 223–237
29. J Haeuser, R Lombard *Tetrahedron*, 1961, **12**(4) 205–214
30. D Do Khac Manh, M Fetizon, J P Flament *Tetrahedron*, 1975, **31**(16) 1897–1902
31. P K Grant, H T L Liau *Aust. J Chem.*, 1978, **31**(8) 1791–1797
32. H R Schenk, H Gutmann, O Jeger, et al. *Helv. Chim. Acta*, 1952, **35**(3) 817–829
33. M A Chirkova, A E Gorbunova, A I Lisina, et al. *Khim. Prir. Soedin.*, 1966, (2) 99–104
34. P F Vlad, A G Russo, Chan Kuang Fan *Zh. Obshch. Khim.*, 1969, **39**(2) 451–457
35. R M Carman, D E Cowley *Tetrahedron Lett.*, 1968, (23) 2723–2724
36. M A Chirkova, V A Pentegova *Khim. Prir. Soedin.*, 1969, (4) 247–251
37. V A Raldugin, V A Pentegova *Khim. Prir. Soedin.*, 1971, (5) 595–597
38. P F Vlad, M N Koltsa, A G Russo *Zh. Obshch. Khim.*, 1973, **43**(3) 650–655
39. V A Raldugin, O V Sudakova, L I Demenkova, et al. *Khim. Prir. Soedin.*, 1988, (4) 601–602
40. M A Chirkova, A K Dzizenko, V A Pentegova *Khim. Prir. Soedin.*, 1967, (1) 86–90
41. L Ruzicka, H Gutmann, O Jeger, et al. *Helv. Chim. Acta*, 1948, **31**(6) 1746–1752
42. M N Koltsa, G N Mironov, A N Aryku, et al. *Khim. Prir. Soedin.*, 1991, (1) 43–50
43. Authors Certificate 1 594 163 USSR; *Byull. Izobret.*, 1990, (25) 130
44. Y Oshima, J I Saito, H Hikino *Phytochemistry*, 1988, **27**(2) 624–626
45. S W Pelletier, S Lajsic, Y Ohtsuka, et al. *J. Org. Chem.*, 1975, **40**(11) 1607–1609
46. W Cocker, B E Cross, S R Duff, et al. *J. Chem. Soc.*, 1953, (9) 2540–2547
47. P F Vlad, M N Koltsa, V E Sibirtseva, et al. *Zh. Obshch. Khim.*, 1980, **50**(1) 213–217
48. G Ohloff, W Giersch, K H Schulte-Elte, et al. *Helv. Chim. Acta*, 1976, **59**(4) 1140–1157
49. M M Janot *Ann. Chim. (Paris)*, 1932, **17** 5–127
50. P F Vlad, A N Aryku, M N Koltsa *Khim. Prir. Soedin.*, 1991, (4) 502–511
51. V N Odinokov, P F Vlad, O S Kukovinets, et al. *Dokl. Akad. Nauk SSSR*, 1983, **269**(4) 853–855
52. A N Aryku, M N Koltsa, P F Vlad, et al. *Khim. Prir. Soedin.*, 1991, (3) 343–349
53. Authors Certificate 1 409 631 USSR; *Byull. Izobret.*, 1988, (26) 94
54. D J Everest, P K Grant, G C Slim, et al. *Aust. J. Chem.*, 1988, **41**(7) 1025–1035
55. J R Hosking, C W Brandt *Chem. Ber.*, 1935, **68**(1) 37–47
56. R C Cambie, A F Preston, P D Woodgate *Aust. J. Chem.*, 1973, **26**(8) 1821–1825
57. G Ohloff *Liebigs Ann. Chem.*, 1958, **617**(1–3) 134–147

58. R C Cambie, K N Joblin, A F Preston *Aust. J. Chem.*, 1972, **25**(8) 1767–1778
59. J A Giles, J N Schumacher, S M Mims *Tetrahedron*, 1962, **18**(1) 169–176
60. S Chandresekharan, T Chakrabartty *J. Indian Chem. Soc.*, 1986, **45**(3) 208–212
61. I C Coste-Maniere, J P Zahra, B Waegell *Tetrahedron Lett.*, 1988, **29**(9) 1017–1020
62. L Ruzicka, C F Seidel, L L Engel *Helv. Chim. Acta*, 1942, **25** 621–630
63. R C Cambie, S H Leong, B D Palmer, et al. *Aust. J. Chem.*, 1980, **33**(1) 155–168
64. R C Cambie, J M Coddington, P S Rutledge, et al. *Austr. J. Chem.*, 1989, **42**(7) 1115–1124
65. J A Giles, J N Schumacher *Tetrahedron*, 1961, **14**(3–4) 246–251
66. M Stoll, M Hinder *Helv. Chim. Acta*, 1950, **33**(5) 1251–1259
67. M Stoll, M Hinder *Helv. Chim. Acta*, 1953, **36**(7) 1984–1995
68. M Hinder, M Stoll *Helv. Chim. Acta*, 1950, **33**(5) 1308–1312
69. A N Aryku, M N Koltsa, P F Vlad *Khim. Prir. Soedin.*, 1991, (2) 209–214
70. R C Cambie, K N Joblin, N K McCallum *Aust. J. Chem.*, 1970, **23**(7) 1439–1455
71. J R Hosking *Chem. Ber.*, 1936, **69**(4) 780–785
72. P K Grant, R Hodges *J. Chem. Soc.*, 1960, (12) 5274–5275
73. J A Barltrop, D Giles, J R Hanson, et al. *J. Chem. Soc.*, 1962, (6) 2534–2636
74. P K Grant, L R Hanton, S F Tsai *Aust. J. Chem.*, 1985, **38**(10) 1461–1470
75. P K Grant, C K Lai, J S Prasad, et al. *J. Chem. Soc.*, 1988, **41**(5) 711–725
76. E Demole *Experimentia*, 1964, **20**(11) 609–610
77. J Haeuser *Bull. Soc. Chim. Fr.*, 1965, (9) 2654
78. P F Vlad, A N Kyl'chik, E N Shmidt *Khim. Prir. Soedin.*, 1986, (5) 577–584
79. E N Shmidt, T V Romanchenko, V A Pentegova, et al. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.*, 1988, (5) Pt. 2, 119–122
80. P F Vlad, A N Aryku, M N Koltsa, et al. *Khim. Prir. Soedin.*, 1987, (4) 524–527
81. S F Khao, A C Oehlschlager, G Ourisson *Tetrahedron*, 1973, **29**(21) 3379–3388
82. Authors Certificate 1 399 302 USSR; *Byull. Izobret.*, 1988, (20) 105
83. A N Aryku, G N Mironov, M N Koltsa, et al. *Khim. Prir. Soedin.*, 1991, (1) 50–53
84. R Ekman, R Sjoholm, K Hannus *Acta Chem. Scand., Ser. B*, 1977, **31**(10) 921–922
85. W Cocker, B E Cross, S R Duff, et al., *J. Chem. Soc.*, 1953, (9) 2540–2547
86. R W Gopinach, T R Covindachari, P C Parthasarathy, et al. *Helv. Chim. Acta*, 1961, **44**(4) 1040–1049
87. M Sumimoto *Tetrahedron*, 1963, **19**(4) 643–655
88. M Sumimoto, Y Tanaka, K Matsufuji *Tetrahedron*, 1964, **20**(6) 1427–1434
89. W G Dauben, V F German *Tetrahedron*, 1966, **22**(2) 679–683
90. E T Rojas, L Rodriguez-Hahn *Phytochemistry*, 1978, **17**(3) 574–575
91. M P Cava, W R Chan, L J Hayes, et al. *Tetrahedron*, 1962, **18**(4) 397–403

Received 16th January 1992

Translated from *Uspekhi Khimii* **61** 1332–1391 (1992) U.D.C. 542.95:547.91

The synthesis of insect juvenile hormones and their analogues

V N Odinokov, O S Kukovinets, R A Zainullin, G A Tolstikov
Institute of Organic Chemistry, Urals Division of the Russian Academy of Sciences

ABSTRACT. **The methods of synthesis of insect juvenile hormones and their natural and synthetic analogues (juvenoids) are considered. Much attention is paid to juvenoids of the 2,4-dienoate class, including oxa and aza derivatives and cyclic and heterocyclic compounds, which display selective activity towards vairous forms of insect.**

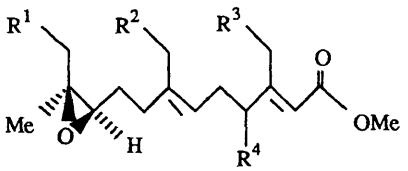
The bibliography contains 263 references.

Contents

I. Introduction 731
II. Synthesis of natural juvenile hormones 731
III. Synthesis of natural analogues of juvenile hormones 735
IV. Synthetic analogues of juvenile hormones 739

I. Introduction

It has been established in the last thirty years that certain terpenoid compounds, referred to as the juvenile hormones (JH), actively participate in the regulation of the development of insects at the larval stage.[1] Five native juvenile hormones have so far been isolated and identified, viz. JH-1, JH-II, JH-III, JH-0 and 4-Me-JH-I.[1–5]



JH-I ($R^1=R^2=Me$, $R^3=R^4=H$); JH-II ($R^1=Me$, $R^2=R^3=R^4=H$); JH-III ($R^1=R^2=R^3=R^4=H$); JH-O ($R^1=R^2=R^3=Me$, $R^4=H$); 4-Me-JH-I ($R^1=R^2=R^4=Me$, $R^3=H$).

The titre of JH in an insect at metamorphosis of the larva to the imago is close to zero. It was shown that the introduction of extraneous JH at this time seemingly affects the fate of a population due to disturbance of the natural cycle of insect development leading to a subsequent reduction in their number. This possible method of regulating the number of insects enables JH to be considered as insecticides of a new generation. They are ecologically safe and act exclusively upon Arthropods.

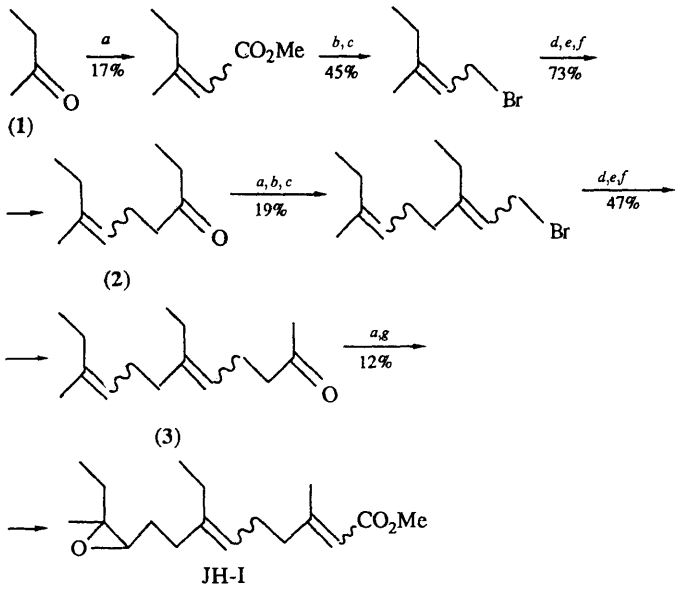
Since JH are present in insects in insignificantly small concentrations, their isolation from natural sources appears to be practically impossible and the only realistic route to obtain them is by chemical synthesis. The promise of the practical use of these regulators of insect development was marked by the discovery that JH action is possessed by certain natural compounds and by a whole series of synthetic compounds close in structure to the native JH. These analogues of the juvenile hormones (AJH) are known as juvenoids. Compounds have been discovered among the large number of AJH with JH activity significantly higher than that of the natural JH. Active juvenoids are found among compounds structurally close to the native JH and among compounds the structure of which only remotely suggests the structure of a JH.

Several monographs and reviews[6–16] have been devoted to the synthesis and study of the biological activity of JH and AJH. However they do not adequately reflect the information on the 2,4-dienoates, their oxa and aza derivatives and on the juvenoids containing hetero- and carbocycles. In addition, new reports of work in this area have recently appeared.

II. Synthesis of natural juvenile hormones

The phosphonate modification of the Wittig reaction, which is usually used to construct a trisubstituted double bond in the synthesis of JH, leads to a mixture of geometric isomers.[17,18] Thus the three-step condensation of trimethyl phosphonoacetate with the initial (**1**) and intermediate (**2**), (**3**) ketones gave JH as a mixture of (*Z*) and (*E*) isomers at the Δ^2 and Δ^6 bonds (Scheme 1).[19]

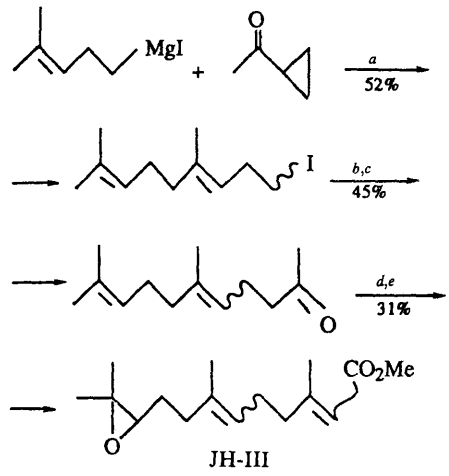
Scheme 1



a: $(MeO)_2P(O)CHCO_2Me$; *b*: $HAlH_4$; *c*: PBr_3; *d*: Mg; *e*: $MeCH_2COCH_2CO_2Et$; *f*: Δ; *g*: 3-$ClC_6H_4CO_3H$

A similar result was obtained in the synthesis of JH-III (Scheme 2).[20]

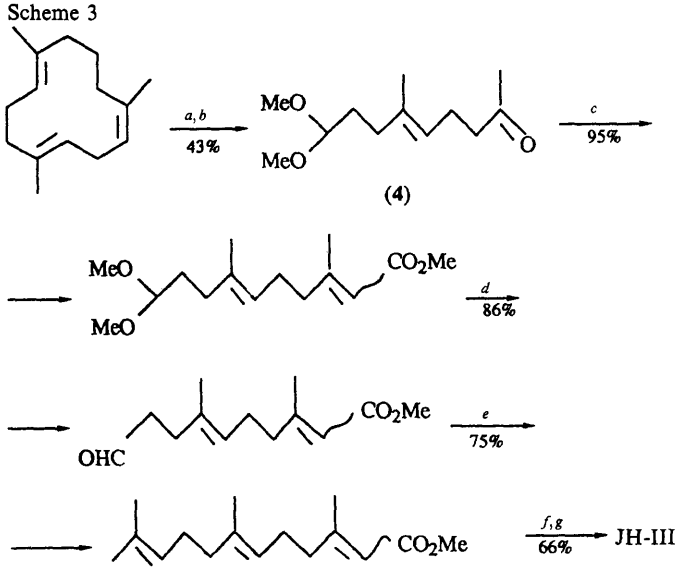
Scheme 2



a: H^+; *b*: Mg/Et_2O; *c*: Ac_2O, −70 °C; *d*: $(MeO)_2P(O)\overset{\ominus}{C}HCO_2Me$; *e*: NBS (*N*-bromosuccinimide)/K_2CO_3.

A mixture of geometric isomers at the Δ^2 bond is formed in the synthesis of JH-III via the selective ozonolysis of (1*E*, 5*E*, 9*E*)-trimethyl-1,5,9-cyclododecatriene and the Petersen reaction with the intermediate ketone (**4**) (Scheme 3).[21]

Scheme 3

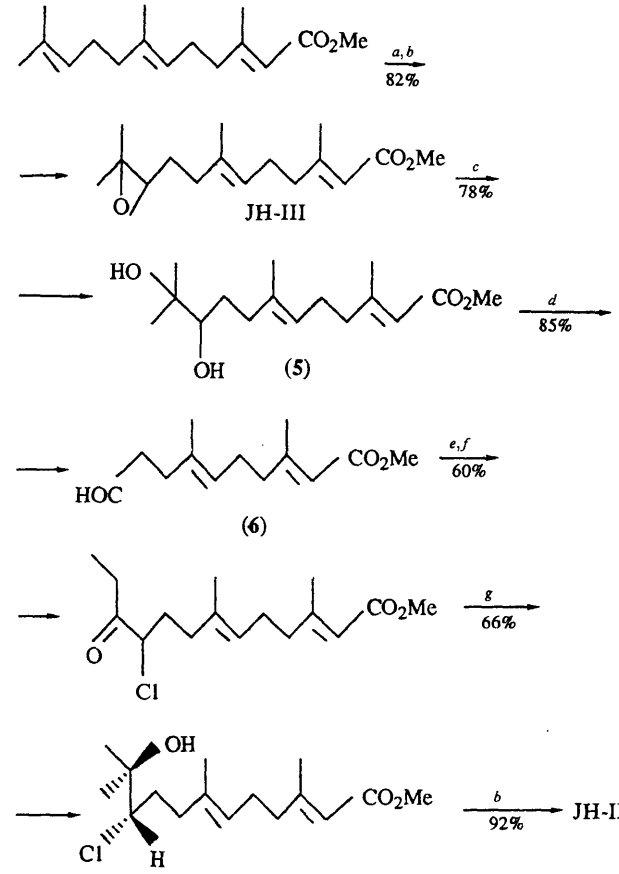


a: O_3/MeOH; *b*: MeOH/NH_4Cl; *c*: $Me_3SiCH_2CO_2Me$/iso-Pr_2NH; *d*: Py.TsOH/Me_2CO; *e*: $Me_2C{=}PPh_3$; *f*: NBS/THF; *g*: K_2CO_3/MeOH.

The individual (2*E*, 6*E*) isomers, which usually display higher activity than the other isomers,[22] were isolated by column chromatography.

Stereospecific syntheses of JH-II have been carried out from (*E*,*E*)-farnesol, methyl (*E*)-geranoate and methyl (*E*,*E*)-farnesenate [methyl (2*E*, 6*E*, 10*E*)-3,7,11-trimethyl-2,6,10-dodecanoate].[18,23] The epoxidation according to Van Tamelen[24] of the terminal double bond in methyl farnesenate gave JH-III. Subsequent opening of the epoxide to the glycol (**5**) and decomposition of the latter with sodium periodate led to the aldehyde (**6**), converted subsequently into the desired JH-II (Scheme 4).[18]

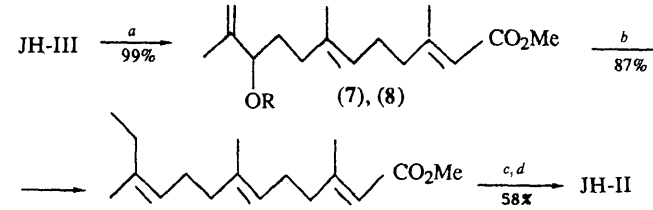
Scheme 4



a: NBS, *b*: K_2CO_3/MeOH; *c*: $HClO_4$; *d*: HIO_4; *b*: $MeCH_2C(OMe){=}PPh_3$; *f*: NCS(*N*-chlorosuccinimide); *g*: MeMgI.

It was established that on distillation JH-III is converted in high yield into the allyl alcohol (**7**), the acetate of which (**8**) is alkylated by lithium dimethylcuprate with the formation of JH-II (Scheme 5).[18,25]

Scheme 5



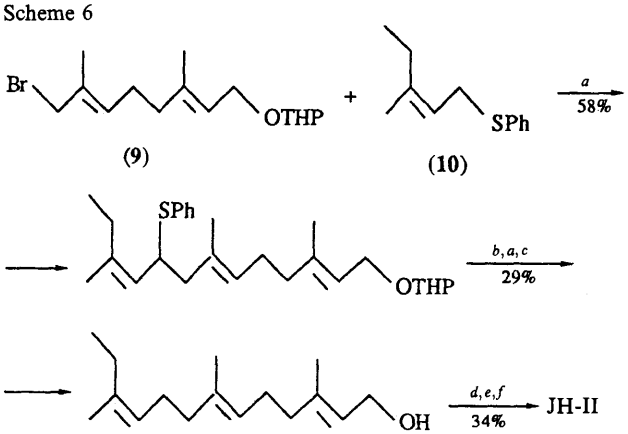
R = H(7), Ac(8).
a: Δ; *b*: Me_2CuLi; *c*: NBS; *d*: K_2CO_3/MeOH.

The syntheses of JH through alkylation of allyl substrates and the *syn*-addition of cuprates and organoaluminium reagents to acetylenes have been discussed in a review.[12] Much attention was paid in the

review to the stereospecific construction of trisubstituted alkenes using sulphur-containing intermediates in the synthesis of JH.

The key stage in one of the syntheses of racemic JH-II is the coupling of the allyl bromide (**9**) with the deprotonated allyl phenyl sulphide (**10**) (Scheme 6).[26,27]

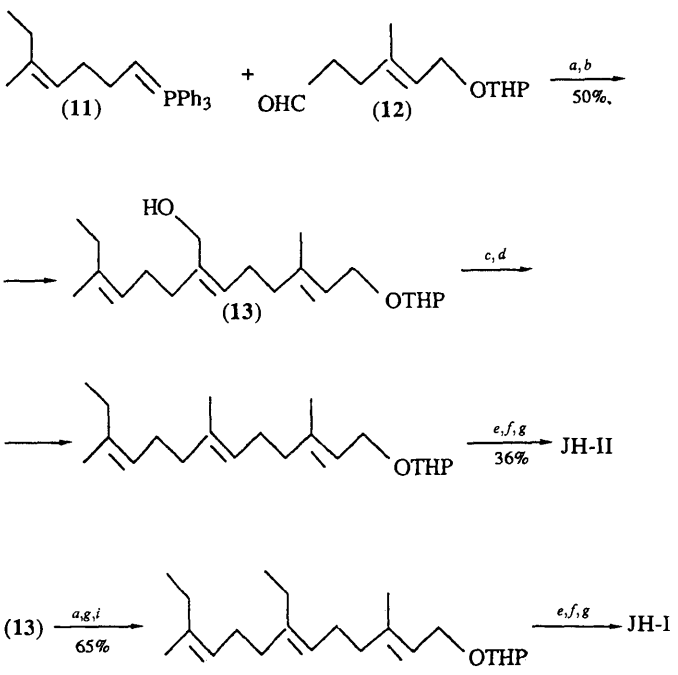
Scheme 6



THP – 2-tetrahydropyran-1-yl; *a*: n-BuLi; *b*: TsOH/MeOH; *c*: Li; *d*: MnO_2; *e*: MnO_2/NaCN/MeOH; *f*: 3-$ClC_6H_4CO_3H$.

Deprotonation of the intermediate in the reaction of phosphorane (**11**) with the aldehyde (**12**) and subsequent treatment with formaldehyde led to compound (**13**) the subsequent transformation of which gave the desired JH-II and JH-I (Scheme 7).[28]

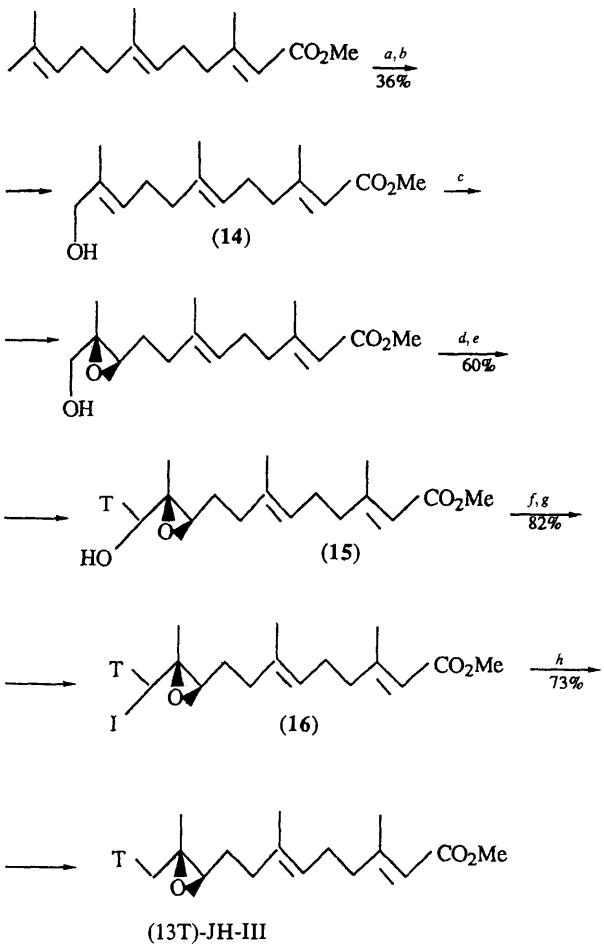
Scheme 7



a: n-BuLi; *b*: CH_2O; *c*: TsCl/Py; *d*: $LiAlH_4$; *e*: MnO_2; *f*: MnO_2/NaCN/MeOH; *g*: 3-$ClC_6H_4CO_3H$; *h*: $CH_2=PPh_3$; *i*: H_2O_2/EtOH/NH_2NH_2.

In 1970 it had already been established that the optically active natural JH have the (10*R*, 11*S*) configuration.[29] Subsequent investigations showed that the synthetic (+) enantiomers corresponding to that configuration displayed higher biological activity than the racemates.[30] One of the synthetic approaches to optically active JH is based on the Sharpless asymmetric epoxidation of allyl alcohols.[31,32] The synthesis of (10*R*, 11*S*)-JH-III containing tritium at C(13) is effected by the allylic oxidation of methyl farnesenate at the terminal position with subsequent asymmetric epoxidation of the resulting allyl alcohol (**14**). The tritiated hydroxy-epoxide (**15**) was deoxygenated via the iodide (**16**) to [13-T]-JH-III (Scheme 8).[33]

Scheme 8

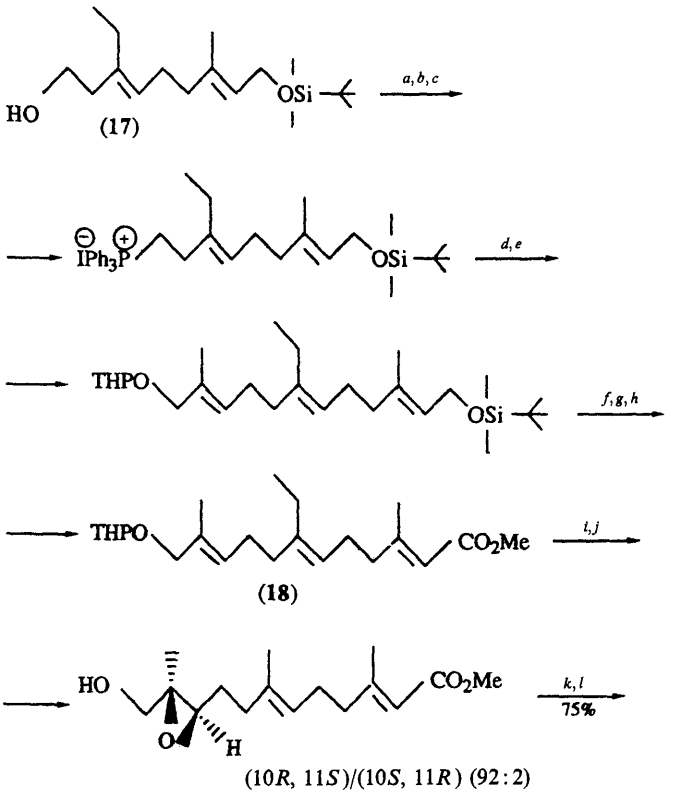


a: BuOOH/SeO_2; *b*: $NaBH_4$; *c*: (iso-PrO)$_4$Ti/t-BuOOH/iso-C_3H_7.OOCCH(OH)CH(OH).$COOC_3H_7$-iso; *d*: CrO_3/Py; *e*: $NaBT_4$; *f*: TsCl/Py; *g*: NaI/Me_2CO; *h*: $NaBH_3CN$.

The asymmetric epoxidation of the triene (**18**) also served as a key stage in the synthesis of optically active (10*R*, 11*S*)-JH-I from the homoallyl alcohol (**17**). Further transformations not affecting the chiral centre led to the (10*R*, 11*S*) enantiomer identical to the

natural JH or to its (12-D, 13-D) analogue.[34] The products obtained had high optical activity (95%) (Scheme 9).

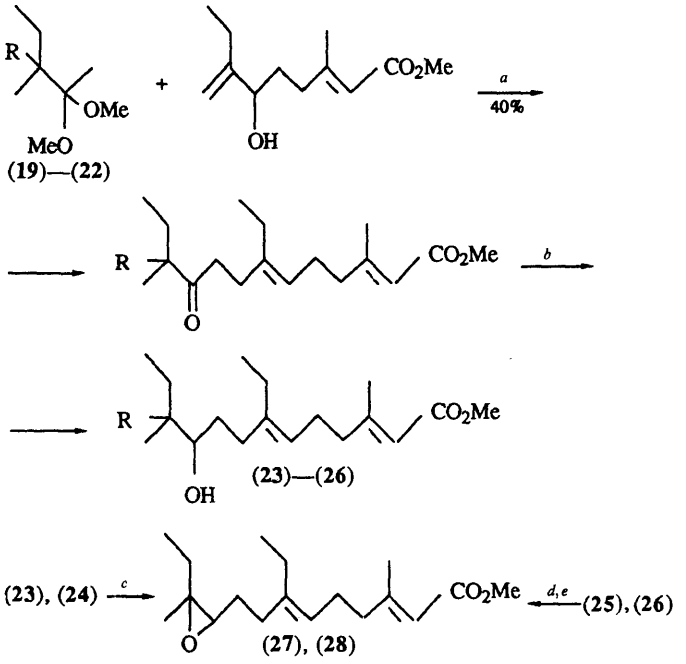
Scheme 9



a: TsCl/Py; *b*: NaI; *c*: Ph_3P; *d*: BuLi; *e*: $MeC(O)CH_2OTHP$; *f*: Bu_4NF; *g*: MnO_2; *h*: $MnO_2-NaCN-MeOH$; *i*: TsOH.Py.MeOH; *j*: t-BuOOH – CH_2Cl_2 – $Ti(OPr\text{-}iso)_4$ – $C_2H_5OOCCH(OH)CH(OH).COOC_2H_5$; *k*: CrO_3/Py; *l*: $Ph_3P=CH_2$; *m*: H_2 or $D_2/Rh(Ph_3P)_3Cl$.

Stereospecific syntheses of the (10*R*,11*S*) (**27**) and (10*R*,11*S*) (**28**) enantiomers of JH-I were effected from the optically active 2,2-dimethoxy-3-methylpentan-3-ols (**19**), (**20**) and 3-chloro-2,2-dimethoxy-3-methylpentanes (**21**) and (**22**). The optical purity of the JH obtained in these syntheses was 80–90% (Scheme 10).[35,36]

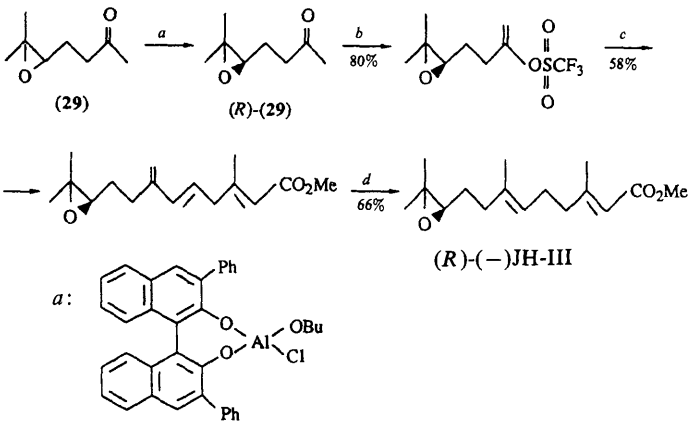
Scheme (10)



R = OH[(*R*)-(**19**), (*S*)-(**20**), (*R*,*R*)-(**23**), (*S*,*S*)-(**24**), (*R*,*S*)-(**27**)]; Cl[(*R*)-(**21**), (*S*)-(**22**), (*R*,*R*)-(**25**), (*S*,*S*)-(**26**), (*S*,*R*)-(**28**)].
a: Δ; *b*: $NaBH_4$; *c*: K_2CO_3/MeOH; *d*: TsCl/Py; *e*: MeONa/MeOH.

Kinetic resolution was used in the reaction of the racemic epoxide (**29**) with the optically active organoaluminium reagent in the synthesis of optically active JH-III.[37] Subsequent conversions of the chiral epoxide (*R*)-(**29**) led to (*R*)-(−)-JH-III (Scheme 11).[37]

Scheme 11



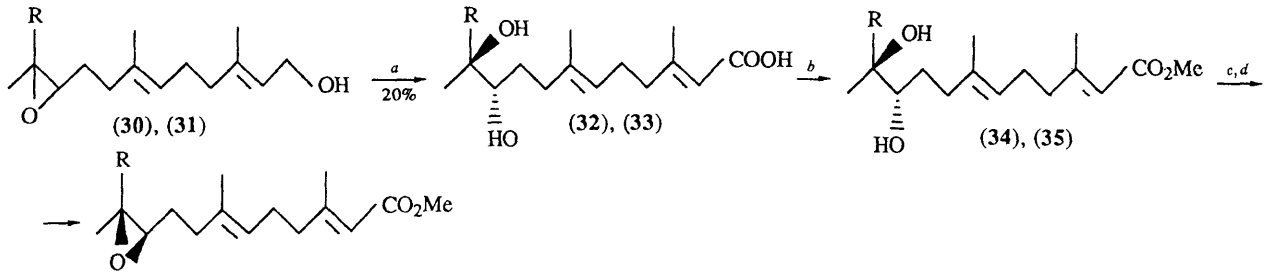
Enzymic reactions were used in the synthesis of optically active JH. Racemic 10,11-epoxyfarnesol (**30**) was converted by the action of a fungal culture of *Helminthosporium sativum* into (−)-*threo*-10,11-dihydroxyfarnesenic acid (**32**) which was then converted further into (10*R*)-JH-III through the ester (**34**).[38] Optically active (10*R*,11*S*)-JH-II was obtained similarly from homofarnesol (**31**) through the intermediates (**33**) and (**35**) (Scheme 12).[39]

The optically active (*R*)-diol (**34**) [containing < 5% (*S*)-isomer] was obtained from methyl farnesenate by treating it with the mould *Colletotrichum nicotianae*.[30] However the yield of the desired compound was low. It was more successful to synthesise enantiomerically pure JH-O, I, II, III from the chiral blocks (**38**) and (**39**) obtained by reduction of the diketones (**36**) and (**37**) with baker's yeast (*Pichia terricola*). The chiral ketones (**38**) and (**39**) were converted in eight steps into the corresponding phenylthio derivatives (**40**) and (**41**) by Baeyer-Villiger oxidation and subsequent ring opening. Further transformations of (**40**) and (**41**) led to enantiomerically pure JH (Scheme 13).[40–42]

III. Synthesis of natural analogues of juvenile hormones

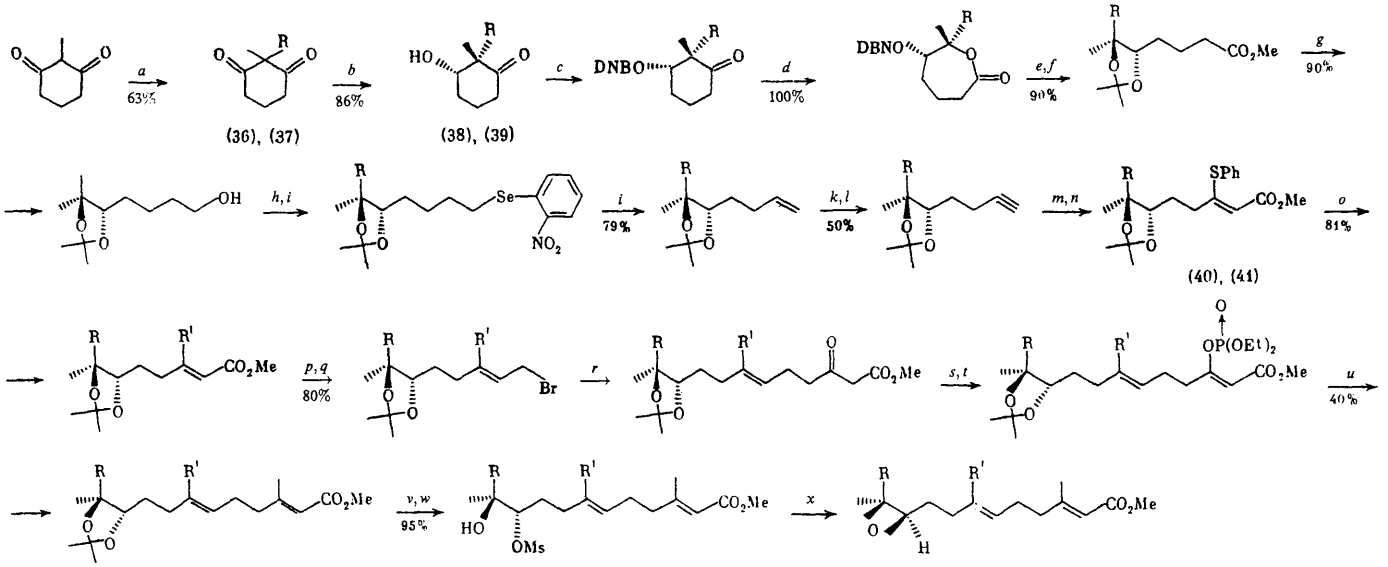
In 1975 an optically active compound was isolated from the North American rudbeckia (*Echinacea angustifolia*) which displayed juvenoid activity in relation to the yellow meal worm (*Tenebrio molitor*). This compound, called echinolone, was identified as (+)-(*E*)-10-hydroxy-4,10-dimethyl-4,11-dodecadien-2-one (**42**).[43]

Scheme 12



R = Me[(10*R*)-JH-II]; Et[(10*R*, 11*S*)-JH-II];
R = Me(**30**), (**32**), (**34**); Et(**31**), (**33**), (**35**);
a: Helm, sativum; *b*: CH_2N_2; *c*: MsCl/Py; *d*: KOH/MeOH.

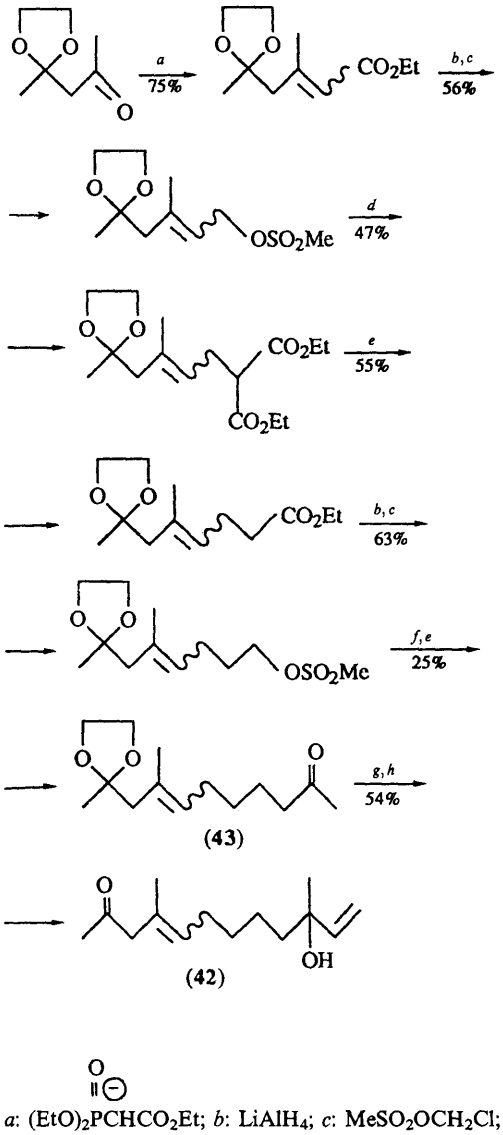
Scheme 13



DNB = 3,5-dinitrobenzoyl;
a: Rl/trilon B; *b*: Pichia tericola; *c*: DNB-Cl; *d*: $3\text{-}ClC_6H_4CO_3H/CH_2Cl_2$; *e*: K_2CO_3/MeOH; *f*: $Me_2C(ONe)_2$/TsOH; *g*: $LiAlH_4$; *h*: $o\text{-}(NO_2)C_6H_4SeCN$; *i*: $(n\text{-}Bu)_2P$; *j*: H_2O_2; *k*: Br_2; *l*: NaH_2/NH_2; *m*: $ClCO_2Me$/n-BuLi; *n*: PhSNa/MeOH; *o*: R^1MgBr/CuI/THF, −65 °C; *p*: $(iso\text{-}C_4H_9)_2AlH$; *q*: MeLi/TsCl/LiCl/HMPA; *r*: $MeCOC.HCO_2Me$; *s*: NaH; *t*: $(EtO)_2POCl$; *u*: MeCuLi; *v*: AcOH; *w*: $MsCl/Et_3N$; *x*: MeONa/MeOH.

Racemic echinolone is synthesised by a sequential build-up from the carbon skeleton of acetylacetone to the diketone monoacetal (**43**) using the Horner double bond reaction. The reaction of the ketoacetal (**43**) with vinylmagnesium bromide led to the desired (+)-echinolone as a mixture of geometric isomers (Scheme 14).[44]

Scheme 14

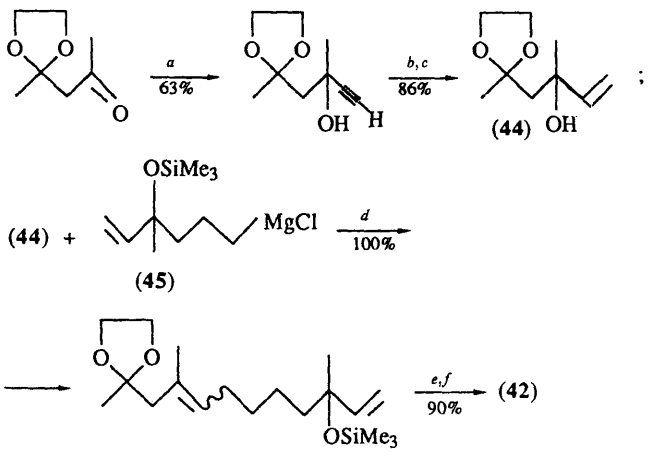


a: $(EtO)_2PCHCO_2Et$; *b*: $LiAlH_4$; *c*: $MeSO_2OCH_2Cl$; *d*: $CH_2(CO_2Et)_2$/NaH; *e*: Δ; *f*: $MeC(O)CH_2CO_2Et$/NaH; *g*: $CH_2=CHMgBr$; *h*: $H^{\oplus}$.

Another synthesis of a mixture (4:1) of the (*E*) and (*Z*) isomers of echinolone (**42**) was convergent with the key stage being the coupling of the two C_7 fragments (**44**) and (**45**).[45] The individual isomers were isolated by HPLC. It is interesting to note that the mixture of geometric isomers of echinolone proved to be more active than each of the individual isomers (Scheme 15).[45]

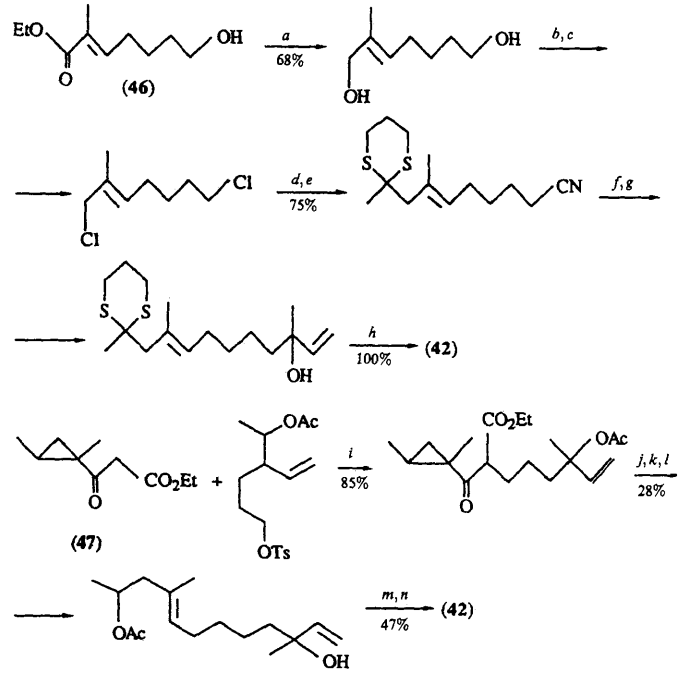
Schemes have been described for the synthesis of echinolone (**42**) from the unsaturated hydroxy-ester (**46**)[46] and from the ketoester (**47**) containing a cyclopropane fragment (Scheme 16).[47]

Scheme 15



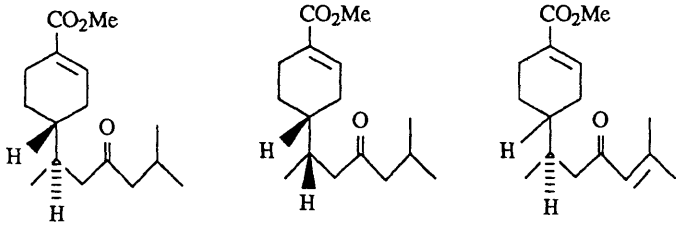
a: $CH\equiv CH/NH_3/KOH$; *b*: Ac_2O; *c*: Pd/ZnO; *d*: CuI/THF; *e*: HPLC; *f*: $H^{\oplus}$.

Scheme 16



a: $Na(OMe)_2(OEt)AlH$; *b*: $MeSO_2Cl/LiCl$; *c*: $Alk_4N^{\oplus}Cl^{\ominus}$; *d*: Me–C–Me (S S); *e*: NaCN; *f*: MeLi; *g*: $CH_2=CHMgBr$; *h*: $HgCl_2/CaCO_3$; *i*: NaH; *j*: $Ba(OH)_2$; *k*: $LiAlH_4$; *l*: HOAc; *m*: K_2CO_3 *n*: $CrO_3/Py/CH_2Cl_2$.

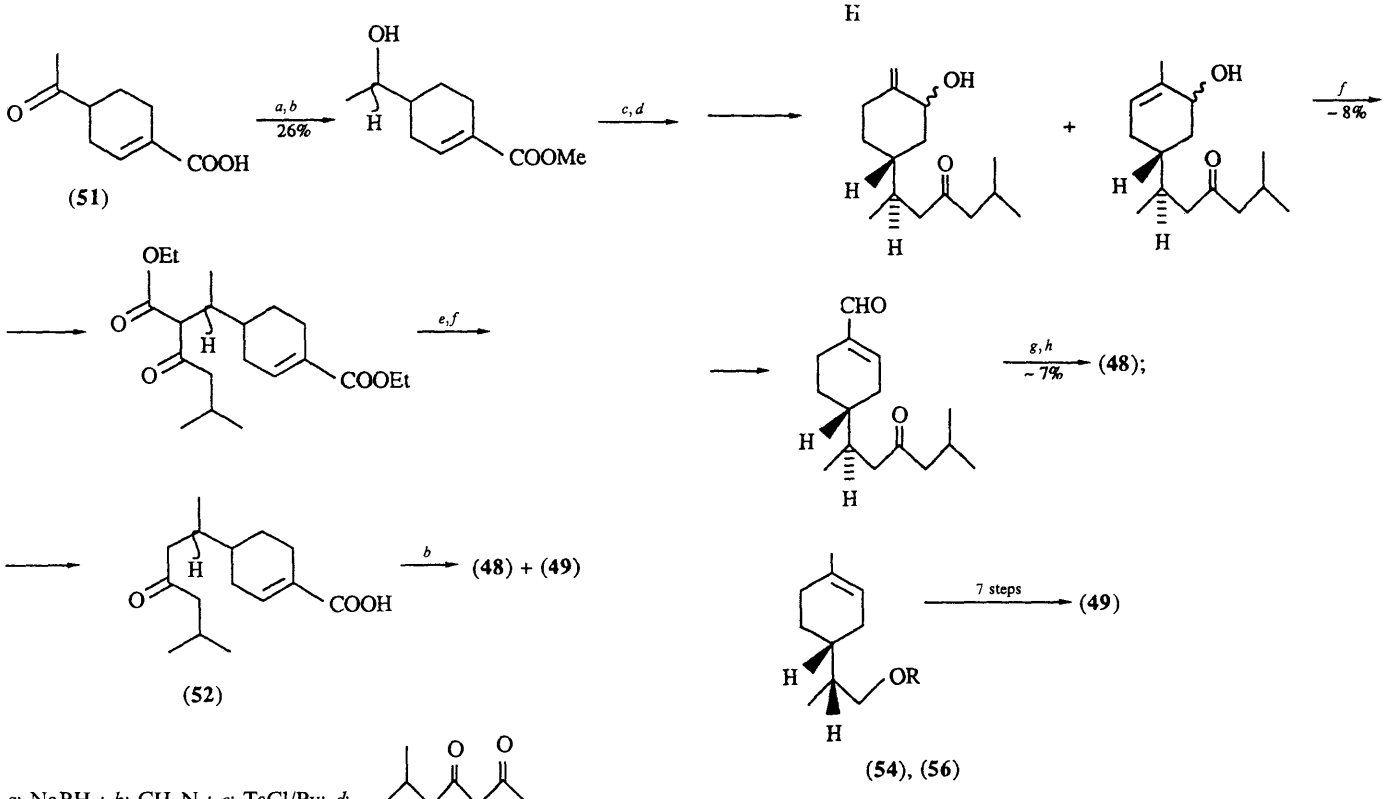
In 1965 Slama and Williams[48] discovered that paper from the wood of the balsam fir (*Abies balsamea*) possessed a JH action. The structure of the active compound proved to be identical to the methyl ester of (+)-todomatuic acid (**48**) with the (*R,R*) configuration at the asymmetric centres.[49,50] The new AJH was called juvabione. A compound of similar structure but with the (*R,S*) configuration was discovered in certain plants and was called epijuvabione (**49**).[51–53] One further active analogue, dehydrojuvabione (**50**), was isolated, together with (+)-juvabione, from Slovak fir.[54]



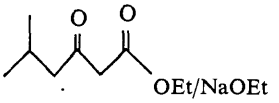
(**48**) (**49**) (**50**)

The shortest of the non-stereospecific routes proposed for synthesising a mixture of juvabione (**48**) and epijuvabione (**49**)[55–58] is that based on conversions of the methyl ester of 4-acetylcyclohexene-1-carboxylic acid (**51**) (Scheme 17).[58]

Scheme 17



a: $NaBH_4$; *b*: CH_2N_2; *c*: TsCl/Py; *d*:

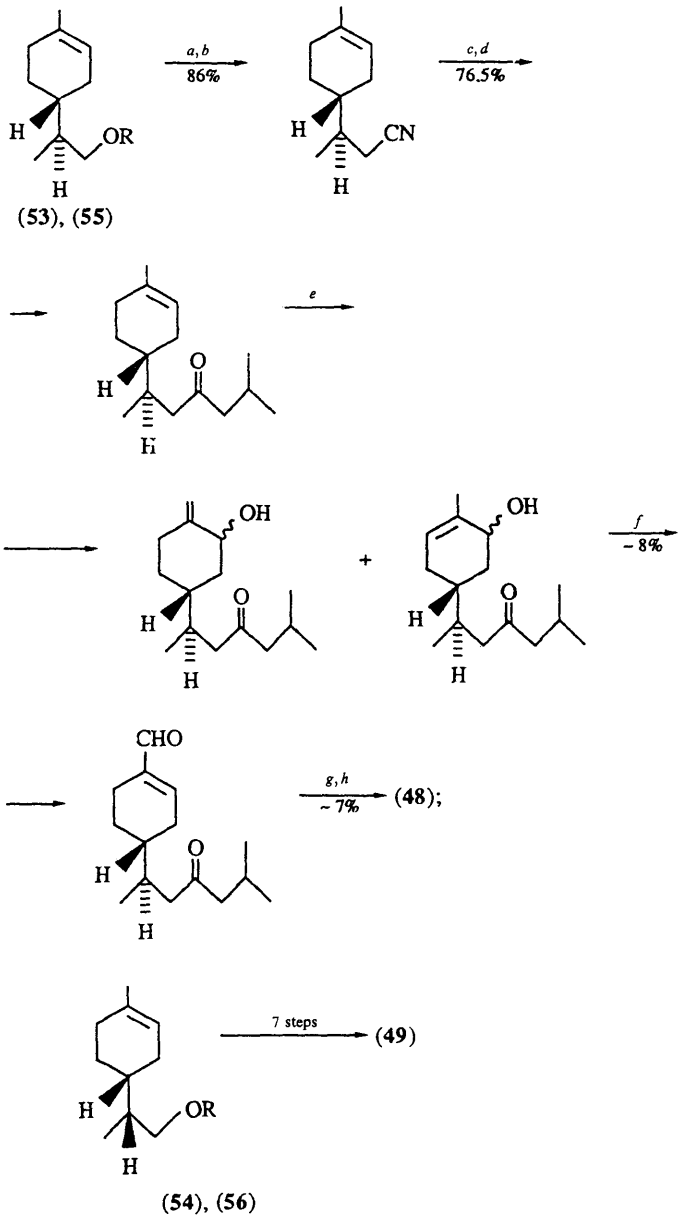


e: KOH/EtOH; *f*: Δ.

The individual epimers (**48**) and (**49**) were obtained by crystallisation of the semicarbazones of the corresponding ketoacids with subsequent esterification.[59,60]

A stereospecific synthesis of the individual (*R,R*)-(**48**) and (*R,S*)-(**49**) diastereomers of juvabione was achieved from the (*R,R*) (**53**) and (*R,S*) (**54**) alcohols, the optical activity of which was increased by fractional crystallisation of their 3,5-dinitrobenzoates (**55**) and (**56**) (Scheme 18).[61]

Scheme 18

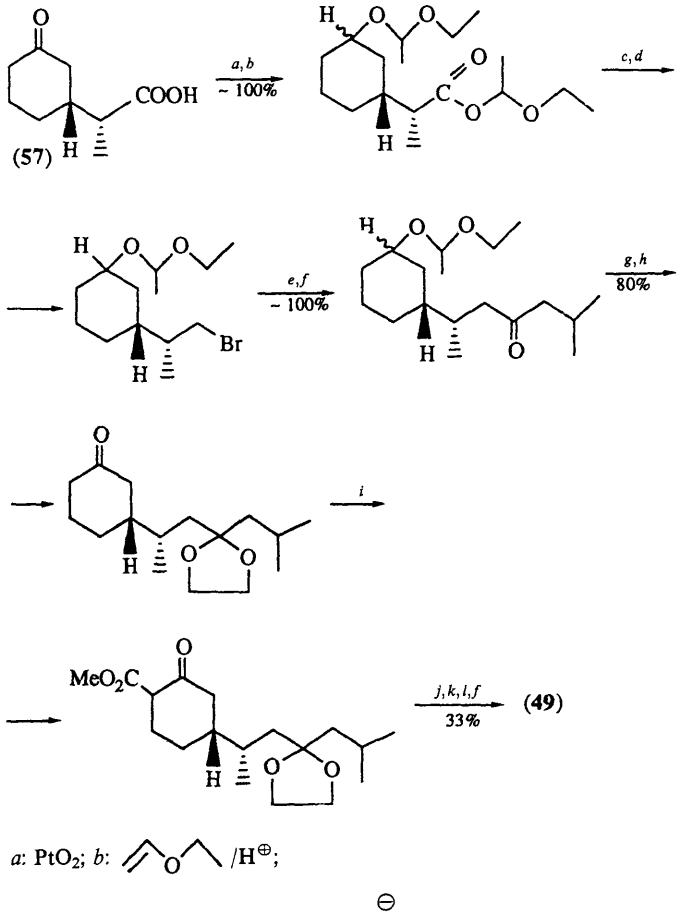


R = H(**53**), (**54**), DNB (**55**), (**56**)

a: TsCl/Py; *b*: NaCN/DMSO; *c*: $(Me)_2CHCH_2Li$; *d*: $H_3O^{\oplus}$; *e*: $O_2/h\nu$; *f*: $Na_2Cr_2O_7/H_2SO_4$/HOAc; *g*: $AgNO_3$; *h*: CH_2N_2.

Two of the stereocontrolled syntheses lead to epijuvabione (**49**).[62,63] In one of them the optically active acid (**57**) serves as starting material (Scheme 19).[62]

Scheme 19

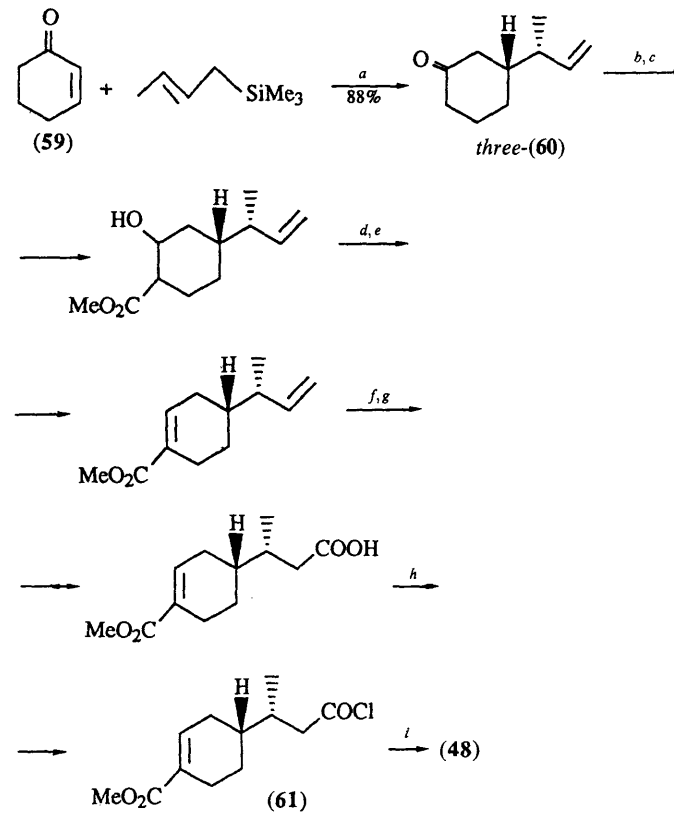


a: PtO_2; *b*: /$H^{\oplus}$;
c: $LiAlH_4$; *d*: PBr_3; *e*: $(Me)_2CH(CH_2)_2\overset{\ominus}{C}H(CN)(OH)$;
f: $H_3^{\oplus}O$; *g*: $(CH_2OH)_2/H^{\oplus}$; *h*: H_2CrO_4/Py; *i*: $(MeO)_2CO$/NaH;
j: $NaBH_4$; *k*: TsCl/Py; *l*: MeONa/MeOH.

Another approach is based on a [3,3] sigmatropic rearrangement applied to the diastereomeric mixture (**58**) with the (*R*) configuration at one of the asymmetric carbon atoms (Scheme 20).[63]

The synthesis[64] of juvabione (**48**) is based on the stereoselective condensation of the enone (**59**) with (*trans*-2-butenyl)trimethylsilane in the presence of $TiCl_4$ leading to the product (**60**) of *threo* configuration, the methoxycarbonylation of which and subsequent transformation through the acid chloride (**61**) gave juvabione (**48**) (Scheme 21).

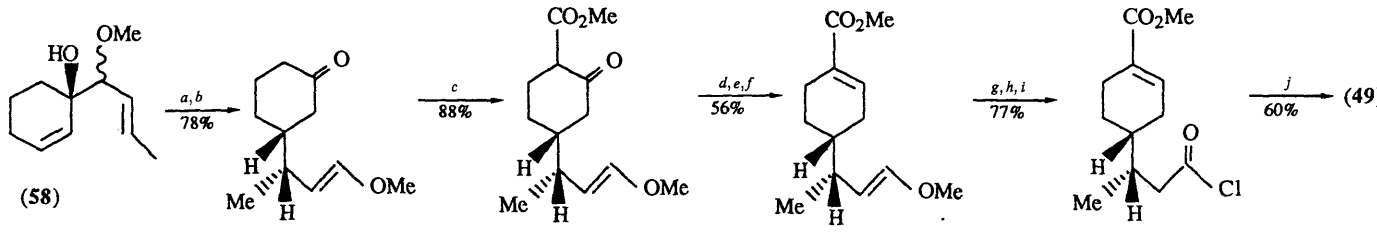
Scheme 21



a: $TiCl_4/CH_2Cl_2$; *b*: $(MeO)_2CO$/NaH; *c*: $NaBH_4$;
d: MsCl; *e*: NaOH/MeOH; *f*: $(C_6H_{11})_2BH$/THF;
g: CrO_3/H_2SO_4; *h*: $(COCl)_2$; *i*: $MeCHCH_2MgBr/Fe(acac)_2$.

The aromatic analogues corresponding to juvabione and epijuvabione have been isolated from natural sources. These are *ar*-juvabiones (**62**) and (**63**) which possess high JH activity.[65]

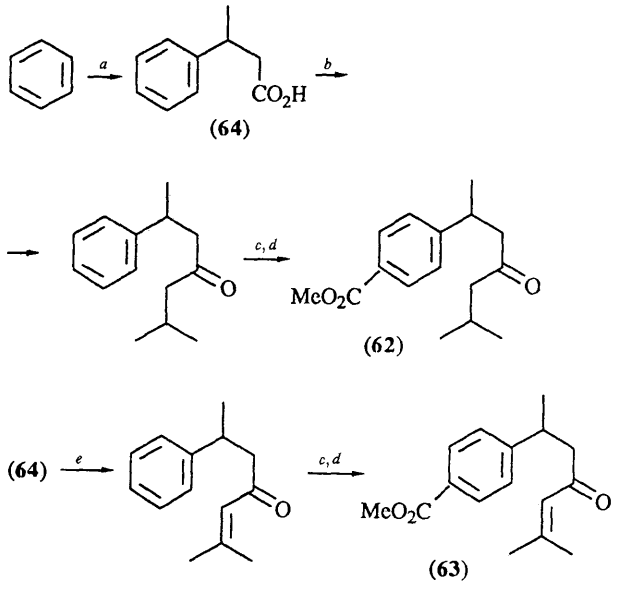
Scheme 20



a: KH, 110 °C; *b*: TLC; *c*: $(MeO)_2CO$/NaH; *d*: $NaBH_4$; *e*: MsCl; *f*: NaOMe/MeOH; *g*: $H^{\oplus}$; *h*: CrO_3/Me_2CO; *i*: $(COCl)_2$; *j*: $(iso\text{-}Bu)_2Cd$.

3-Phenylbutanoic acid (**64**) served as the key synthon in the synthesis of racemic (**62**) and (**63**) (Scheme 22).[66,67]

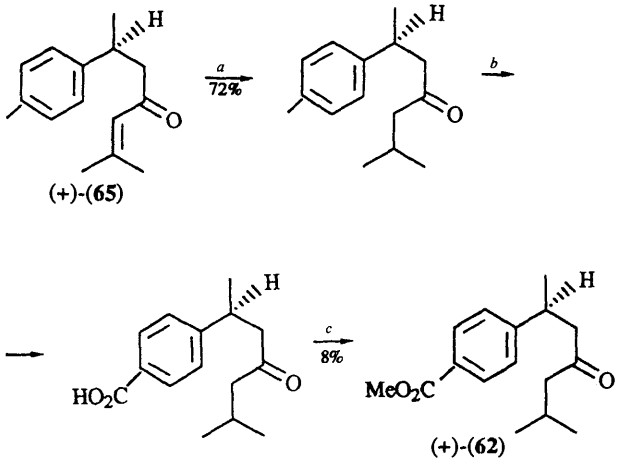
Scheme 22



a: MeHC=CHCOOH; *b*: Me_2CHCH_2Li; *c*: $(COCl)_2/AlCl_3$; *d*: MeOH; *e*: $Me_2C=CHLi$.

(+)-*ar*-Turmerone (**65**) was used for the synthesis of optically active (+)-*ar*-juvabione (**62**) (Scheme 23).[55]

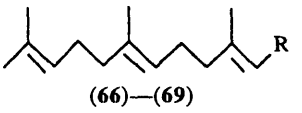
Scheme 23



a: H_2IPd-C; *b*: $CrO_3/AcOH$; *c*: MeOH/KOH/Me.

IV. Synthetic analogues of juvenile hormones

It was discovered in 1961[68] that farnesol (**66**) and farnesal (**67**) possess high juvenoid activity, comparable with that of the natural JH, but the methyl ester (**68**) and the diethylamide (**69**) of farnesenic acid proved to be even more active.[69–71]



(66)—(69)

R = CH_2OH (**66**), CHO (**67**), CO_2Me (**68**), $CONEt_2$ (**69**) .

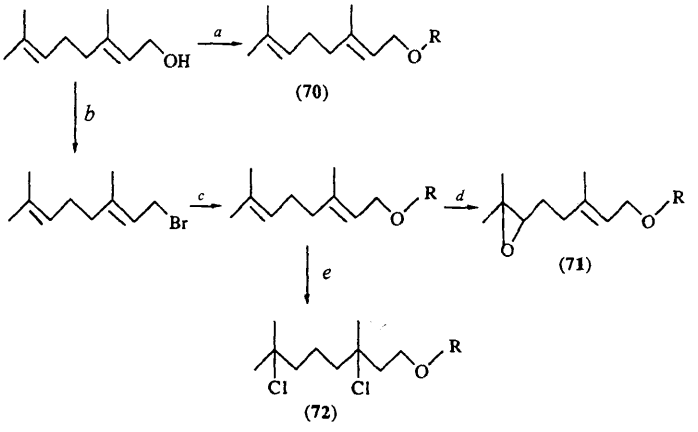
Intensive investigations then followed which were directed towards the search for active AJH and their synthesis. Several types of juvenoids emerged as a result of a widespread search. Highly active AJH were found chiefly among acyclic compounds with isoprenoid fragments in the chains, including derivatives of farnesenic acid and geraniol ethers. The most active juvenoids appeared among the esters of isoprenoid 2,4-dienoic acids (the 2,4-dienoates). Juvenoids of selective action were discovered among aliphatic compounds containing a heteroatom or a cyclic fragment in the carbon chain.

1. Acyclic juvenoids

a) Geraniol derivatives

When investigating the biological activity of alkyl ethers of geraniol (**70**), and of the epoxy (**71**) and dichloro (**72**) derivatives[72–74] in relation to the red cotton stainer bug (*Dysdercus koenigii*), it became apparent that the length of the alkyl chain (R) had considerable importance (the optimum was from four to six carbon atoms). Branching in the radical R causes a small increase in biological activity. Epoxydation of the terminal double bond in the geraniol portion of the molecule [compounds of the (**71**) series] reduces the juvenoid activity (Scheme 24).

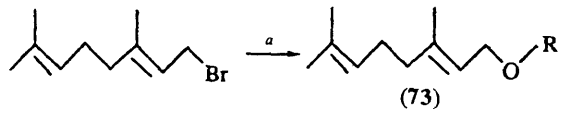
Scheme 24



R = n-Bu, CH_2CHMe_2, $(CH_2)_4Me$, $(CH_2)_2CHMe_2$, $CH_2CH=CMe_2$; *a*: $RBr/OH^{\ominus}$; *b*: PBr_3; *c*: RONa; *d*: $3\text{-}ClC_6H_4CO_3H$; *e*: HCl.

The most active were compounds with a total of 14–18 carbon atoms.[73] The geranyl ethers (**73**) or (**74**) were synthesised by the reaction of geranyl bromide with alcohols or geraniol with alkyl bromides in the presence of alkali (Scheme 25).[75–77]

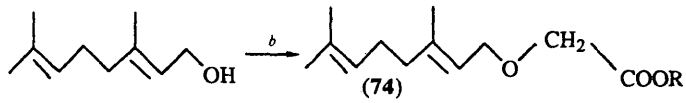
Scheme 25



(**73**)

R = $(CH_2)_2OMe$, $(CH_2)_2OCH_2Me$,

$(CH_2)_2O(CH_2)_2Me$, CH_2–CH(–)–OCH_2

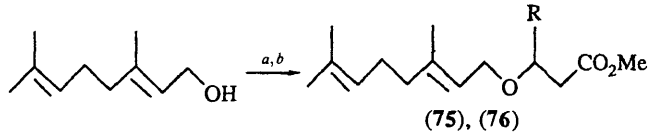


(**74**)

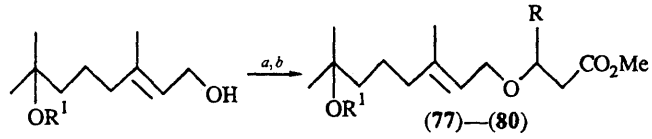
R = Me, Et, Pr, iso-Pr; *a*: $ROH/OH^{\ominus}$; *b*: $BrCH_2COOR/OH^{\ominus}$.

Catalytic addition of geraniol or of its 7-alkoxy derivatives to the activated double bond of methyl crotonate[74] or methyl 2-pentenoate[78,79] was used for the synthesis of compounds (**75**)–(**80**) (Scheme 26). It was noted that the introduction of methoxyl and ethoxyl groups at the terminal position of these compounds increases their JH activity.

Scheme 26



(**75**), (**76**)



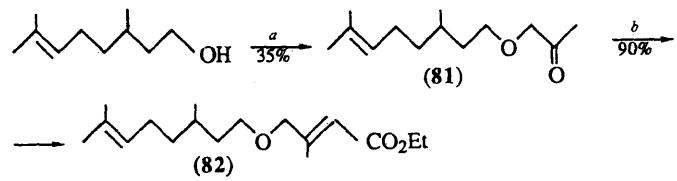
(**77**)—(**80**)

R = Me(**75**), (**77**), (**79**); Et (**76**), (**78**), (**80**);
R^1 = Me (**77**), (**80**); Et (**78**), (**79**);

a: R–CH=CH–$CO_2Me/OH^{\ominus}$; *b*: MeOH/TsOH.

An interesting approach to the synthesis of such a series of AJH is the olefination of compound (**81**), itself obtained by the reaction of citronellol with a diazoketone.[80–82] The ether (**82**), for example, was synthesised in this way (Scheme 27).

Scheme 27



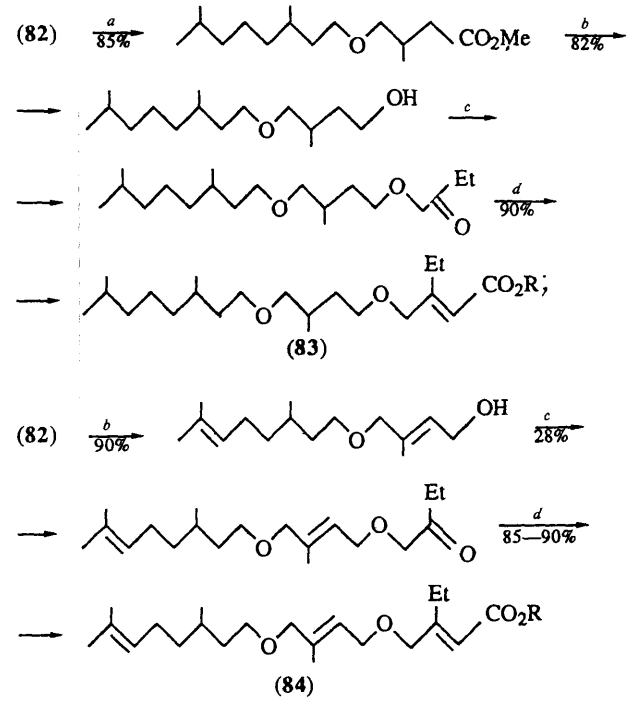
(**81**)

(**82**)

a: $MeC(O)CH_2N_2/BF_3$; *b*: $Ph_3P=CH_2CO_2Et$.

Transformations analogous to those carried out for compound (**82**) led to the ethers (**83**)[83–86] and (**84**)[84–86] with an oxygen atom in the alkyl chain of the citronellol derivative (Scheme 28).

Scheme 28

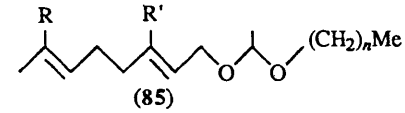


(**83**)

(**84**)

R = Me, Et, iso-Pr;
a: $H_2/Pd-C$; *b*: $LiAlH_4$; *c*: $EtC(O)CH_2N_2/BF_3$;
d: $Ph_3P=CHCO_2R$.

Some compounds of this series display a selective action. Compounds of the (**85**) series proved to be effective juvenoids in relation to the Mexican pea beetle.[87]



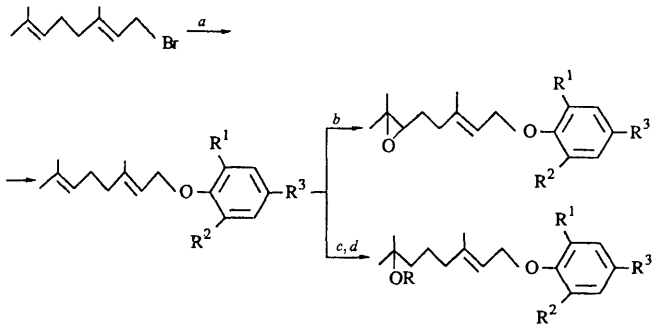
(**85**)

R, R' = Me, Et; *n* = 0, 1.

Juvenoids with a high morphogenetic effect were discovered in a series of phenyl ethers of geraniol and also their 6,7-epoxy, 7-hydroxy and 7-alkoxy derivatives.[9] The greatest effect on juvenoid activity was shown by substituents in the 4 and 2 positions of the phenyl group and also by hydroxyl and methoxyl groups in the 7 position of the chain.[88–110] Some of these compounds, containing for example ethyl, propyl and cyclopropyl groups in the 4 position of the phenyl ring, proved to be 100 or more times more active than the alkyl ethers of geraniol in relation to *Tenebrio molitor*, *Culex pipiens* and *Aedes aegypti*.[88,90,92,93,95] The greatest activity among

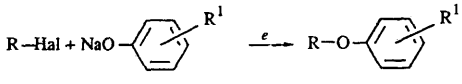
the 7-hydroxy and 7-methoxy derivatives is displayed by compounds with ring ethoxy and propoxy groups (Scheme 29).[88,93]

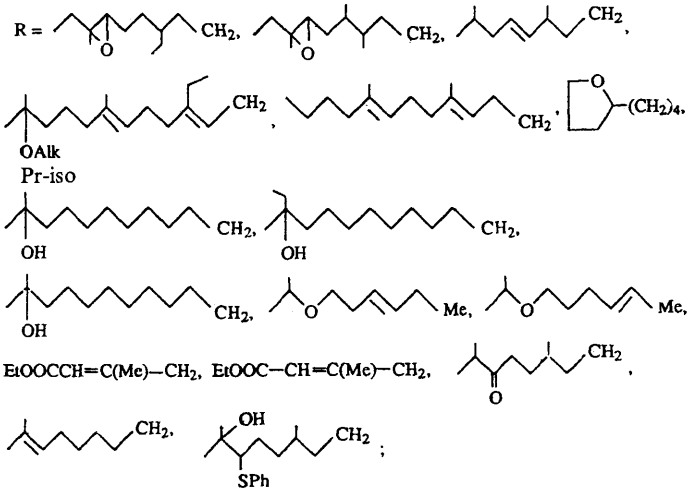
Scheme 29



R = H, Me, Et, Pr, iso-Pr, CH_2Ph; R^1 = H, Me, iso-Pr, Cl, OMe; R^2 = H, Cl, NO_2; R^3 = H, Et, Pr, iso-Pr, CH_2-CH (O), CH(OH)Et, EtC=

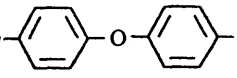
=NOH, CHO, MeCO, EtCO, OMe, SMe, NO_2, Cl;





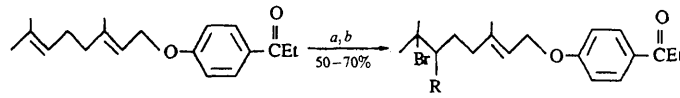
R = Bu, NO_2;

a: Mg; *b*: ; *c*: $MeC(OEt)_3$; *d*: $LiAlH_4$; *e*: TsCl/Py;

f:  .

The introduction of a halogen atom, a hydroxy or an alkoxy group into the terpene portion of the molecule did not change significantly the biological activity of the initial geraniol ether (Scheme 32).[114]

Scheme 32

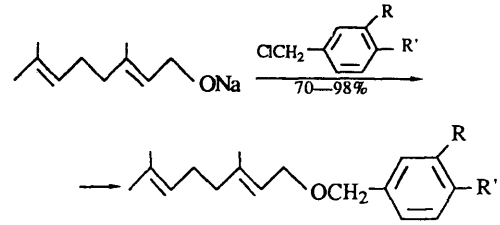


R = OH, OMe, iso-Pr;

a: NBS; *b*: ROH.

Benzyl ethers of geraniol proved to be less active than phenyl ethers (Scheme 33).[115,116]

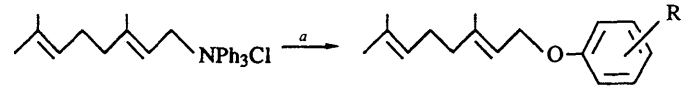
Scheme 33



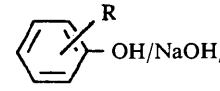
R = H, OH, Cl; R' = H, CMe_3, OMe, OEt, SMe, SEt, Cl, Br.

The method proposed for obtaining the phenyl ethers of geraniol is the reaction of the appropriate alkali metal phenoxide with geranyltriphenylammonium chloride (Scheme 30).[111,112]

Scheme 30

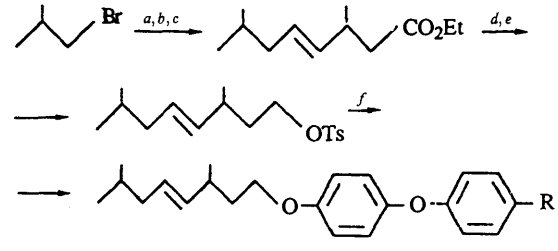


R = 3-Me, 4-Me, 4-Et, 3,4-Me_2, 4-iso-Pr, 2-iso-Pr, 5-Me, 2-OMe, 3-OMe, 4-NO_2, 4-Cl;

a: 

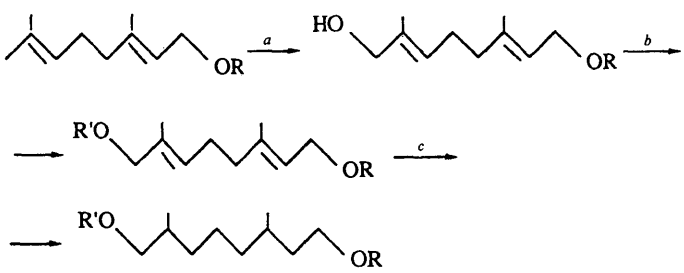
Juvenoid activity is increased significantly for the phenoxyphenyl ethers (Scheme 31).[113]

Scheme 31



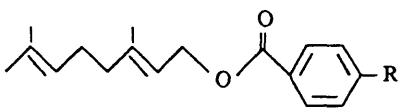
The diethers of (2*E*, 6*E*)-3,7-dimethyl-2,6-octadiene-1,8-diol and their tetrahydro derivatives shows high activity in relation to mosquitoes and the red cotton stainer bug (Scheme 34).[117]

Scheme 34



R = Me, Et, Ph, Bz, 4-MeC_6H_4; R′ = Me, Et, Ph, 4-ClPh, Bz, 4-MeC_6H_4; *a*: SeO_2; *b*: R′Hal – NaH; *c*: H_2/PtO_2 – Et.

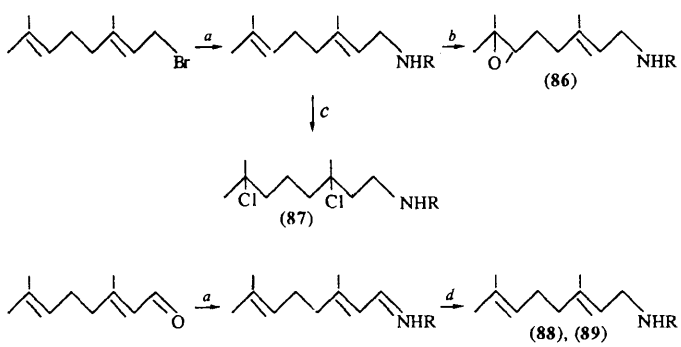
The geranyl esters of 4-substituted benzoic acids display high activity.[118]



R = OMe, Cl, NO_2.

The derivatives of geranylamine (**86**)–(**89**) have been investigated as potential juvenoids. However they proved to be less active than the corresponding oxygen-containing analogues (Scheme 35).[73,119]

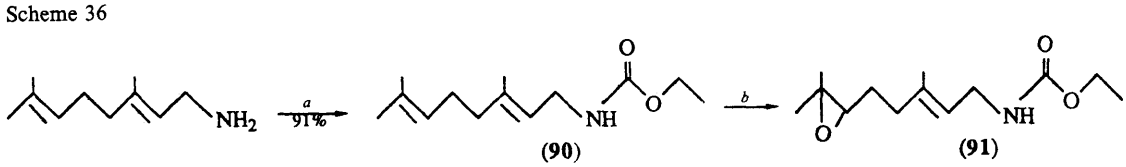
Scheme 35



R = C_nH_{2n+1} (n = 1 to 9) (**86**), (**87**); 4-$(EtO_2C)C_6H_4$ (**88**), 4-(HO_2C).C_6H_4 (**89**);
a: RNH_2; *b*: 3-$ClC_6H_4CO_3H$; *c*: HCl; *d*: KBH_4.

On the other hand the geranyl derivatives of carbamic acid (**90**) and (**91**), obtained by the reaction of ethyl chloroformate with geranylamine,[120] display high juvenoid activity in relation to the yellow meal worm (*Tenebrio molitor*) (Scheme 36).[120]

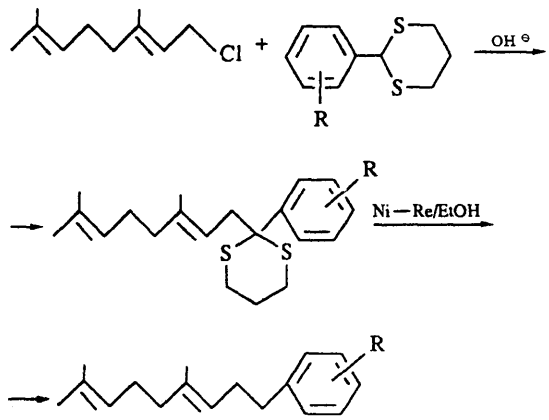
Scheme 36



a: $ClCO_2Et$; *b*: 3-$ClC_6H_4CO_3H$.

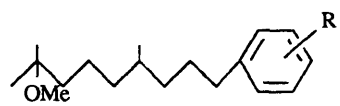
The reaction of geranyl chloride with dithiianes of substituted benzaldehydes and subsequent reduction of the dithiiane group gave geranyl benzyl derivatives (Scheme 37).[121]

Scheme 37



R = 3-Br, 4-Br, 4-F, 4,5-Cl_2, 4-CN, 4-CO_2Et, 4-NMe_2.

The methoxy substituted tetrahydro derivatives of the series (**92**)–(**94**) display high juvenoid activity against the house-fly.[122] Compound (**94**) proved to be the most active.

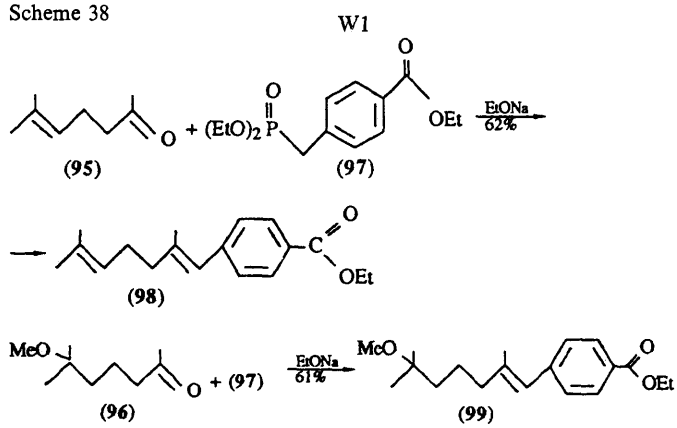


(**92**)—(**94**)

R = Et (**92**), Pr (**93**), iso-Pr (**94**).

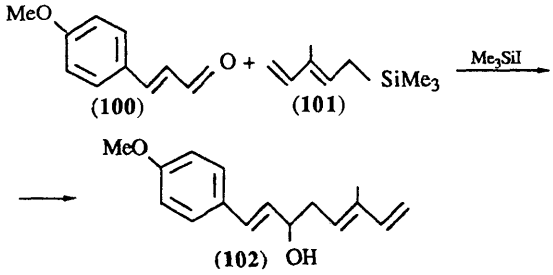
Compounds (**98**) and (**99**), obtained from ketones (**95**) and (**96**) and the phosphonate (**97**), display selective JH activity in relation to *Diptera* (Scheme 38).[123]

Scheme 38



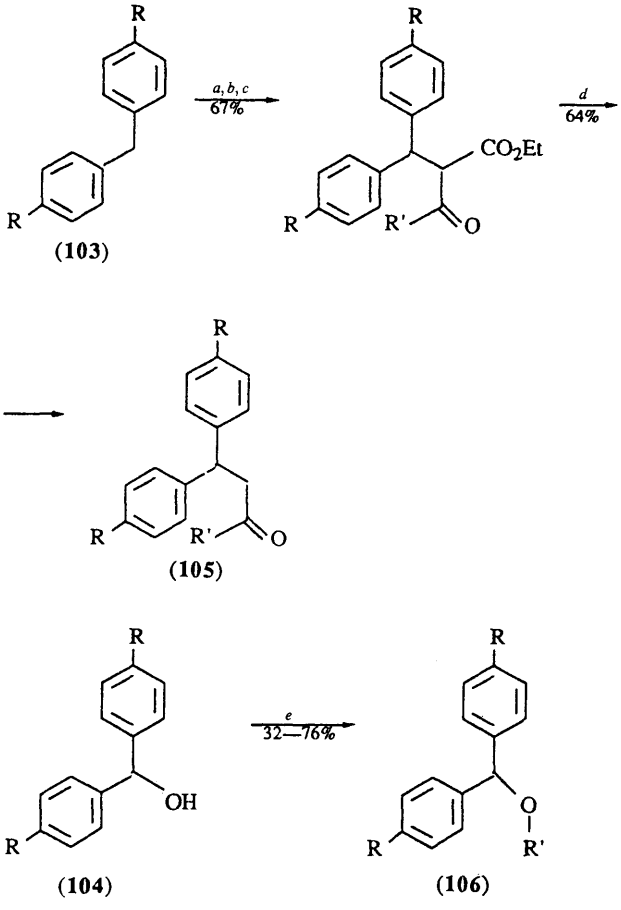
The product (**102**) from the reaction of 4-methoxycinnamaldehyde (**100**) and the allylsilane (**101**) shows juvenoid activity (Scheme 39).[124]

Scheme 39



The activity of the substituted diarylmethanes (**105**) and (**106**), synthesised[12] from the symmetrical diphenylmethanes (**103**) and (**104**), depends on the length of the alkyl chain R'. Compounds with eight carbon atoms in the side chain have the highest JH activity (Scheme 40).

Scheme 40

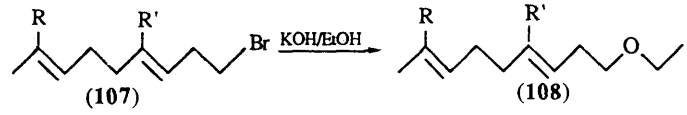


R = Cl, CO_2Me; R' = Me, Et, iso-Pr, iso-Bu, $COCCl_3$, $COCH_2CHMe_2$, $Me_2C{=}CH(CH_2)_2CH(Me)(CH_2)_2$;
a: NBS; *b*: $R'CCH_2CO_2Et$ (R'C(=O)CH_2CO_2Et); *c*: K_2CO_3/DMF; *d*: NaCl–DMSO;
e: R'X/Py.

b) Oxa and aza derivatives

The interesting results obtained for geranyl ethers stimulated the search for active JH analogues in other compounds of the ether type referred to as oxa analogues of JH in the literature.[16] The oxa-AJH (**108**) were synthesised from the homologues of geranyl bromide (**107**) (Scheme 41).[126]

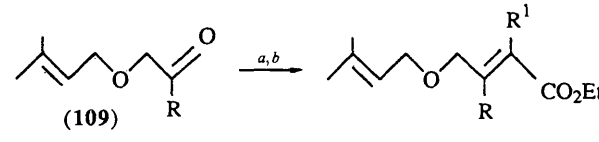
Scheme 41



R, R' = Me, Et, Pr.

However, compounds containing a Δ^2-double bond conjugated with the ester group were more promising. Compounds of this class with oxygen at various positions in the chain were synthesised. The 5-oxa analogues of JH were obtained, for example, by the Reformatsky reaction from the ketoethers (**109**) and α-haloacids with subsequent dehydration of the resulting β-hydroxyesters (Scheme 42).[127]

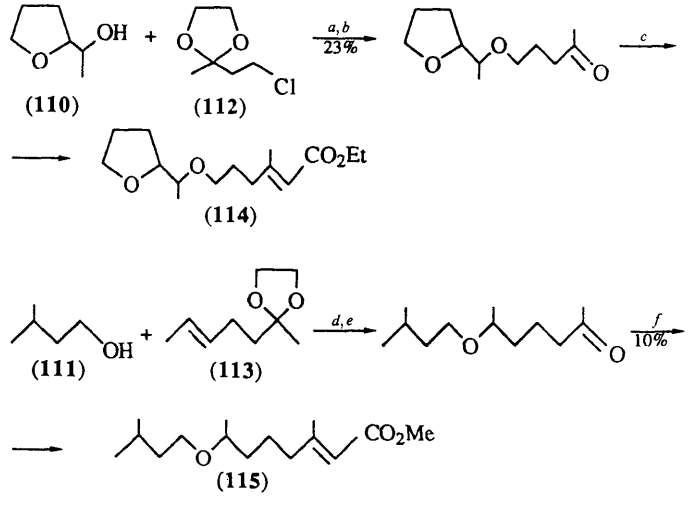
Scheme 42



R, R^1 = Me, Et, Pr;
a: $R^1CH_2(Br)COOEt$; *b*: $POCl_3$.

Compounds (**114**) and (**115**) were obtained by the reaction of the alcohols (**110**) and (**111**) with the acetals (**112**) and (**113**) respectively with subsequent Horner olefination (Scheme 43).[128,129]

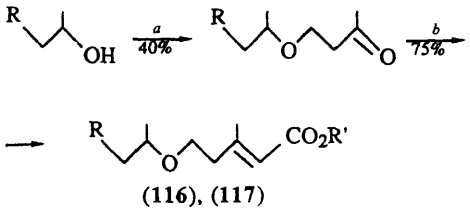
Scheme 43



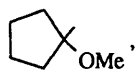
a: NaOH; *b*: H_3O^+; *c*: $(EtO)_2P(O)CHCO_2Et$; *d*: $NaBH_4$; *e*: TsOH;
f: $(MeO)_2P(O)CHCO_2Me$.

The key step in the synthesis of esters of the 6-oxa derivatives of (2*E*)-3,7-dimethyl-2-alkenoic acids (**116**) and (**117**) is the addition, catalysed by mercuric oxide and boron trifluoride etherate, of alcohols to methyl vinyl ketone with subsequent Horner olefination of the resulting ketones (Scheme 44).[130,131]

Scheme 44



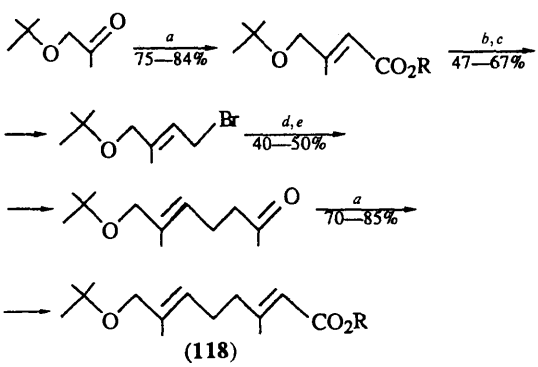
(**116**), (**117**)

(**116**): R = , R' = Me; (**117**): R =  , R' = Et;

a: , $HgO/BF_3.Et_2O$; *b*: $(EtO)_2P(O)CHCO_2R'$.

9-Oxa derivatives of (2*E*,6*E*)-2,6-undecadienoic acid (**118**) have been synthesised using two olefination stages (Scheme 45).[132,133]

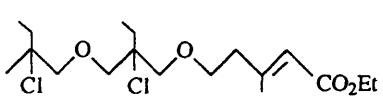
Scheme 45



(**118**)

R = Me, Et, iso-Pr;
a: $Ph_3P{=}CH_2CO_2R$; *b*: $LiAlH_4$; *c*: PBr_3; *d*: $MeC(O)CH(Na)CO_2Et$; *e*: Δ.

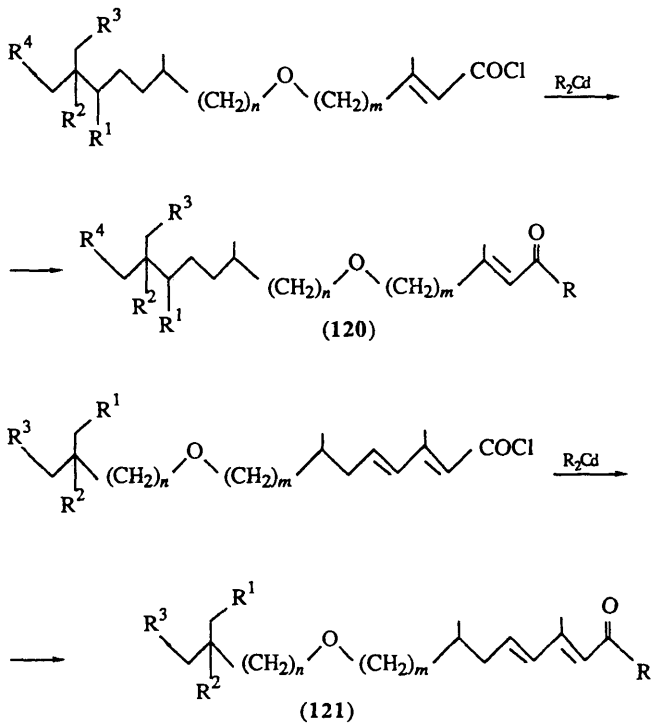
The juvenoid activity of compounds (**114**)–(**118**) proved to be less than that of the corresponding deoxy derivatives.[134] However some oxa derivatives show a selective action on particular species. Thus the ethyl ester of (2*E*)-8,12-dichloro-8-ethyl-12-methyl-6,10-dioxa-2-tetradecenoic acid (**119**) is an effective juvenoid in relation to *Dysdercus cingulatus*. The dose of compound enabling 50% intermediate forms to develop under standard conditions (specimens with part-larva part-pupa features) (UD_{50}) was 0.06 μg per specimen.[84]



(**119**)

Several mono- (**120**) and dienoketones (**121**) containing an oxygen atom in the main chain show high juvenoid activity towards the yellow meal worm, the domestic fly and *Eurygaster integriceps*.[135,136] These compounds were obtained by the reaction of the acid chlorides of the appropriate carboxylic acids with organocadmium compounds (Scheme 46).

Scheme 46



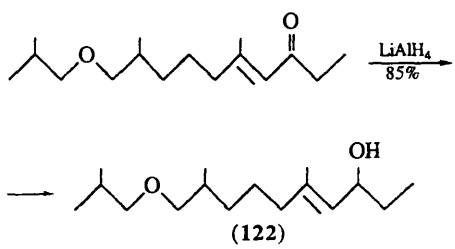
(**120**)

(**121**)

R, R^1, R^2, R^3, R^4 = H, Me, Et, Pr; *m* = 1,2; *n* = 0,1.

The oxa compound (**122**), obtained by reduction of the corresponding α,β-unsaturated ketone, displays high JH activity on the same insect species (Scheme 47).[137]

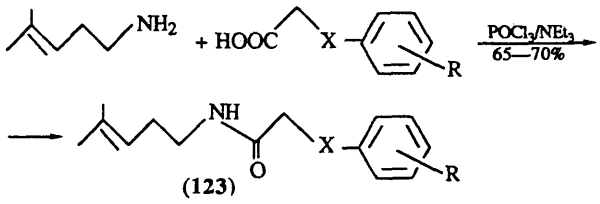
Scheme 47



(**122**)

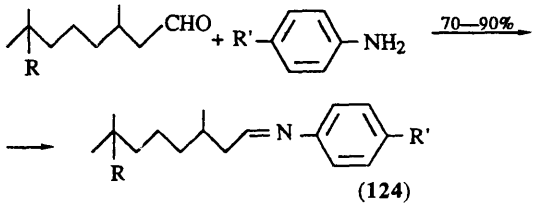
It was discovered that compounds (**123**)–(**128**), containing a nitrogen atom in the chain, display low juvenoid activity (Scheme 48).[138–140]

Scheme 48



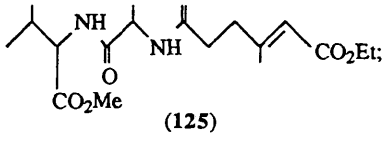
(**123**)

X = O, S; R = H, 4-Me, 4-Et, 2-Cl, 4-Cl, 4-Br.

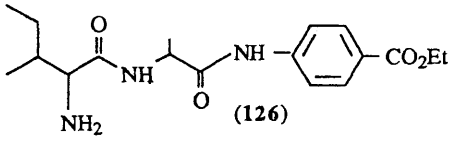


(**124**)

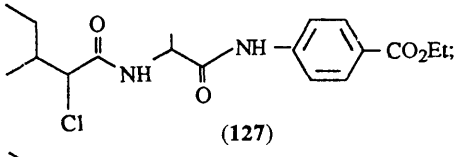
R = OH, OMe; R' = H, Me, Cl, CO_2H, NO_2.



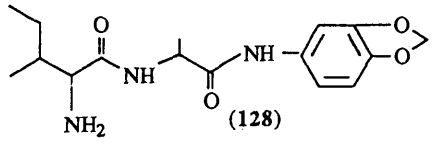
(**125**)



(**126**)



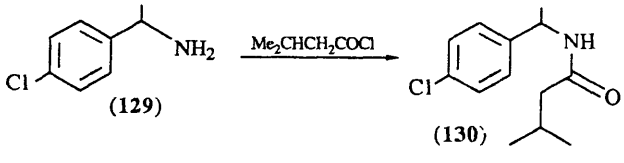
(**127**)



(**128**)

It was however established that the aza analogues of juvabione[141] display selectively high activity in relation to *Dysdercus fasciatus*. The most active proved to be compound (**130**) obtained by the acylation of the amine (**129**) (Scheme 49).

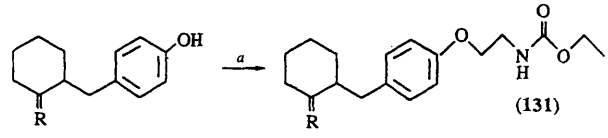
Scheme 49



(**129**) (**130**)

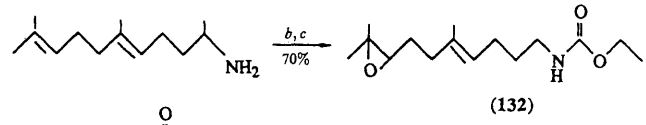
The compounds (**131**) and (**132**), containing oxygen and nitrogen atoms in the chain, display selective activity towards termites (Scheme 50).[142,143]

Scheme 50

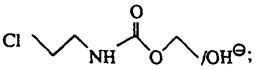


(**131**)

R = O (50%); OCH_2CH_2O (23%)

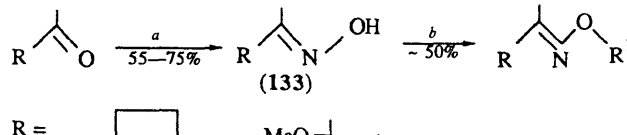


(**132**)

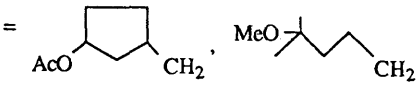
a:  ; *b*: $ClCO_2Et$; *c*: $3\text{-}ClC_6H_4CO_3H$.

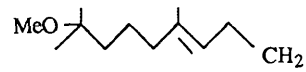
The reaction of oximes (**133**) and (**134**) with the appropriate halogen derivative[144–151] or chloroformate ester[143] may serve as an efficient method of obtaining juvenoids containing two heteroatoms, nitrogen and oxygen, in the same structure (Scheme 51).

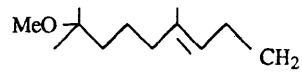
Scheme 51

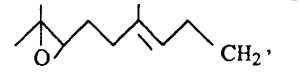


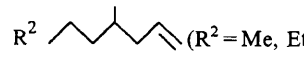
(**133**)

R = 

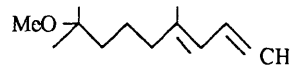
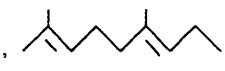


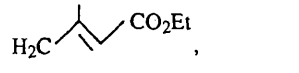
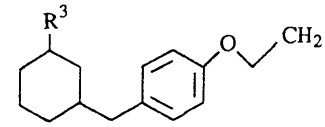




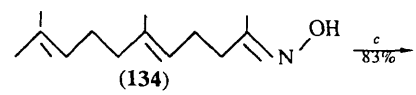


R^2 (R^2 = Me, Et, Pr, iso-Bu, MeC=CH, alkenyl)

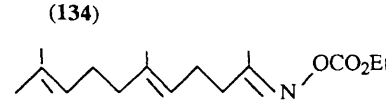
 ,  ; R^1 = Alk,

 ,  ;

R^3 = O, OH, OCH_2CH_2O.



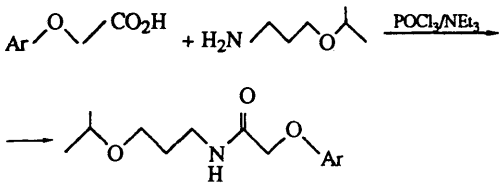
(**134**)



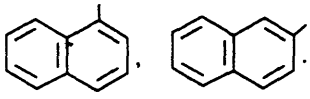
a: $H_2NOH.HCl$; *b*: Na/R'Br; *c*: $ClCO_2Et$.

Amides of unsaturated carboxylic acids with an oxygen atom in the chain, obtained by the reaction of acids with amines in the presence of $POCl_3$, display high JH activity in relation to the yellow meal worm (Scheme 52).[152–156]

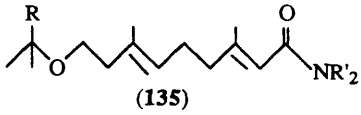
Scheme 52



Ar = 4-EtC_6H_4, 2-FC_6H_4, 2-ClC_6H_4, 3-EC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4,



The JH activity of compounds of the (135) series is ~0.01 μg per specimen.[157]

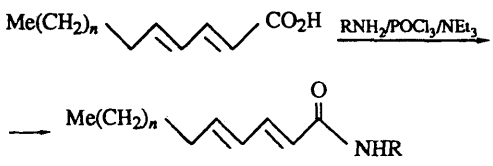


(135)

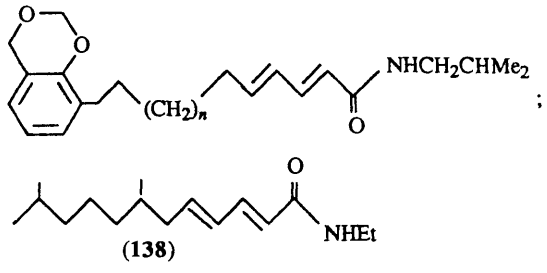
R, R′ = C_1–C_5-alkyl or C_2–C_5-alkenyl.

It was noted that the juvenoid activity of the amides was reduced in the series NR_2 > NHR > NH_2 (R = Alk, Ar)[9,158] and tertiary arylamides are more active than aliphatic amides. The amides of 2,4-dienoic acids are more active than the corresponding derivatives with isolated double bonds. A series of dienoates (136)–(138) was prepared, the action of which on *Callosobruchus maculatus*[159] and *Boophilus decoloratus*[160] exceeds that of methoprene (Scheme 53).

Scheme 53



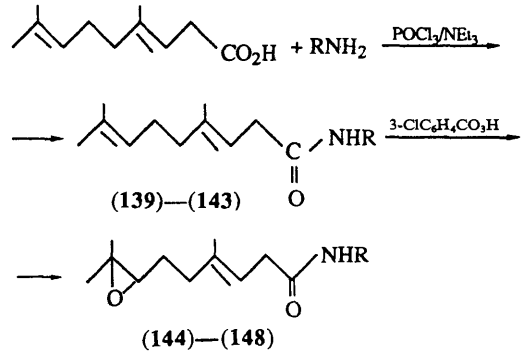
R = Me, Et, Pr, iso-Pr; n = 4 to 6.



(136), n = 5; (137), n = 3.

It was established that the epoxy derivatives (144)–(148) are more active than the initial amides (139)–(143) (Scheme 54).[155]

Scheme 54



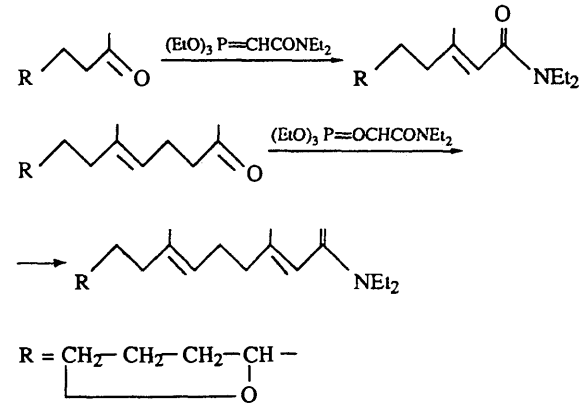
(139)—(143)

(144)—(148)

R = Ph (139), (144); 4-MeC_6H_4 (140), (145); 4-$MeOC_6H_4$ (141), (146); 4-$EtOC_6H_4$ (142), (147); 4-ClC_6H_4 (143), (148).

The Horner reaction is used for the synthesis of the α,β-unsaturated amides (Scheme 55).[152,153]

Scheme 55



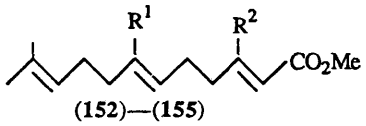
R = CH_2–CH_2–CH_2–CH(O)–

Highly active juvenoids of the amide type were obtained by the reaction of the corresponding alcohols with isocyanates,[161] or of amines with a chloroformate ester.[143,162] Compounds (149)–(151) display high activity towards the yellow meal worm (UD_{50} = 0.1 μg per specimen) but their activity in relation to *Dysdercus cingulatus* exceeds that of methoprene (UD_{50} = 0.008 and 0.04 μg per specimen respectively) (Scheme 56).

c) Derivatives of isoprenoid acids

Comparison of the methyl ester of farnesenic acid (152) and its C(3) and C(7) methylated analogues (153) and (154)[163] showed that the presence of the substituent at C(7) has little effect on juvenile hormone action but the absence of a methyl group at C(3) leads to an attenuating effect as indicated by the low activity of compound (154). On the other hand a stronger juvenoid is obtained by replacement of the methyl group at C(3) by trifluoromethyl [compound (155)].[164] It was also established that activity is increased in a series of farnesenic acid esters from methyl to propyl: CO_2Me < CO_2Et < CO_2Pr.[165,166] Replacement of the ester group

by amide reduces the juvenoid action of the obtained compound on *Bombyx mori* while the susceptibility of the yellow meal worm is increased.[167]

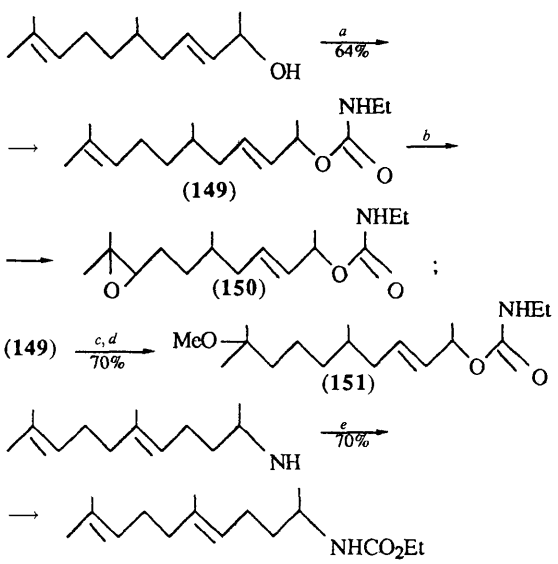


(152)—(155)

R^1 = H (153); Me (152), (154); CF_3 (155);
R^2 = H (154); Me (152), (153).

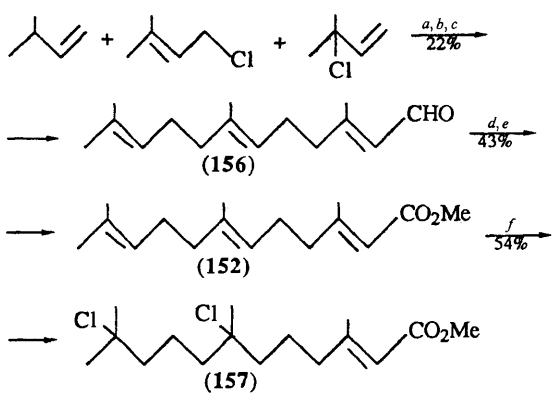
Methyl farnesenate (**152**) may be obtained mixed with other compounds by the telomerisation of isoprene, 1-chloro-3-methyl-2-butene and 3-chloro-3-methyl-1-butene with formaldehyde and subsequent oxidation of the aldehyde (**156**).[168] On treatment with hydrogen chloride the dichloride (**157**) is given and proved to be 1000 times more active in relation to *Antheraea polyphemus* than the natural JH (Scheme 57).[169]

Scheme 56



a: EtN=C=O; *b*: 3-$ClC_6H_4CO_3H$; *c*: $Hg(OAc)_2$; *d*: $NaBH_4$/NaOH; *e*: $ClCO_2Et$.

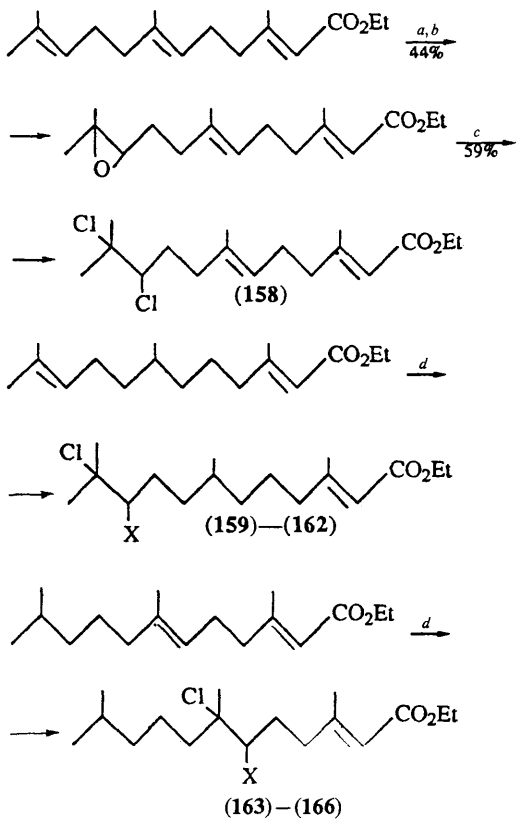
Scheme 57



a: $SnCl_4$; *b*: urofropin; *c*: CH_2O; *d*: $AgNO_2$; *e*: Me_2SO_4; *f*: HCl/MeOH.

It was shown that of the compounds (**159**)—(**166**) the activity of the 10,11-dichloro derivative (**158**) towards *Eurygaster integriceps* was greater than that of the 6,7- (**163**) and 7,11- (**157**) dichlorides. The thio analogues (**160**), (**161**), (**164**) and (**165**) were less active than the corresponding dichlorides (Scheme 58).[168,170]

Scheme 58



X = Cl (**159**), (**163**); SMe (**160**), (**164**); SPh (**161**), (**165**); 4-ClC_6H_4 (**162**), (**166**).
a: NBS; *b*: K_2CO_3; *c*: CCl_4/Ph_3P; *d*: $CuCl_2$/MeCN or RSCl.

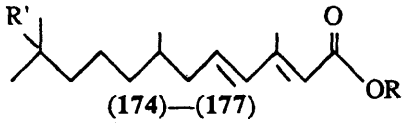
According to literature data[171] the presence of a fluorine atom in an organic compound inhibits its oxidative metabolism. This stimulated the synthesis of the fluorinated analogue (**169**) of JH-III. The fluorine-containing ester (**167**) served as starting material and was converted into the ester of 6-fluorogeranic acid (**168**) by a Claisen—Cope rearrangement. Further transformations led to the desired compound (**169**) (Scheme 59).[172]

The antipodes of the optically active juvenoids (**172**) and (**173**), which were obtained from the nitrile (**170**), possess different juvenoid activity in relation to *Dysdercus cingulatus*.[173,174] The racemic secondary alcohol (**171**), formed by the reaction of the nitrile (**170**) with propylmagnesium bromide was resolved into optical antipodes by Sharpless asymmetric epoxidation. Depending on whether (+) or (−) diisopropyl tartrate was used either the (*S*)-(−)- or the (*R*)-(+)-alcohol (**171**) respectively react and the unreacted (*R*)-(+) or (*S*)-(−) (**171**) enantiomer is isolated. The optical purity of the (*R*)-(+)-(**171**) and (*S*)-(−)-(**171**) alcohols was 88 and 74%

respectively. A Claisen rearrangement with an alkyl orthoformate in the presence of propionic acid[175] gave the juvenoids (172) and (173) of the (*R*) or (*S*) configuration (Scheme 60).[174]

Analogues of farnesenic acid of similar structure are comparable in juvenoid activity to the natural JH.[176–185] For example, a significant growth in JH activity was detected for esters of (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoic acid on changing from the α,β-enoates to the corresponding 2,4-dienoates.[1,186]

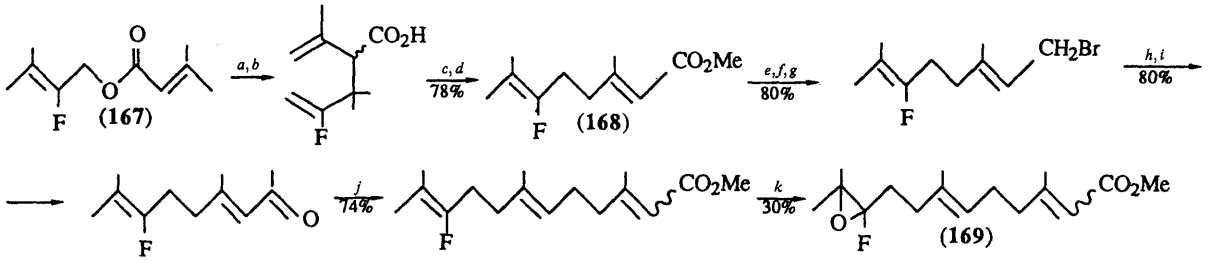
Compounds with very high juvenoid activity were found among the esters of (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoic acid. The ethyl ester (174) (hydroprene) and the propargyl ester (175) (kinoprene) are amongst these. The introduction of a methoxyl group at the 11 position of the isopropyl ester (176) gave an increase of almost one order of magnitude in juvenoid activity. Methoprene proved to be non-toxic to warm blooded animals and man. On the other hand this compound displayed high juvenoid activity towards the house ant *Monomorium pharaonis*,[187] the mosquito *Culex nigripalpus*,[188] the house-fly and the dung fly and also towards many agricultural pests of the orders *Lepidoptera* and *Hemiptera*.[13,189] The addition of 0.01% methoprene to bird feed led to 99% destruction of flies on poultry farms. Hydroprene (174)[189,190] and kinoprene (175)[189,191] are also of practical use.



(174)—(177)

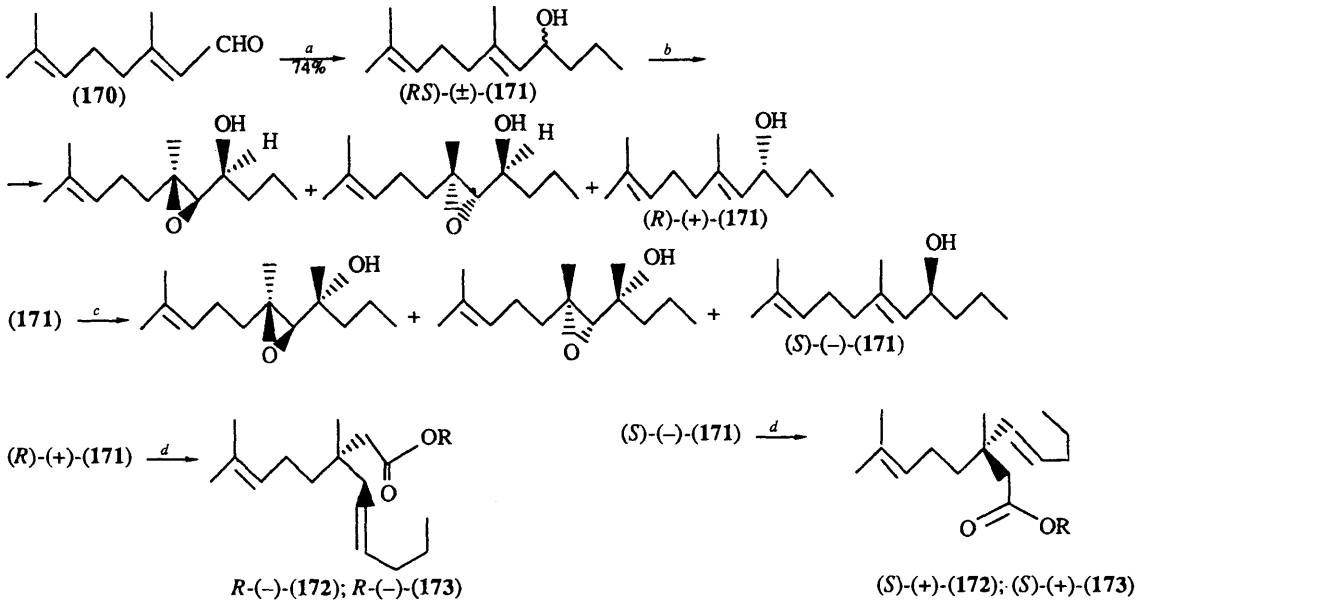
R = Et (174); $CH_2C{\equiv}CH$ (175); $CHMe_2$ (176), (177);
R' = H (174)—(176); OMe (177).

Scheme 59



a: LDA/THF, −75 °C; *b*: Me_3SiCl; *c*: DMFA, Δ; *d*: MeI/K_2CO_3/Me_2CO; *e*: $LiAlH_4$; *f*: $(CF_3CO)_2O$/Py; *g*: LiBr/THF; *h*: t-BuOK/Me.$COCH_2CO_2Et$; *i*: DMSO/H_2O/NaCl; *j*: $(MeO)_2P(O)CH_2CO_2Me$/NaH; *k*: 3-$ClC_6H_4CO_3H$.

Scheme 60



R = Me (172), Et (173);

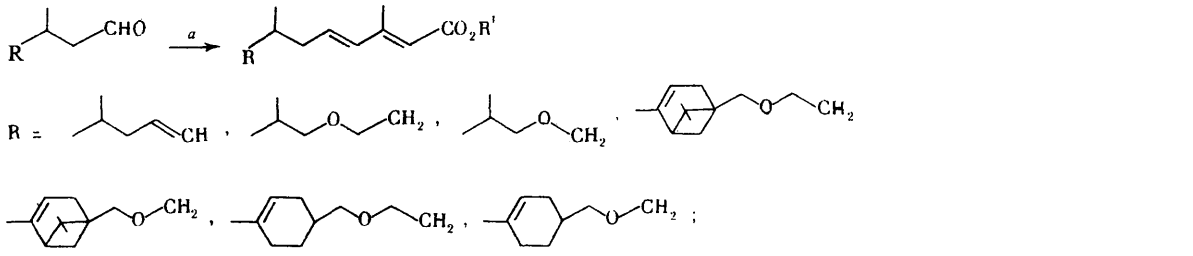
a: $Me(CH_2)_2MgBr$; *b*: t-BuOOH/(iso-OPr)$_4$Ti/(+)-PrOOCCH(OH)CH(OH)COOPr; *c*: t-BuOOH/(iso-OPr)$_4$Ti/(−)-PrOOCCH(OH)CH.(OH)COOPr; *d*: $MeC(OR)_3$/$MeCH_2COOH$.

The key stage in the synthesis of the 2,4-dienoates is usually the Emmons modification of the Wittig reaction (Scheme 61).[134,186,192–196]

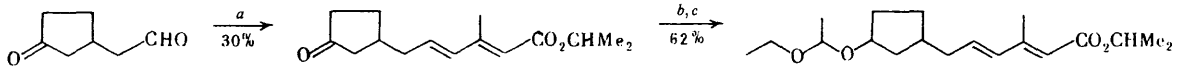
A review[13] has been devoted to the synthesis and properties of methoprene (**177**). Hydroprene (**174**), as a mixture of the (2*E*,4*E*) and (2*Z*,4*E*) isomers, was synthesised for the (2*E*) unsaturated ketone (**178**) and ethyl bromoacetate by the Reformatsky reaction,[197] using the Iotsich–Preobrazhenskii reagent[198] or by the reaction with acetic acid di-anion.[199]

The individual (2*E*,4*E*) isomer of the methyl ester (**181**) was obtained by elimination of acetic acid from the homoallyl acetate (**180**), which was itself obtained by the reaction of tetrahydrocitral (**179**) with the di-anion generated from 3-methyl-3-buten-1-ol (Scheme 63).[200]

Scheme 61

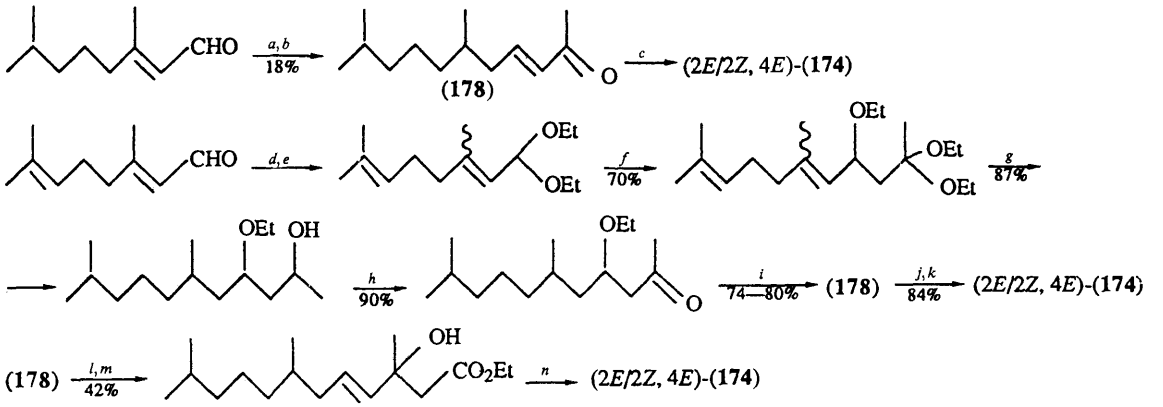


R^1 = OMe, OEt, iso-Pr, SEt.



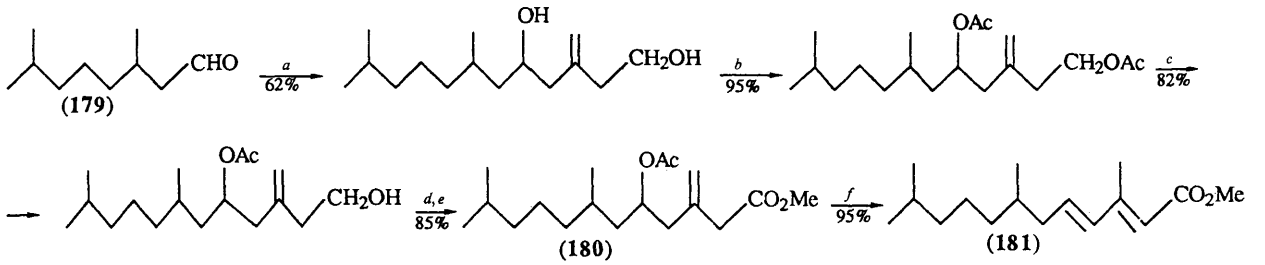
a: $(R'O)_2P(O)CHCMe{=}CHCO_2CHMe_2$; *b*: $NaBH_4$; *c*: $EtOCH{=}CH_2$.

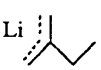
Scheme 62



a: Me_2CO; *b*: KOH/EtOH; *c*: $BrCH_2CO_2Et/Zn$; *d*: $HC(OEt)_3$; *e*: $HClO_4$; *f*: $CH_2{=}C(Me)OMe/ZnCl_2$; *g*: H_2/Ni; *h*: PY.CrO_3.HCl; *i*: Ts.OH/quinoline; *j*: HC≡COEt/EtMgBr; *k*: 10% H_2SO_4; *l*: $LiCH_2CO_2Li$; *m*: $EtOH/H^{\oplus}$; *n*: P_2O_5.

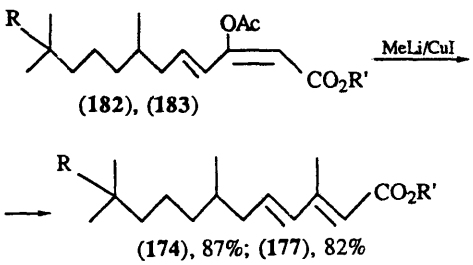
Scheme 63



a:  CH_2OLi; *b*: AcCl; *c*: $Na_2CO_2/EtOH$; *d*: CrO_3/Me_2CO; *e*: CH_2N_2; *f*: NaH.

Hydroprene (174) and methoprene (177) are obtained from compounds (182) and (183) by replacing the acetoxy group by methyl accompanied by isomerisation of the double bond (Scheme 64).[201]

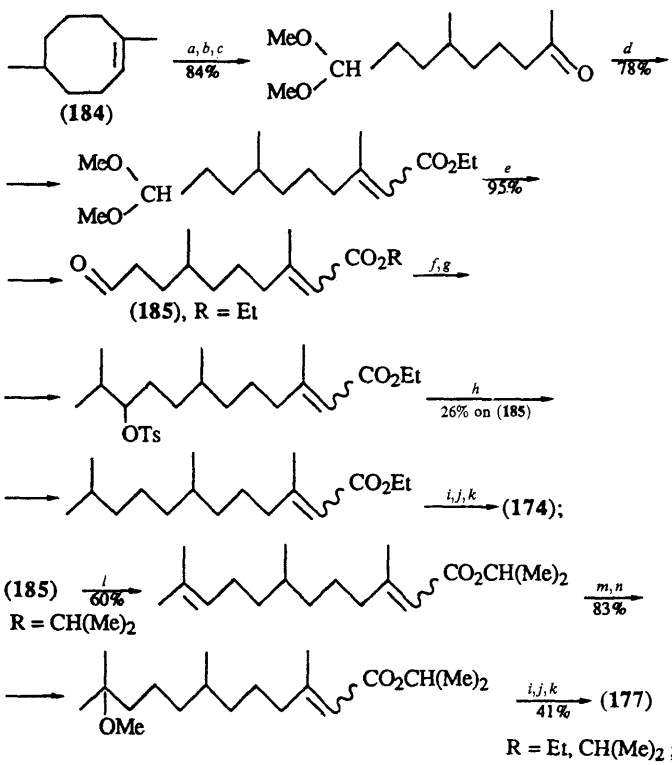
Scheme 64



R = H (174), (182); R = OMe (177), (183);
R' = Et (174), (182); $CHMe_2$ (177), (183).

A complete synthesis of hydroprene (174) and methoprene (177) was effected from the products of the ozonolysis of 1,5-dimethyl-1-cyclooctene (184).[202,203] The aldehyde (185) is the key synthon in both cases. The individual (2*E*,4*E*) isomers (174) and (177) were isolated by preparative HPLC (Scheme 65).

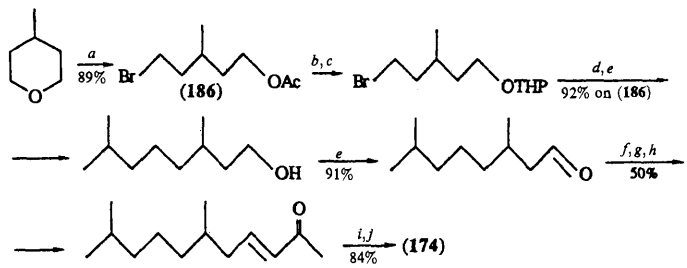
Scheme 65



a: O_3/MeOH; *b*: H_2/Pd–$CaCO_3$–PbO; *c*: NH_4Cl/MeOH; *d*: $(Me)_3$.$SiCH_2CO_2R$/$(iso\text{-}Pr)_2NH$; *e*: $H^{\oplus}$; *f*: $(Me)_2CHMgBr$; *g*: TsCl/Py; *h*: Zn/NaI/THF; *i*: NBS/$(BzO)_2$; *j*: Li_2CO_3/LiBr/DMF; *k*: HPLC; *l* $Me_2C{=}PPh_3$; *m*: $Hg(OAc)_2$/MeOH; *n*: $NaBH_4$/NaOH.

The synthon (186), readily available from 4-methyltetrahydropyran, was used for the preparation of hydropropene (174) (Scheme 66).[204]

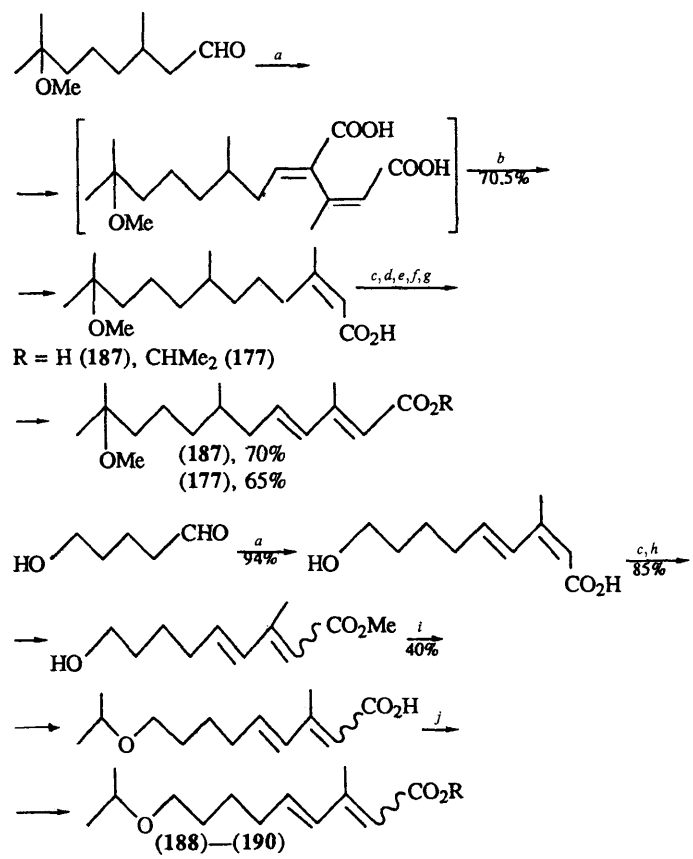
Scheme 66



a: AcBr/$ZnCl_2$; *b*: KOH/MeOH; *c*: DHP(3,4-dihydro-2H-pyran)/Ts.OH; *d*: Me_2CHCH_2MgBr; *e*: Py.CrO_3.HCl; *f*: $CH_2{=}CH{-}CH_2Mg$.Br; *g*: $O_2/PdCl_2/CuCl$; *h*: $H^{\oplus}$; *i*: $BrMgC{\equiv}COEt$; *j*: H_2SO_4.

The syntheses of methoprene (177) from 7-methoxycitronellal have been discussed.[13] The isolation of the (2*E*,4*E*) isomer was effected as the ammonium salt of the acid (187).[205,206] A similar methodology was used in the synthesis of the other 2,4-dienoates (188)–(190) (Scheme 67).[207,208]

Scheme 67

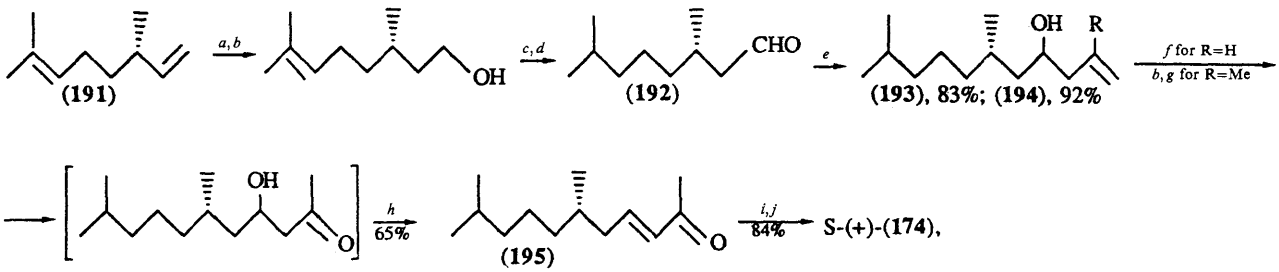


R = Me (188), 30%; $CHMe_2$ (189), 50%; $CH_2C{\equiv}CH$ (190), 58%;

a: EtO_2C CO_2Et; *b*: Δ; *c*: PhSH; *d*: NH_3; *e*: $H^{\oplus}$; *f*: $SOCl_2$;

g: $Me_2CHOH/H^{\oplus}$; *h*: CH_2N_2; *i*: $Me_2CHBr/OH^{\ominus}$;
j: $C_6H_{11}NHC(OR){=}NC_6H_{11}$(R = Me, $CHMe_2$, $CH_2C{\equiv}CH$).

Scheme 68

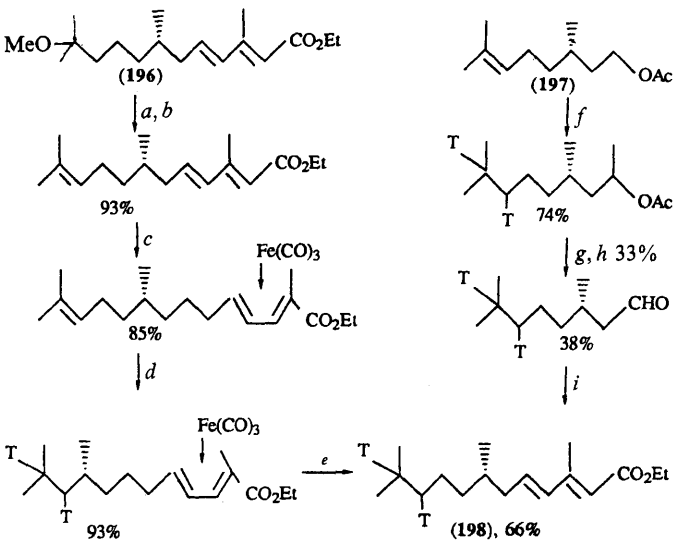


a: $(iso\text{-}Bu)_2AlH$; *b*: O_3/O_2; *c*: H_2-Pd/C; *d*: $Py.CrO_3.HCl$; *e*: $CH_2=C(R)-CH_2MgCl$; *f*: $O_2/PdCl_2-CuCl_2$; *g*: Me_2S; *h*: $H^{\oplus}$; *i*: $EtOC\equiv CH/Et.MgBr$; *j*: H_2SO_4.

It is known that the (7*S*)-(+) enantiomer of hydroprene (**174**) displays higher activity than the (7*R*)-(−) antipode.[209] Enantiomerically enriched hydroprene (**174**) (enantiomeric excess ~50%) is obtained from dihydromyrcene (**191**) through (*S*)-(+)-3,7-dimethyloctanal (**192**) which was treated with allyl- or methallylmagnesium chloride and gave the alcohols (**193**) or (**194**), each of which was converted into the conjugated ketone (**195**) then transformed by the usual route into the desired (*S*)-(+)-hydroprene (Scheme 68).[210]

The synthesis of 10,11-ditritiohydroprene (**198**), used for investigating the metabolism of juvenoids *in vivo*, was effected from the (*S*)-(+)-dienoate (**196**) in which the Δ^{10} double bond was tritiated after protecting the diene system as the iron carbonyl complex. Another route is based on tritiation of the double bond of (*S*)-(+)-citronellyl acetate (**197**) before constructing the diene system (Scheme 69).[211]

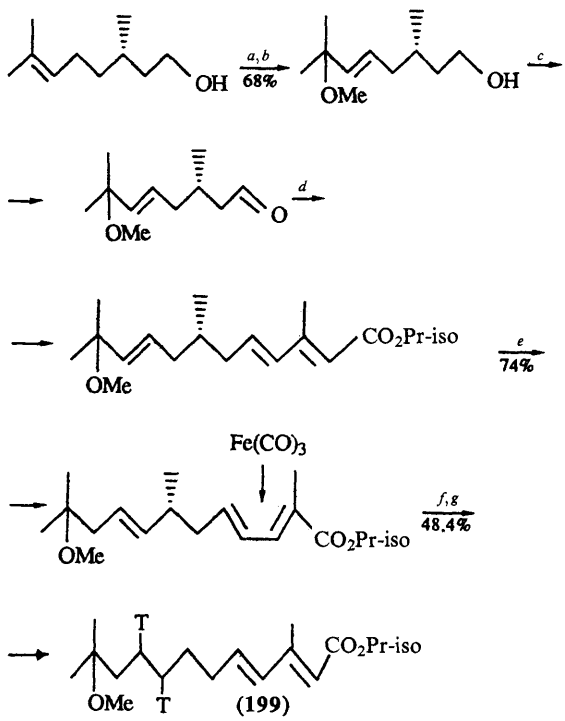
Scheme 69



a: NaOEt/EtOH; *b*: H_2SO_4; *c*: $Fe_3(CO)_{12}$; *d*: $T_2/Ph[Ph_3P]_3Cl$; *e*: $(NH_4)_2Ce(NO_3)_2$; *f*: T_2/Pd; *g*: NaOH/MeOH; *h*: CrO_3/Py; *i*: $Et_2.OCCH=C(Me)CH_2P(O)(OEt)_2$.

A similar approach was used in the synthesis of 8,9-ditritiomethoprene (**199**) used as a tracer for characterising protein receptors in insects (Scheme 70).[212]

Scheme 70

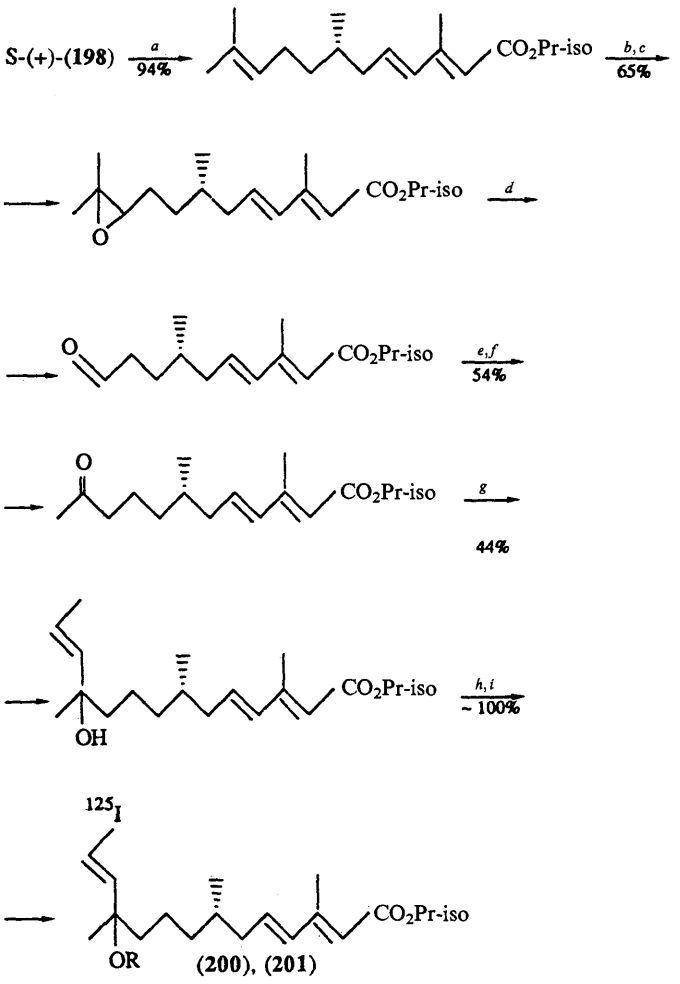


a: NBS/MeOH; *b*: $Ph_3CK/CH_2(OMe)_2$; *c*: $Py.CrO_3.HCl$; *d*: $(iso\text{-}PrO)_2P(O)CH_2CH(Me)=CHCO_2Pr\text{-}iso$; *e*: $Fe(CO)_{12}$; *f*: $T_2/Rh-C$; *g*: $Ce(NH_4)_2(NO_3)_2$.

In order to study the mechanism of binding juvenoids to protein, an iodomethyl group labelled with radioactive ^{125}I, which is stable to metabolism, was introduced into the methoprene molecule

[compounds (200) and (201)].[213] The resulting analogue (201) proved to be four times as active as methoprene (Scheme 71).

Scheme 71

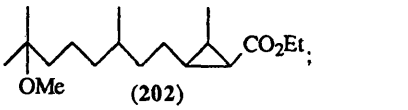


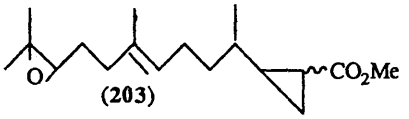
R = H(200), Me (201);
a: H_2SO_4; *b*: NBS; *c*: K_2CO_3; *d*: H_2IO_6; *e*: $Ph_3P=C(Me)OMe$; *f*: $H^{\oplus}$/MeOH; *g*: (*E*)-$Bu_3SnCH=CHSnBu_2$, BuLi/THF; *h*: $Na^{125}I/H_2O_2$/AcOH; *i*: $NaHSO_3$.

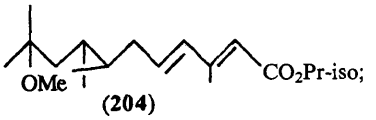
2. Juvenoids containing cyclic residues in the carbon chain

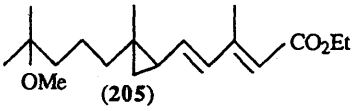
a) Juvenoids containing carbon rings

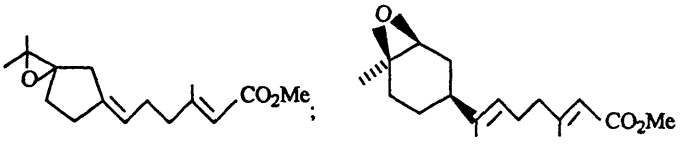
Compounds containing cyclic residues in various parts of the carbon chain of the AJH molecule have been synthesised with the aim of studying the mechanism of action and of searching for new active juvenoids. It was established that the introduction of a cyclopropane ring into the head portion of the molecule [compounds (202), (203)[214,215]] or its heart [compounds (204), (205)[216,217]] did not change the biological activity while the presence of an alicycle in the tail portion of the molecule [compounds (206)–(209)] reduces JH activity compared with the corresponding compounds containing no cyclic fragments.[218–221]

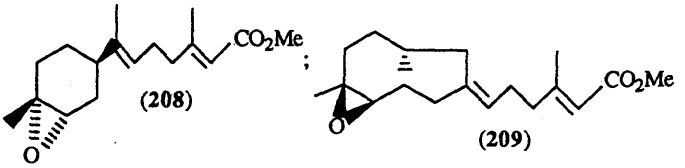






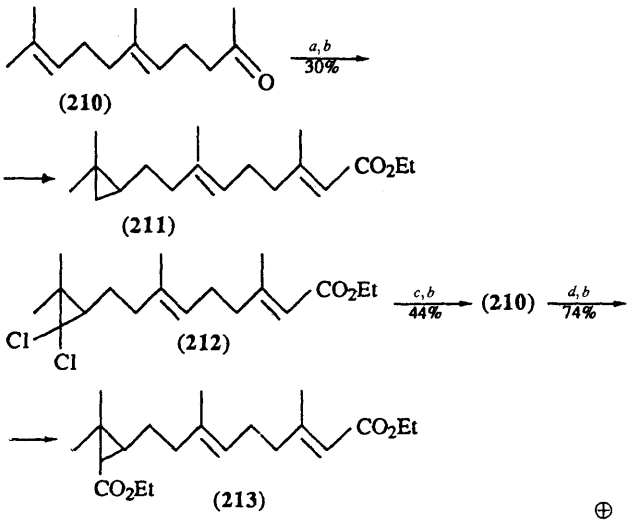






Compounds (211)–(213) were obtained by the cyclopropanation of geranylacetone (210) and subsequent Horner olefination (Scheme 72).[221]

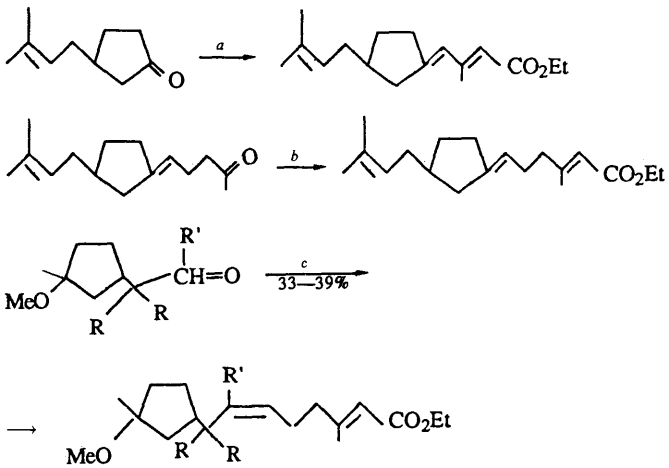
Scheme 72



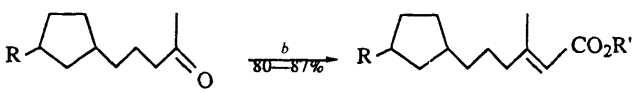
a: $CH_2I_2/Zn/CuO$; *b*: $(EtO)_2P(O)CH_2CO_2Et$; *c*: $CHCl_3/Et_3BuNCl^{\ominus}$; *d*: $EtO_2CCH_2N_2$.

A typical route for the synthesis of juvenoids containing a carbocyclic residue is the olefination of cyclic ketones or ketones and aldehydes containing a cyclic fragment in the carbon chain (Scheme 73).[222–232]

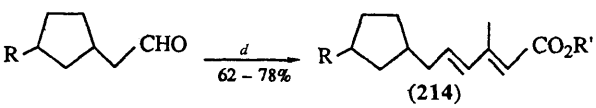
Scheme 73



R = H, Me; R' = H, Me;

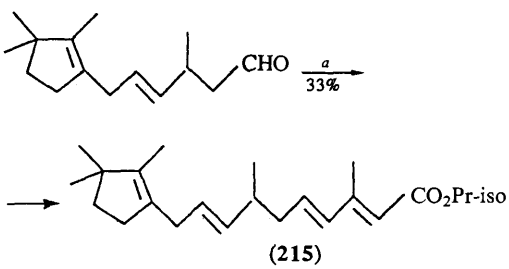


R = $CH(Me)_2$; $C(Me)_3$; $HOCMe_2$; R' = Et, $CHMe_2$;

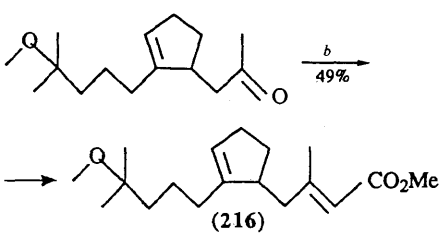


(214)

R = OAc, $MeC(OMe)-CH_2-CH_2$; R' = Et, Pr-iso;

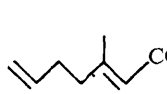


(215)



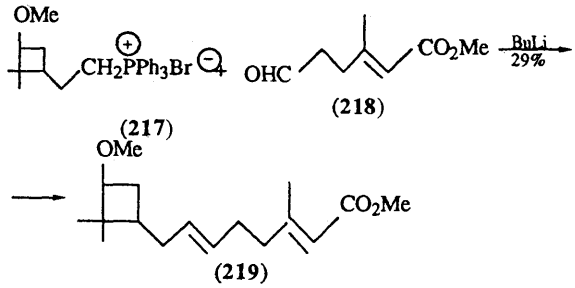
(216)

a: $(EtO)_2P(O)CHC(Me)=CHCO_2Et$, *b*: $(EtO)_2P(O)CHCO_2Et$;

c: Ph_3P  CO_2Et; *d*: $Br^{\ominus}(Ph_3)PC$ $CO_2R'/BuLi$

The juvenoid (**219**) was obtained by the reaction of the aldehyde (**218**) with the phosphonium salt (**217**) containing a cyclobutane residue (Scheme 74).[233]

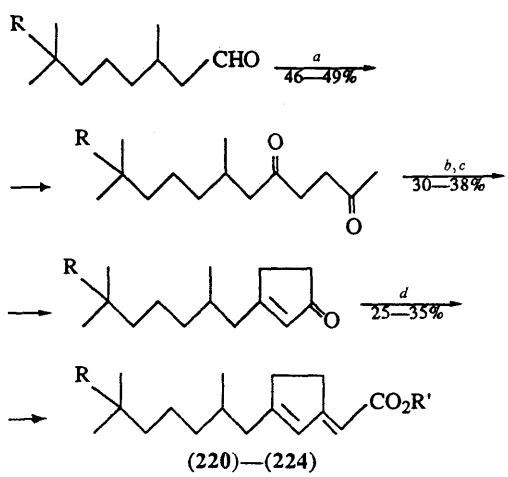
Scheme 74



It may be concluded from the existing literature data that AJH containing an alicyclic residue possess lower juvenoid activity than compounds without these fragments. The dienoates (**214**) do not have significant advantages over the unconjugated or α,β-unsaturated esters. The presence of a double bond in a cyclopentane ring does not increase biological activity [compounds (**215**), (**216**)]. Juvenoids containing cyclobutane rings proved to be selectively active towards *Tribolium costaneum*.[233,234]

The ethyl bridge between atoms C(3) and C(5) in the 2,4-dienoates (**220**)–(**224**) leads to high morphogenetic activity, two to three times greater than the activity of methoprene (**177**) and hydroprene (**174**) on the pupa of the Cabbage White butterfly (*Pieris brassicae*).[235–237] The methoxy derivatives of the 2,4-dienoates of this series are selectively active towards *Diptera*, while compounds without the methoxy group display higher activity towards *Lepidoptera* (Scheme 75).[236]

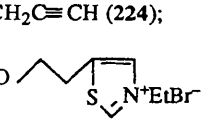
Scheme 75



(220)—(224)

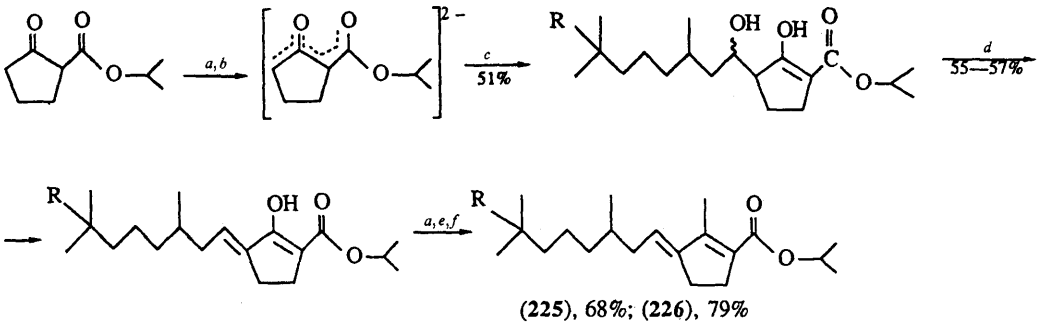
R = H (**220**), (**221**); OMe (**222**)—(**224**); R' = H (**220**), (**222**);

$CHMe_2$ (**221**), (**223**); $CH_2C{\equiv}CH$ (**224**);

a: $H_2C=CHC(O)Me/HO$  ; *b*: iso-$PrNH_2$; *c*: NaH;

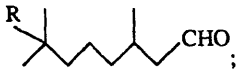
d: $Me_3SiCH_2CO_2R'$ or $(R^1O)_2P(O)CH_2CO_2R^1$.

Scheme 76



(225), 68%; (226), 79%

R = H (225), OMe (226);

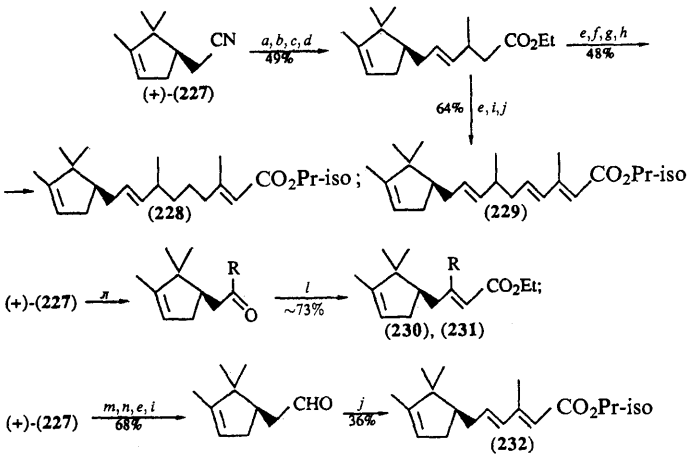
a: NaH; *b*: AlkLi; *c*:  ; *d*: HCl; *e*: Et_2PCl; *f*: $LiCuAlk_2$.

The following route is proposed for the synthesis of 2,4-dienoates (**225**) and (**226**) with an ethylene bridge between the C(2) and C(4) atoms (Scheme 76).[238]

The optically active compounds (**228**)–(**232**), obtained from (+)-1-cyanomethyl-2,2,3-trimethyl-3-cyclopentane (**227**), displayed higher juvenoid activity than the corresponding racemates (Scheme 77).[239,240]

Juvenoids of medium activity (**234**) and (**235**), containing a cyclobutane ring, were obtained by the partial ozonolysis of caryophyllene (**233**) (Scheme 78).[241]

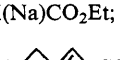
Scheme 77



R = Me (230), Et (231);

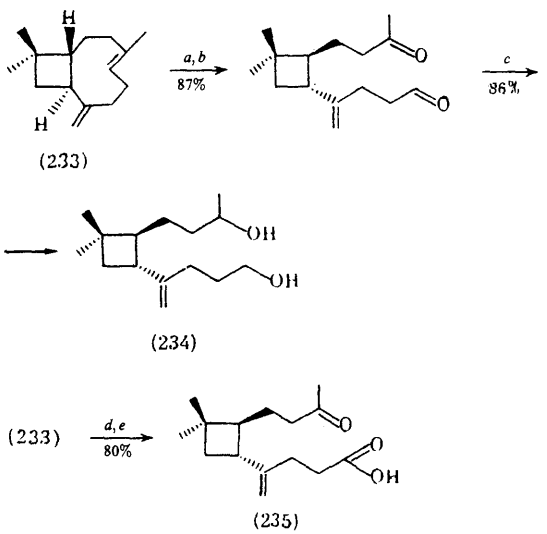
a: $CH_2=CHMgBr$; *b*: $Et_3N/EtOH$; *c*: iso-BuAlH; *d*: $MeC(OEt)_3$;

e: $LiAlH_4$; *f*: PBr_3; *g*: $AcCH(Na)CO_2Et$; *h*: $(EtO)_2P(O)\overset{\ominus}{C}HCO_2Pr$-iso;

i: $Py.CrO_3.HCl$; *j*: $(EtO)_2P(O)$  CO_2Pr-iso; *k*: RMgX;

l: $(EtO)_2P(O)\overset{\ominus}{C}HCO_2Et$; *m*: KOH/H_2O; *n*: TsOH/EtOH.

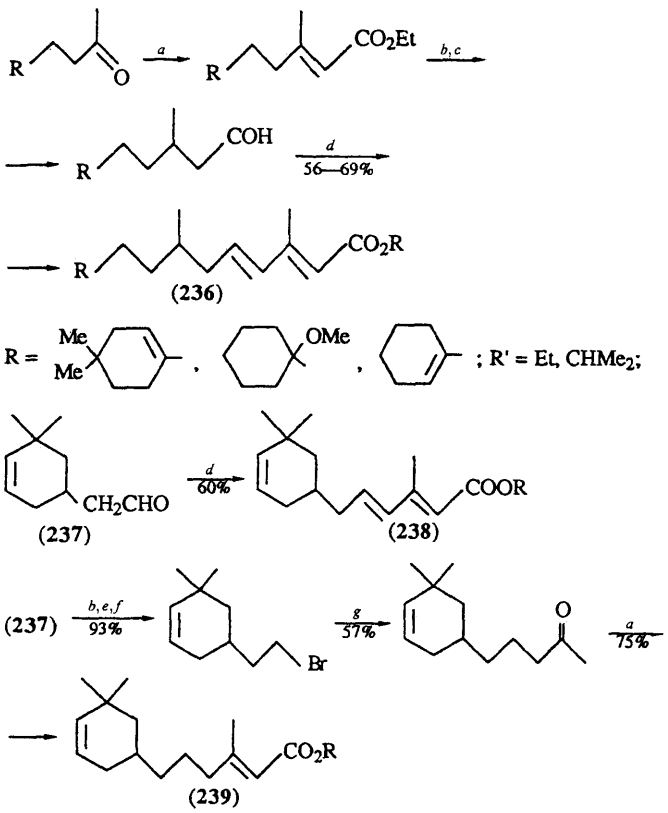
Scheme 78



a: O_3/MeOH; *b*: H_2/Pd.$CaCO_3$.PbO; *c*: $NaBH_4$; *d*: O_3/AcOH; *e*; AcOH/AcONa.

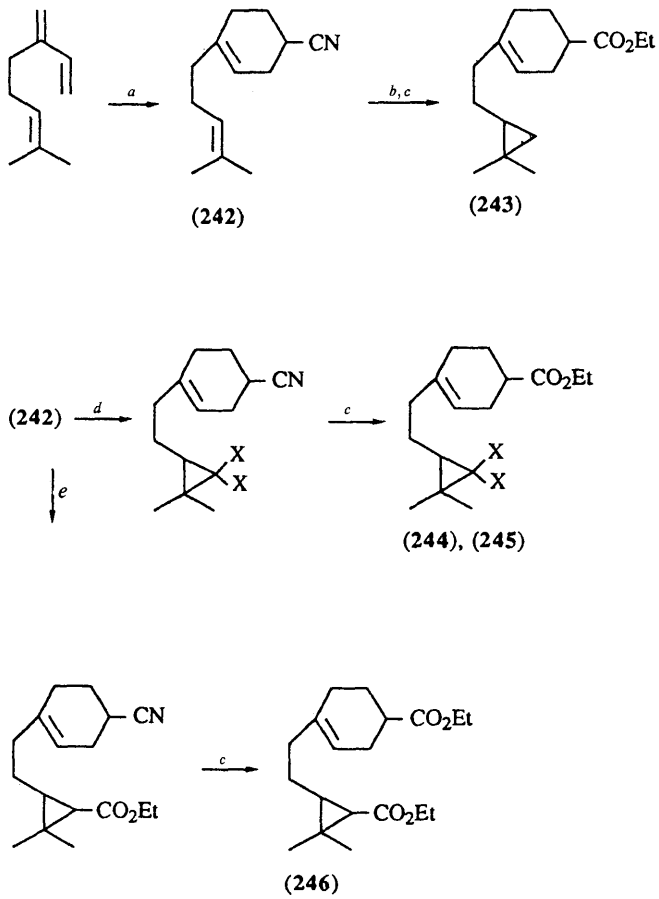
The juvenoids (**236**) with a six-membered ring, like the related compounds (**238**)–(**241**) obtained from the aldehyde (**237**), are not active towards the yellow meal worm and are ten times less active than their acyclic analogues towards *Dysdercus cingulatus* (Scheme 79).[123,217,242–245]

Scheme 79



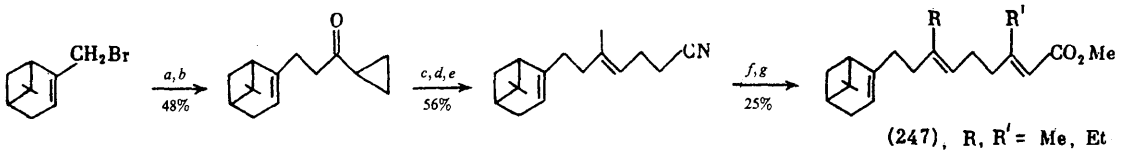
The compounds (**243**)–(**246**) obtained from compound (**242**) and containing cyclohexene and cyclopropane fragments proved to be active towards *Dysdercus koenigii* (Scheme 80).[246]

Scheme 80

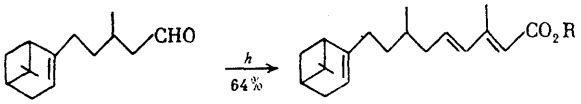


Several AJH have been synthesised with pinene (**247**) and (**248**) and norbornene (**249**) bicyclic fragments.[217,247–249] The AJH (**251**)–(**253**) were synthesised from camphene (**250**) (Scheme 81).

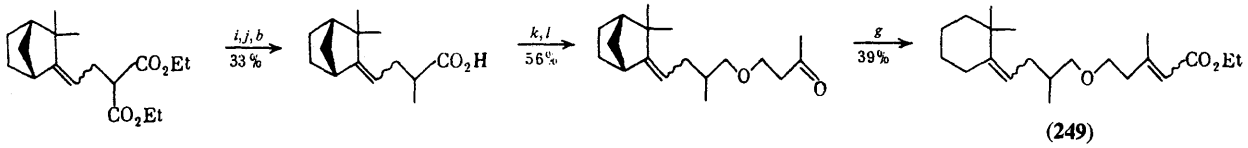
Scheme 81



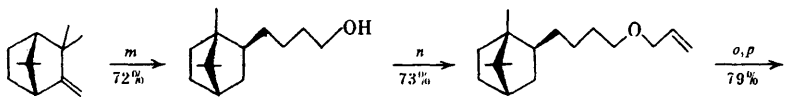
(247), R, R' = Me, Et



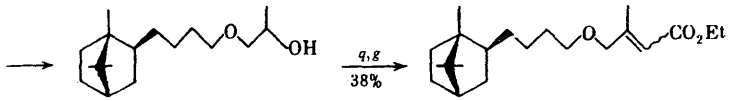
(248), R = Et, $CHMe_2$



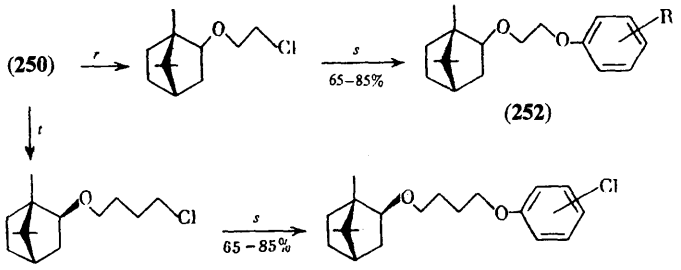
(249)



(250)



(251)



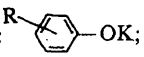
R = 4-Et; 2-iso-Pr; 2-Me; 4-iso-Pr; 2-Me; 4-Ac; 4-Cl; 4-Br; 2,4,6-Cl_3; 4-NO

a: $EtO_2CCH_2\overset{O}{\overset{\|}{C}}/EtONa$; *b*: Δ; *c*: RMgI; *d*: HBr; *e*: NaCN; *f*: R_1MgBr;

g: $(EtO)_2\overset{\ominus}{P}(O)CHCO_2Me$; *h*: $(EtO)_2\overset{\ominus}{P}(O)CH-C(CH_3)=CHCO_2R$;

i: Na/MeI; *j*: $OH^{\ominus}$; *k*: $LiAlH_4$; *l*; $CH_2=CH-C(O)-Me$;

m: $HO(CH_2)_3OH/HClO_4$; *n*: $CH_2=CH-CH_2I$; *o*: $Hg(OAc)_2$;

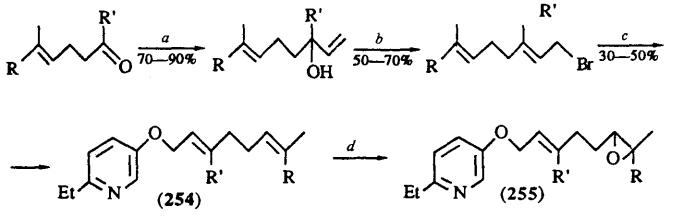
p: $NaBH_4/OH^{\ominus}$; *q*: CrO_3/Py; *r*: $HO(CH_2)_2Cl/HClO_4$; *s*: 

t: $HO(CH_2)_4Cl/HClO_4$.

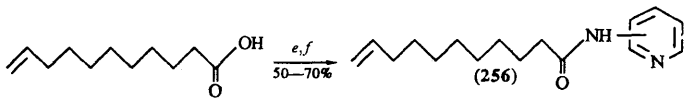
b) Juvenoids containing heterocycles

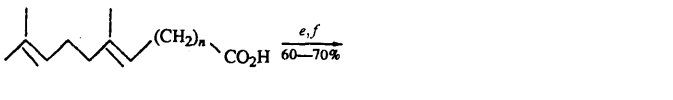
Compounds containing heterocycles have been investigated as AJH. The AJH (**254**)–(**257**) have been obtained with a pyridine ring in the molecule and also compound (**258**) containing a pyrrolidine ring as well (Scheme 82).[250–252]

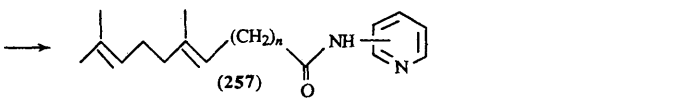
Scheme 82



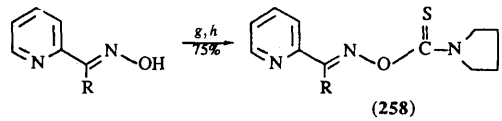
R = $Me(CH_2)_2$, $Me(CH_2)_3$; R' = Me, Et;



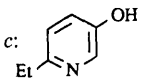




n = 0,1



R = Me, Me_2CH;

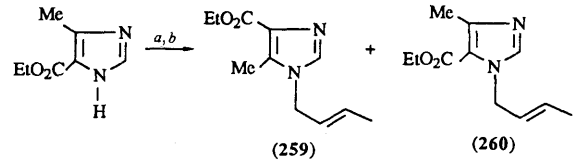
a: $CH_2=CHMgBr$; *b*: HBr; *c*:  ; *d*: $3\text{-}ClC_6H_4CO_3H$; *e*: $SOCl_2$;

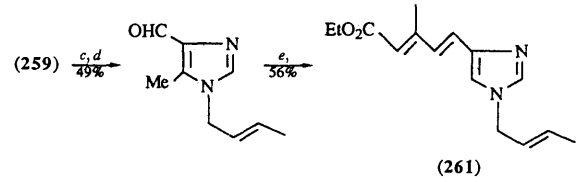
f: ; *g*: $CSCl_2/Et_3N$; *h*: .

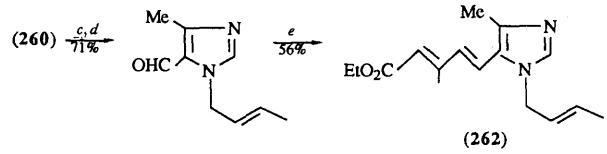
It was established that the introduction of a pyridine ring reduced JH activity significantly. A similar result was obtained for the imidazole derivatives (**261**) and (**262**) synthesised from compounds (**259**) and (**260**) (Scheme 83).[157,253]

Highly active AJH have been discovered among compounds (**263**)–(**266**) containing oxygen in the heterocycle and also for compounds (**267**) and (**268**) containing both nitrogen and oxygen in the rings (Scheme 84).[254,255]

Scheme 83

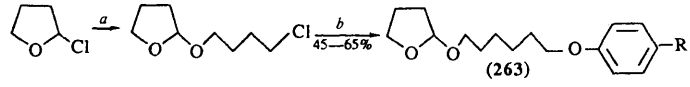




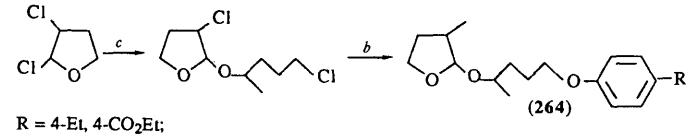


a: NaH; *b*: $Me_2C=CH-CH_2Cl$; *c*: $LiAlH_4$; *d*: MnO_2; *e*: $(EtO)_2-\overset{\ominus}{C}H.-C(Me)=CHCO_2Et$.

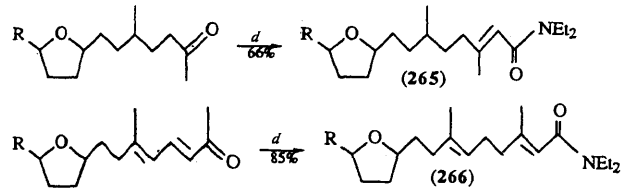
Scheme 84



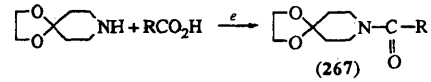
R = 4-H, 3-Me, 4-OMe, 4-SMe, 4-COMe, 4-COEt, 4-CO_2Me, 4-CO_2Et, 4-Cl, 4-NO_2.

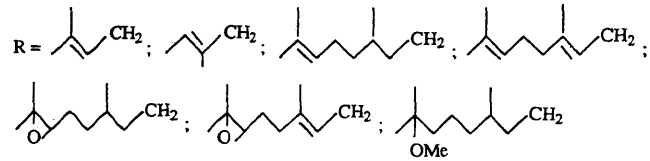


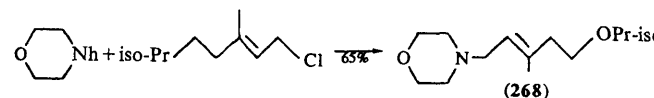
R = 4-Et, 4-CO_2Et;

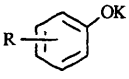
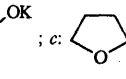


R= H, Me;



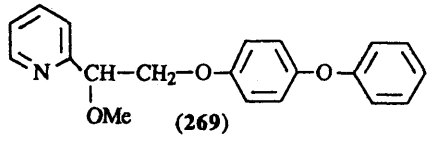




a: $HO(CH_2)_4Cl$; *b*: R-  ; *c*:  ; *d*: $(EtO)_2P(O)\overset{\ominus}{C}HCONEt_2$;

e: $Ph_2P(O)Cl$.

It turned out that the JH activity of compound (**269**) exceeded that of methoprene (**177**) in relation to *Aedes aegypti, Galleria mellonella, Tenebrio molitor* and *Musca domestica*.[256]

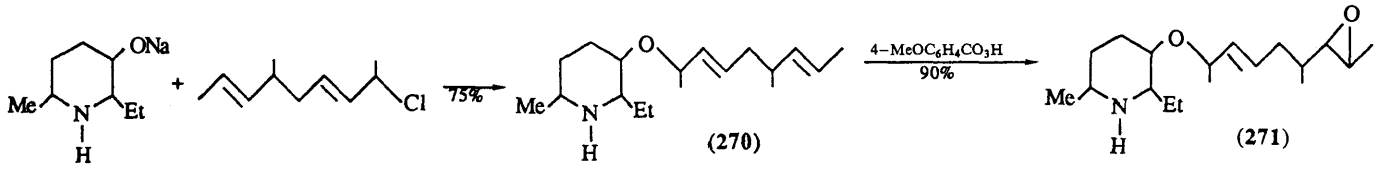


(**269**)

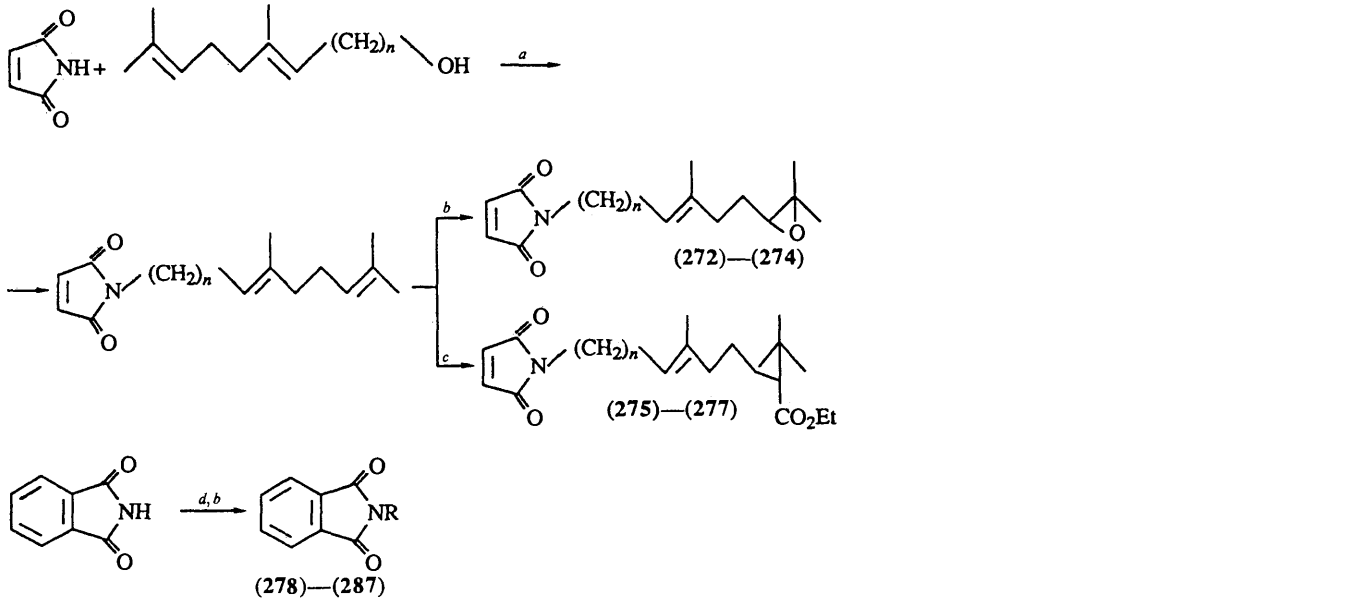
Oxa-AJH containing a piperidine ring (**270**) and (**271**) displayed selective activity towards *Coleoptera* (Scheme 85).[257]

Of the other AJH containing nitrogen heterocycles it is necessary to mention the derivatives of maleimide (**272**)–(**277**) and phthalimide (**278**)–(**287**).[258,259] Compounds (**278**)–(**287**) were tested for JH activity against *Dysdercus koenigii* and proved to be 1.5–2 times more active than methyl faranesenate (**152**). Compounds (**283**)–(**287**), containing an epoxy group in the isoprenoid group R, display higher activity (Scheme 86).

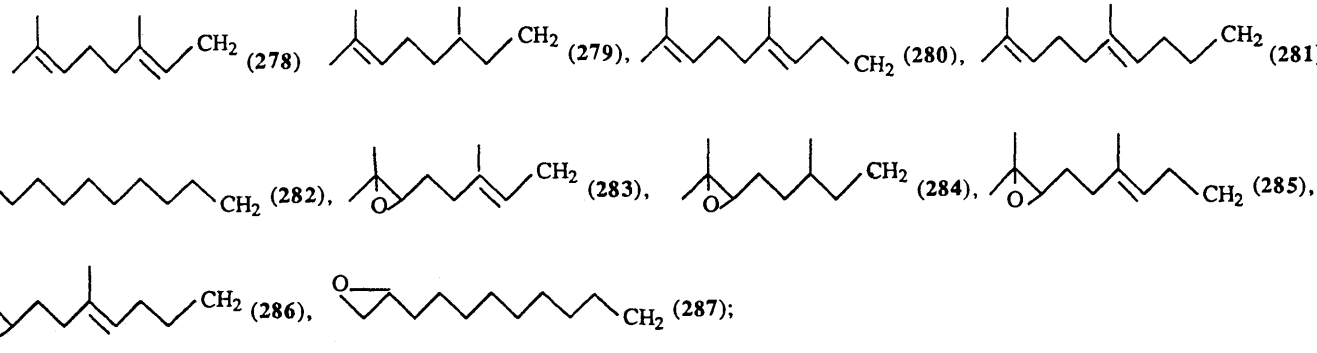
Scheme 85



Scheme 86

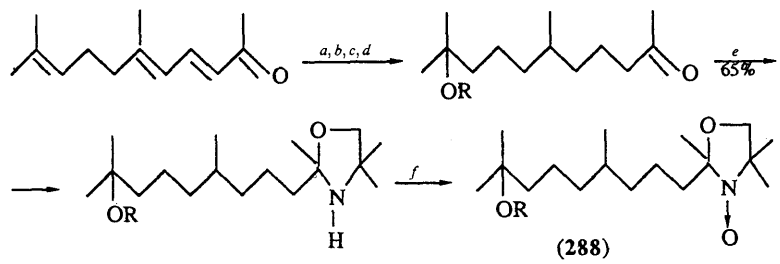


n = 1 (**272**), (**275**); 2 (**273**), (**276**); 3 (**274**), (**277**);

R =  (**278**), (**279**), (**280**), (**281**), (**282**), (**283**), (**284**), (**285**), (**286**), (**287**);

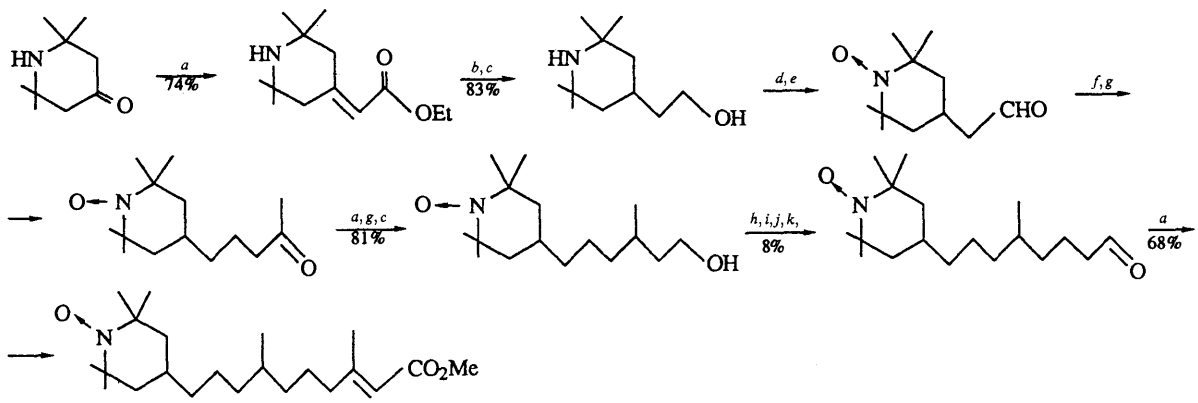
a: $PhP/N_2(CO_2Et)_2$; *b*: $3\text{-}ClC_6H_4CO_3H$; *c*: $N_2C(CO_2Et)_2$; *d*: ROH/PPh_3; $N_2(CO_2Et)_2$.

Scheme 87



(288)

R = Me, Et;
a: Ni–Re; *b*: $Hg(OAc)_2/ROH$; *c*: $NaOH/NaBH_4$; *d*: CrO_3; *e*: $Me(NH_2)_2C-CH_2OH$; *f*: $3\text{-}Cl-C_6H_4CO_3H$.

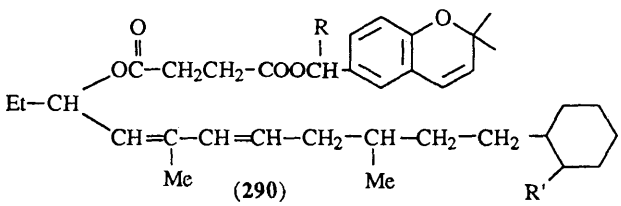


(289)

a: $(EtO)_2P(O)^{\ominus}CHCO_2Et$; *b*: $H_2/Ni-Re$; *c*: $LiAlH_4$; *d*: H_2O_2; *e*: CrO_3/Py; *f*: $Ph_3P=CHCH_2C(O)Me$; *g*: $H_2/Pd-BaSO_4$; *h*: TsCl/Py; *i*: NaI/. .acetone; *j*: $MeC(O)CH_2CO_2Et$; *k*: Δ.

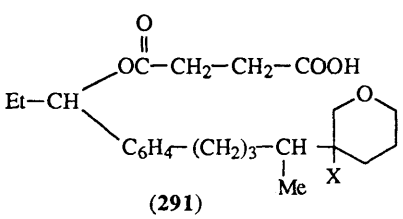
AJH with stable nitroxyl radicals in oxazolidine (**288**)[260] or piperidine (**289**)[261] rings have been synthesised and display high juvenoid activity (Scheme 87).[260,261]

The mixed succinic acid esters (**290**) and (**291**) proved to be active analogues of JH.[262,263]



(290)

R = Me, Et, Pr; R′ = H, Me, Et, Pr, iso-Pr:



(291)

X = H, Cl

To date, stereospecific methods of synthesising the natural juvenile hormones have been developed. Active analogues of the juvenile hormones, such as farnesal, methyl farnesenate, echinolone and juvabione, have been isolated from natural sources. The discovery in nature of JH analogues has stimulated investigation of the synthesis and study of the biological activity of compounds of various structures. Highly active juvenoids have become apparent in various classes of organic compounds. The most active juvenoids were found among the isoprenoid 2,4-dienoates and the aryl ethers of geraniol. The search for highly active and readily available JH analogues has been actively pursued since juvenoids are already recommended as effective and ecologically safe agents for regulating the insect population and an extension of their use for this purpose must be expected.

References

1. J J Menn *Zashchita Rastenii i Rastenievodstvo: Dokl. Mezhdunarodnogo Simpoziuma* (Plant Protection and Plant Cultivation: Reports of the International Symposium), Moscow, 1984, p. 80
2. H Roller, K H Dahm, C C Sweeley, B H Trost *Angew. Chem.*, 1967, **79** 190
3. A S Meyer, D H Schneidermann, E Hanzmann *Proc. Natl. Acad. Sci. USA*, 1968, **60** 853
4. K I Judy, D H Schooley, L L Duhman, et al. *Proc. Natl. Acad. Sci. USA*, 1973, **70** 1509
5. T Koyama, K Ogura, F C Baker, et al. *J. Am. Chem. Soc.*, 1987, **209** 2853

6. G T Brooks, A W Johnson *Chemicals and Insects: Interdisciplinary Science Reviews*, 1979, Vol. 4, p. 279
7. V N Burov, N N Gamper, A P Sazonov *Gormonal'nye Preparaty v Bor'be s Vrednymi Nasekomymi* (Hormonal Preparations in the Fight Against Harmful Insects), VNIITEIsel'khoz MSKh SSSR, Moscow, 1974, 58 pp
8. Yu S Tsizin, A A Drabkina *Usp. Khim.*, 1970, **39**(6) 1074 [English translation in *Russ. Chem. Rev.*, 1970(6)]
9. K Slama, M Romanuk, F Sorm *Insect Hormones and Bioanalogues*, Springer Verlag, Wien, New York, 1979, 477 pp
10. C Wawrzenczyk *Pr. Nauk Insect. Chem. Org. Fiz. Politech. Wroclaw*, 1985, 147 pp
11. J J Menn, M Beroza *Insect Juvenile Hormones*, Academic Press, New York, London, 1972, 50 pp
12. A V Lozanova, A M Moiseenkov *Khim. Prir. Soedin.*, 1988, 133
13. E P Serebryakov, V K Promonenkov *Itogi Nauki i Tekhniki. Ser. Organicheskaya Khimiya* (Progress in Science and Technology. Organic Chemistry Series), AN SSSR VINITI, Moscow, 1989, Vol. 9, p. 102
14. A F Granov, M Ya Pushina *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1988, **33** 661
15. Z Wimmer, M Romanuk *Collect. Czech. Chem. Commun.*, 1989, **54** 2302
16. M Romanuk *Pestycydy*, 1988, 14
17. M Z Krimer, V I Spektor, G E Muntyan, A A Shamshurin *Zh. Org. Khim.*, 1974, **10** 1614
18. R J Anderson, C A Henrick, J B Siddall, R Zurfluh *J. Am. Chem. Soc.*, 1972, **94** 5379
19. K H Dahm, B M Trost, H Roller *J. Am. Chem. Soc.*, 1967, **89** 5292
20. W Biernicki *Pol. J. Chem.*, 1980, **54** 777
21. V N Odinokov, O S Kukovinets, N I Sakharova, G A Tolstikov *Zh. Org. Khim.*, 1985, **21** 1180
22. K H Dahm, H Roller, B M Trost *Life Sci.*, 1968, 129
23. C A Henrick, F Schaub, J B Siddall *J. Am. Chem. Soc.*, 1972, **94** 5374
24. E E Van Tamelen, T I Curphey *Tetrahedron Lett.*, 1962, 121
25. R J Anderson, C A Henrick, J B Siddall *J. Am. Chem. Soc.*, 1970, **92** 735
26. K Mori, M Ohki, M Matsui *Agric. Biol. Chem.*, 1972, **36** 1085
27. K Mori, M Ohki, M Matsui *Tetrahedron*, 1974, **30** 715
28. E J Corey, H Yamamoto *J. Am. Chem. Soc.*, 1970, **92** 6636
29. A S Meyer, E Hanzmann *Biochem. Biophys. Res. Commun.*, 1970, **41** 891
30. K Imai, S Marumo, T Ohtaki *Tetrahedron Lett.*, 1976, 1211
31. K B Sharpless, R C Michaelson *J. Am. Chem. Soc.*, 1973, **95** 6136
32. S Tanaka, H Yamamoto, H Nozaki, et al. *J. Am. Chem. Soc.*, 1974, **96** 5254
33. W Eng, G D Prestwich *J. Labelled Compd. Radiopharm.*, 1988, **25** 627
34. G D Prestwich, C Wawrzenczyk *Proc. Natl. Acad. Sci. USA*, 1985, **82** 5290
35. P Loew, S Johnson *J. Am. Chem. Soc.*, 1971, **93** 3765
36. D J Faulkner, M R Petersen *J. Am. Chem. Soc.*, 1971, **93** 3766
37. Y Naruse, T Esaki, H Yamamoto *Tetrahedron*, 1988, **44** 4747
38. Y Suzuki, K Imai, S Marumo, T Mitsui *Agric. Biol. Chem.*, 1972, **36** 1849; *Chem. Abs.*, 1973, **78** 79948 g
39. K Imai, S Marumo, K Mori *J. Am. Chem. Soc.*, 1974, **96** 5925
40. K Mori, M Fujiwhara *Tetrahedron*, 1988, **44** 343
41. K Mori, M Fujiwhara *Liebigs Ann. Chem.*, 1989, 41
42. K Mori, H Mori *Tetrahedron*, 1987, **43** 4097
43. M Jacobson, R E Redfern, G D Mills *Lloydia*, 1975, **38** 473; *Chem. Abs.*, 1976, **85** 1961f
44. O P Vig, S D Sharma, S S Bari, V K Handa *Indian J. Chem., Sect. B*, 1977, **15** 1078
45. M V Mavrov, Nguen Kong Khao, I M Vol'pin, et al. *Bioorg. Khim.*, 1986, **12** 961
46. F Orsini, F Pelizzoni *J. Org. Chem.*, 1980, **45** 4726
47. M P Cooke *J. Org. Chem.*, 1979, **44** 2461
48. K Slama, C H Williams *Proc. Natl. Acad. Sci. USA*, 1965, **54** 411
49. W S Bowers, H M Fales, M J Thompson, E C Uebel *Science*, 1966, **154** 1020
50. J F Manville *Can. J. Chem.*, 1975, **53** 1579
51. J F Blount, B A Pawson, G Saucy *J. Chem. Soc., Chem. Commun.*, 1969, 715
52. I M Roger, J F Manville *Can. J. Chem.*, 1974, **52** 1192
53. P A Bartlett *Tetrahedron*, 1980, **36** 61
54. V Cerny, L Dolejs, L Labler, F Sorm *Tetrahedron Lett.*, 1967, 1053
55. K S Ayyar, G S K Rao *Can. J. Chem.*, 1968, **46** 1467
56. B M Trost, Y Tamaru *J. Am. Chem. Soc.*, 1977, **99** 3101
57. A J Birch, P L Macdonald, V M Powel *J. Chem. Soc., C*, 1970, 1469
58. A A Drabkina, Yu S Tsizin *Zh. Obshch. Khim.*, 1973, **43** 689
59. K Mori, M Matsui *Tetrahedron*, 1986, **24** 3127
60. E Negishi, M Sabanski, J J Katz, H C Brown *Tetrahedron*, 1976, **32** 925
61. B A Pawson, H C Cheung, S Curbaxani, G Saucy *J. Am. Chem. Soc.*, 1970, **92** 336
62. J Ficini, J d'Angelo, J Noire *J. Am. Chem. Soc.*, 1974, **96** 1213
63. D A Evans, J V Nelson *J. Am. Chem. Soc.*, 1980, **102** 774
64. T Tokoroyama, L Pan *Tetrahedron Lett.*, 1989, **30** 197
65. J F Manville, L Greguss, K Slama, E Rudloff *Collect. Czech. Chem. Commun.*, 1977, **42** 3658
66. R B Mane, G S K Rao *Indian J. Chem.*, 1974, **12** 936
67. B P Kavitake, U V Desai, D G Desai, R B Mane *Indian J. Chem., Sect. B*, 1986, **25** 178
68. P Schmialek *Z. Naturforsch, B*, 1962, **16** 461; *Chem. Abs.*, 1962, **57** 7751f
69. P Schmialek *Z. Naturforsch, B*, 1961, **15** 513
70. G H Cardillo, M Contento, A Umani-Ronchi, M Panunzion *Chem. Ind. (London)*, 1977, 873
71. Author's Certificate 153934 ChSSR; *Ref. Zh .Khim.*, 1976, 12O323P
72. A Kogerman, K Ammon, K Leets, et al. *Izv. Akad. Nauk EstSSR, Khimiya*, 1984, **33** 131
73. R S Deshpande, H P Tipnis, V M Kulkarni *Indian J. Chem., Sect. B*, 1976, **14** 979
74. M M Patil, S A Patwardhan, A S Gupta *Indian J. Chem., Sect. B*, 1978, **16** 625
75. US P. 4014901; *Ref. Zh. Khim.*, 1977, 22O302P
76. US P. 3960902; *Ref. Zh. Khim.*, 1977, 3O361P
77. US P. 3970688; *Ref. Zh. Khim.*, 1977, 7O353P
78. S A Patwardhan, A S Gupta, A Aggarwal, R N Sharma *Indian J. Chem., Sect. B*, 1982, **21** 156
79. M K Moorthy, A S Gupta, B P Sexena, O Koul *Indian J. Chem., Sect. B*, 1979, **18** 563
80. Author's Certificate 155864 ChSSR; *Ref. Zh. Khim.*, 1977, 5O353P

81. Author's Certificate 155 862 ChSSR; *Ref. Zh. Khim.*, 1977, 5O351P
82. V Jarolim, F Sorm *Collect. Czech. Chem. Commun.*, 1974, **39** 587
83. Author's Certificate 156 636 ChSSR; *Ref. Zh. Khim.*, 1977, 5O349P
84. Author's Certificate 156 635 ChSSR; *Ref. Zh. Khim.*, 1977, 5O350P
85. V Jarolim, F Sorm *Collect. Czech. Chem. Commun.*, 1977, **42** 1894
86. V Jarolim, F Sorm *Collect. Czech. Chem. Commun.*, 1977, **42** 3490
87. US P. 3 959 264; *Ref. Zh. Khim.*, 1977, 2O319P
88. US P. 4 054 667; *Ref. Zh. Khim.*, 1978, 10O303P
89. US P. 3 970 758; *Ref. Zh. Khim.*, 1977, 8O312P
90. US P. 4 051 262; *Ref. Zh. Khim.*, 1978, 10O307P
91. US P. 3 910 894; *Ref. Zh. Khim.*, 1976, 12O322P
92. US P. 3 907 783; *Ref. Zh. Khim.*, 1976, 14O388P
93. US P. 3 953 607; *Ref. Zh. Khim.*, 1977, 2O317P
94. Czech. P. 148 960; *Ref. Zh. Khim.*, 1977, 5O348P
95. O P Vig, G L Kad, S Kumari, J Singh *J. Indian Chem. Soc.*, 1984, **61** 344
96. A A Svishchuk, V I Sheiko, I N Oleshchenko *Fiziol. Akt. Veshchestva*, 1977, **9** 37
97. J Kahovcova, M Romanuk *Collect. Czech. Chem. Commun.*, 1981, **46** 1413
98. Austrian P. 341 774; *Ref. Zh. Khim.*, 1978, 16O247P
99. Polish P. 120 901; *Ref. Zh. Khim.*, 1984, 4H158P
100. Author's Certificate 200 330 ChSSR; *Ref. Zh. Khim.*, 1983, 15O329P
101. Japanese P. 57-52342; *Ref. Zh. Khim.*, 1984, 17O321P
102. Author's Certificate 209 622 ChSSR; *Ref. Zh. Khim.*, 1984, 5O322P
103. K Leets, M Shmidt, T Kaal, et al. *Izv. Akad. Nauk EstSSR, Khimiya*, 1986, **35** 223
104. O P Vig, I R Trehan, A L Bedi, S Kumari *Indian J. Chem., Sect. B*, 1982, **21** 159
105. K Leets, M Shmidt, T Vyalimyae, et al. *Izv. Akad. Nauk EstSSR, Khimiya*, 1987, **3** 297
106. US P. 4 661 617; *Ref. Zh. Khim.*, 1988, 5O374P
107. Author's Certificate 253 350 ChSSR; *Ref. Zh. Khim.*, 1989, 9O339P
108. Author's Certificate 239 408; *Ref. Zh. Khim.*, 1987, 23O338P
109. O V Shekhter, Yu S Tsizin *Zh. Org. Khim.*, 1977, **13** 993
110. Author's Certificate 241 705 ChSSR; *Ref. Zh. Khim.*, 1988, 18O323P
111. A Kogerman, K Ammon, Kh Rang, K Leets *Izv. Akad. Nauk EstSSR, Khimiya*, 1977, **28** 257
112. Author's Certificate 533 585; *Byull. Izobret.*, 1976, (40) 62
113. C Wawrzenczyk, Z Przepiorka, A Zabra *Pol. J. Chem.*, 1981, **55** 819
114. J Kahovcova, M Romanuk *Collect. Czech. Chem. Commun.*, 1981, **46** 2742
115. Author's Certificate 529 760; *Byull. Izobret.*, 1978, (35) 184
116. A P Phadnis, B Nanda, S A Patwardhan, A S Gupta *Indian J. Chem., Sect. B*, 1984, **23** 1098
117. A P Phandis, S A Patwardhan, P V Powar, R N Sharma *Indian J. Chem., Sect. B*, 1988, **27** 600
118. Japanese P. 55-38921; *Ref. Zh. Khim.*, 1981, 13O323P
119. N V Kuznetsov, N Kh Mikryukova, R Yu Selens *Respublikanskii Mezhvuzovskii Sbornik* (Republican Inter-University Symposium), 1977, 27; *Ref. Zh. Khim.*, 1977, 2OE20
120. US P. 3 904 773; *Ref. Zh. Khim.*, 1976, 12O319P
121. US P. 396 282
122. M Schwarg, R W Miller *J. Med. Entomol.*, 1979, **15** 300; *Ref. Zh. Khim.*, 1979, 21O340
123. L Borowiecki, A Kazubski, E Reca, W Wodzki *Liebigs Ann. Chem.*, 1985, 929
124. F Szurdoki, L Novak, B Majoros, C Szantay *Acta Chim. Acad. Sci. Hung.*, 1987, **124** 511
125. R B Mane, U V Desai, G D Hebbalkar *Collect. Czech. Chem. Commun.*, 1988, **53** 646
126. US P. 3 904 763; *Ref. Zh. Khim.*, 1976, 12O312P
127. Author's Certificate 155 864 ChSSR; *Ref. Zh. Khim.*, 1977, 5O353P
128. W Biernacki, W Sobotka *Pol. J. Chem.*, 1979, **53** 461
129. W Biernacki, W Sobotka *Rocz. Chim.*, 1977, **51** 469
130. M Kozlowska, W Sobotka, J Daroszewski, R Sterzycki *Rocz. Chim.*, 1977, **51** 1133
131. V Jarolim, F Sorm *Collect. Czech. Chem. Commun.*, 1974, **39** 596
132. Author's Certificate 155 757 ChSSR; *Ref. Zh. Khim.*, 1976, 17O404P
133. V Jarolim, F Sorm *Collect. Czech. Chem. Commun.*, 1975, **40** 1059
134. O V Shekhter, N L Sergovskaya, Yu S Tsizin, E A Pridantseva *Zh. Org. Khim.*, 1982, **18** 755
135. Author's Certificate 189 383 ChSSR; *Ref. Zh. Khim.*, 1983, 24O337P
136. Author's Certificate 189 384 ChSSR; *Ref. Zh. Khim.*, 1983, 24O338P
137. Author's Certificate 194 577 ChSSR; *Ref. Zh. Khim.*, 1985, 21O451P
138. A A Gupta, A Rastogi, M M Gupta, et al. *Indian J. Chem., Sect. B*, 1983, **22** 948
139. O P Vig, I R Trehan, S Kumari, M S Grewal *Indian J. Chem., Sect. B*, 1980, **19** 784
140. M Zaoral, K Slama *Science*, 1970, **170** 92
141. R K Mahajan, N Gupta, S Uppal, R Bhardway *Indian J. Exp. Biol.*, 1987, **25** 86
142. Z Wimmer, L Streinz, M Romanuk *Collect. Czech. Chem. Commun.*, 1985, **50** 2453
143. J B Rodrigues, T G Gros, A M Stoka *Z. Naturforsch., B*, 1988, **43** 1038
144. W Biernacki, A Gdula *Pol. J. Chem.*, 1981, **55** 1063
145. W Biernacki, W Sobotka *Rocz. Chim.*, 1977, **51** 979
146. W Biernacki, A Gdula *Pol. J. Chem.*, 1982, **56** 527
147. Japanese P. 60-181064; *Ref. Zh. Khim.*, 1986, 21O403P
148. W Biernacki, A Gdula *Pol. J. Chem.*, 1982, **56** 1365
149. W Biernacki, W Sobotka *Rocz. Chim.*, 1976, **50** 1323; *Ref. Zh. Khim.*, 1977, 6E35
150. W Biernacki, W Sobotka *Pol. J. Chem.*, 1979, **53** 1283
151. Z Wimmer, D Saman, J Smolikova, M Romanuk *Liebigs Ann. Chem.*, 1988, 1091
152. K Hejno, F Sorm *Collect. Czech. Chem. Commun.*, 1976, **41** 1225
153. K Hejno, F Sorm *Collect. Czech. Chem. Commun.*, 1980, **45** 1734

154. S D Sharma, R C Aggarwal, B R Soni, M L Sharma *Indian J. Chem., Sect. B*, 1979, **18** 81
155. O P Vig, I R Trehan, G L Kad, et al. *J. Indian Chem. Soc.*, 1985, **62** 391
156. O P Vig, I R Trehan, G L Kad, S Kumari *Indian J. Chem., Sect. B*, 1982, **21** 781
157. Author's Certificate 155 395 ChSSR; *Ref. Zh. Khim.*, 1976, 14O389P
158. S Bernasconi, M Ferrari, P Gariboldi, et al. *Experientia*, 1980, **32** 1337
159. H C F Su, R Horvat *J. Agric. Food Chem.*, 1981, **29** 115
160. K R Solomon, A A Evans *J. Med. Entomol.*, 1977, **14** 433
161. Japanese P. 60-181062; *Ref. Zh. Khim.*, 1986, 21O402P
162. US P. 4 608 389; *Ref. Zh. Khim.*, 1987, 10O428P
163. K Mori, T Takigawa, Y Manabe, et al. *Agric. Biol. Chem.*, 1975, **39** 249; Ref. Zh. Khim., 1975 14E167
164. F Camps, R Canela, J Coll *Tetrahedron*, 1978, **34** 2179
165. Y Ozawa, K Mori, M Matsui *Agric. Biol. Chem.*, 1973, **37** 2373; *Chem. Abs.*, 1974, **80** 37321h
166. G R Nilles, et al. *J. Agric. Food Chem.*, 1973, **21** 342; *Chem. Abs.*, 1973, **79** 61833b
167. P A Cruickshank, R M Palmere *Nature (London)*, 1971, **233** 488; *Chem. Abs.*, 1972, **76** 54516k
168. K Leets, A Kogerman, K Ammon *Izv. Akad. Nauk EstSSR, Khimiya*, 1978, **27** 36
169. J H Law, C Yunn, C M Williams *Proc. Natl. Acad. Sci. USA*, 1966, **55** 576
170. M Z Krimer, et al. *Zh. Org. Khim.*, 1979, **15** 713
171. W R Dolbier, K S Medinger, A Greenberg, J F Liebman *Tetrahedron*, 1982, **38** 2415
172. F Camps, A Messeguer, F Sanchez *Tetrahedron*, 1988, **44** 5161
173. E Galera, A Zabra *Bull. Pol. Acad. Sci., Chem.*, 1977, **25** 615
174. C Wawrzenczyk, A Zabra, M Aniol *Liebigs Ann. Chem.*, 1989, 5
175. W S Johnson, L Wertemann, W R Bartlett, et al. *J. Am. Chem. Soc.*, 1970, **92** 741
176. W Biernacki, W Sobotka *Rocz. Chim.*, 1977, **51** 2369; *Ref. Zh. Khim.*, 1978, 10E118
177. W Biernacki, W Sobotka *Pol. J. Chem.*, 1978, **52** 965
178. E Galera, A Zabra *Bull. Pol. Acad. Sci., Chem.*, 1978, **26** 427
179. V B Deodhar, V S Dalavoy, U B Nayak *Indian J. Chem., Sect. B*, 1979, **17** 375
180. Polish P. 120 008; *Ref. Zh. Khim.*,. 1984, 9O269P
181. V B Deodhar, V S Dalavoy, U R Nayak *Indian J. Chem., Sect. B*, 1979, **17** 507
182. G A Tolstikov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 874
183. G A Tolstikov, O A Rozentsvet *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1647
184. F Campe, I Coll, M E Seba *Ann. Quim. Publ. Real. Soc. Esp. Fis. y Quim., C*, 1980, **76** 65; *Ref. Zh. Khim.*, 1983, 22E141
185. US P. 3 911 025; *Ref. Zh. Khim.*, 1976, 12O326P
186. C A Henrick, G B Staal, J B Siddal *J. Agric. Food. Chem.*, 1973, **21** 354
187. J P Edwards, B Clarke *Int. Pest. Contr.*, 1978, **20**(1); *Ref. Zh. Khim.*, 1978, 17O347
188. C B Rathburn, et al. *Mosquito News*, 1980, **40** 19; *Ref. Zh. Khim.*, 1981, 13O275
189. J P Edwards, J J Menn *Chemie der Pflanzenschutz und Schadlingsbekampfungen* (Edited by R Herausg, Wegler), Springer-Verlag, Berlin, Heidelberg, New York, 1981, Vol. 6, p. 185
190. Japanese P. 61-152603; *Ref. Zh. Khim.*, 1987, 14O366P
191. *J. Food Sci.*, 1977, **14** 132; *Ref. Zh. Khim.*, 1987, 17O3446P
192. US P. 3 969 385; *Ref. Zh. Khim.*, 1977, 6O403P
193. B P. 1 414 607; *Ref. Zh. Khim.*, 1976, 14O390P
194. Polish P. 120 009; *Ref. Zh. Khim.*, 1984, 8O267P
195. L Borowiecki, A Kazubski, E Reca *Liebigs Ann. Chem.*, 1986, 1428
196. Author's Certificate 164 629 ChSSR; *Ref. Zh. Khim.*, 1978, 10O304P
197. A Maasalu *Izv. Akad. Nauk EstSSR, Khimiya*, 1983, **32** 170
198. L A Yanovskaya *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2790
199. C A Henrick, W E Willy, D R McKean, et al. *J. Org. Chem.*, 1975, **40** 8
200. G Cardillo, M Contento, S Sandri, M Panunzio *J. Chem. Soc., Perkin Trans. 1*, 1979, 1729
201. Hungarian P. 181 239; *Ref. Zh. Khim.*, 1986, 3O421P
202. V N Odinokov, et al. *Zh. Org. Khim.*, 1988, **24** 1365
203. V N Odinokov, O S Kukovinets *Zh. Org. Khim.*, 1989, **25** 725
204. V N Odinokov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1923
205. C A Henrick, W E Willy, J W Baum *J. Org. Chem.*, 1975, **40** 1
206. Author's Certificate 247 395 ChSSR; *Ref. Zh. Khim.*, 1988, 21H22P
207. O V Shekhter, N L Sergovskaya, Yu S Tsizin *Zh. Org. Khim.*, 1979, **15** 260
208. M Kozlowska, W Sobotka *Pol. J. Chem.*, 1978, **52** 347
209. C A Henrick *J. Agric. Food Chem.*, 1978, **26** 542; *Chem. Abs.*, 1978, **88** 184558j
210. V N Odinokov, G Yu Ishmuratov, R Ya Kharisov, et al. *Khimiya Prirodnykh Nizkomolekulyarnykh Bioregulyatorov* (Chemistry of Natural Low Molecular Bioregulators), Erevan, 1990, p. 50
211. M F Boehm, G D Prestwich *J. Org. Chem.*, 1987, **52** 1349
212. M F Boehm, G D Prestwich *J. Labelled Compd. Radiopharm.*, 1988, **25** 653; *Ref. Zh. Khim.*, 1988, 22E190
213. M F Boehm, G D Prestwich *J. Org. Chem.*, 1986, **52** 5447
214. Polish P. 91 345; *Ref. Zh. Khim.*, 1979, 4O411P
215. G Baan, P Vinczer, L Novak, C Szantay *Tetrahedron Lett.*, 1985, **26** 4261
216. M Kozlowska, W Sobotka *Pol. J. Chem.*, 1980, **54** 957
217. L Borowiecki, A Kazubski, E Reca *Liebigs Ann. Chem.*, 1982, 1766
218. C Wawrzenczyk, A Zabra *Liebigs Ann. Chem.*, 1987, 169
219. C Wawrzenczyk, A Zabra *Tetrahedron*, 1980, **36** 3091
220. H A Patel, S Dev *Tetrahedron*, 1981, **37** 1577
221. O P Vig, G L Kad, A L Bedi, S D Kumari *Indian J. Chem., Sect. B*, 1978, **16** 452
222. L Streinz, M Romanuk *Collect. Czech. Chem. Commun.*, 1978, **43** 647
223. M Kozlowska, W Sobotka *Pol. J. Chem.*, 1979, **53** 1805
224. M Kozlowska, W Sobotka *Pol. J. Chem.*, 1978, **52** 581
225. Polish P. 106 137; *Ref. Zh. Khim.*, 1981, 7O325P
226. Polish P. 135 154; *Ref. Zh. Khim.*, 1987, 20O405P
227. Polish P. 135 243; *Ref. Zh. Khim.*, 1987, 20O404P
228. Polish P. 131 155; *Ref. Zh. Khim.*, 1987, 3O392P
229. Polish P. 135 756; *Ref. Zh. Khim.*, 1987, 13O394P
230. E Chojecka-Koryn, W Sobotka *Pol. J. Chem.*, 1981, **55** 1241
231. W Biernacki, W Sobotka, M Kocor *Rocz. Chem.*, 1976, **50** 895
232. C Wawrzenczyk *Pol. J. Chem.*, 1984, **58** 135
233. R Sterzycki, W Sobotka, M Kocor *Rocz. Chem.*, 1977, **51** 735

234. I Ribas, et al. *Rev. Agroquim. y Technol. Alim.*, 1980, **20** 347; *Ref. Zh. Khim.*, 1981, 80254
235. C A Henrick *Bioorg. Chem.*, 1978, **7** 235; *Chem. Abs.*, 1978, **89** 124523e
236. J Fekete, L Varjas, V Szantay, et al. *Liebigs Ann. Chem.*, 1986, 509
237. L Novak, J Ronaly, G Galik, et al. *Magy. Kem. Foly.*, 1987, **93** 304; *Ref. Zh. Khim.*, 1988, 8E336
238. L Novak, J Ronaly, P Kolonits *Liebigs. Ann. Chem.*, 1982, 1173
239. C Wawrzenczyk, K Derdzinski, A Zabra *J. Prakt. Chem.*, 1984, **326** 213
240. H Derdzinski, C Wawrzenczyk, A Zabra *J. Prakt. Chem.*, 1984, **326** 196
241. V N Odinokov, et al. *Zh. Org. Khim.*, 1985, **21** 992
242. C Wawrzenczyk, S Lochynski *Monatsh. Chem.*, 1985, 99
243. L Borowiecki, A Kazubski *Pol. J. Chem.*, 1978, **52** 1447
244. C Wawrzenczyk, S Lochynski *J. Prakt. Chem.*, 1988, **33** 261
245. Polish P. 136250; *Ref. Zh. Khim.*, 1988, 2O382P
246. O P Vig, I R Trehan, G L Kad, A L Bedi *Indian J. Chem., Sect. B*, 1978, **16** 455
247. L Borowiecki, E Reca *Liebigs Ann. Chem.*, 1982, 1775
248. L Borowiecki, M Welniak, W Wodzki *Pol. J. Chem.*, 1988, **62** 739
249. L Borowiecki, M Welniak *Pol. J. Chem.*, 1988, **62** 235
250. Y Ichikawa *Agric. Biol. Chem.*, 1980, **44** 2709; *Ref. Zh. Khim.*, 1981, 9E29
251. L K Pedersen *Pestic. Sci.*, 1984, **15** 462; *Ref. Zh. Khim.*, 1985, 10O349
252. O P Vig, I R Trehan, G L Kad *Indian J. Chem., Sect. B*, 1982, **21** 1052
253. J G Bernasconi, R Pagliarin, P Tavercchia *J. Heterocycl. Chem.*, 1989, **25** 725
254. K Leets, M Shmidt *Izv. Akad. Nauk EstSSR, Khimiya*, 1985, **34** 176
255. J Kahovcova, M Romanuk, F Sorm *Collect. Czech. Chem. Commun.*, 1978, **43** 1502
256. Itaya Nobushige *J. Synth. Org. Chem. Jpn.*, 1987, **45** 36; *Ref. Zh. Khim.*, 1988, 11O353
257. Author's Certificate 1066993; *Byull. Izobret.*, 1984, (2) 93
258. O P Vig, I R Trehan, G L Kad, et al. *J. Indian Chem. Soc.*, 1985, **62** 238
259. O P Vig, I R Trehan, G L Kad, J Ghose *Indian J. Chem., Sect. B*, 1983, **22** 515
260. J Szykula, A Zabza *Liebigs Ann. Chem.*, 1987, 709
261. E Galera, J Szykula, A Zabza *Liebigs Ann. Chem.*, 1987, 777
262. Author's Certificate 250588 ChSSR; *Ref. Zh. Khim.*, 1989, 4O362P
263. Author's Certificate 213702 ChSSR; *Ref. Zh. Khim.*, 1984, 24O367P

Translated from *Uspekhi Khimii* 61 1395–1420 (1992) U.D.C. 547.221

The chemistry of perfluoroalkyl-substituted dicyanoethylenes

A V Fokin, V Yu Tyutin, N D Chkanikov
A N Nesmeyanov Institute of Heteroorganic Compounds, Russian Academy of Sciences

ABSTRACT. Fundamental data on the means of obtaining and on the reactivity of perfluoroalkyl-substituted dicyanoethylenes are correlated. The principal ways of using these compounds in organic synthesis are shown. Examples are given of the practical application of perfluoroalkyl-substituted dicyanoethylenes and of the compounds derived from them.

The bibliography contains 72 references.

Contents

I. Introduction 766
II. Methods of synthesising perfluoroalkyl-substituted dicyanoethylenes 766
III. π-Complexes of perfluoroalkyl-substituted dicyanoethylenes with aromatic compounds 767
IV. Oxidation–reduction reactions of perfluoroalkyl-substituted dicyanoethylenes 767
V. Cycloaddition reactions of perfluoroalkyl-substituted dicyanoethylenes 768
VI. Reactions of perfluoroalkyl-substituted dicyanoethylenes with olefins involving an allylic hydrogen 772
VII. Reactions of perfluoroalkyl-substituted dicyanoethylenes with nucleophiles 774
VIII. Other reactions of perfluoroalkyl-substituted dicyanoethylenes 777
IX. Applications of perfluoroalkyl-substituted dicyanoethylenes and compounds derived from them 777

I. Introduction

The needs of medicine, agriculture and various modern technologies for new organic compounds possessing specific properties have enabled organofluorine chemistry to be integrated into organic chemistry in recent years. An important route for such an amalgamation is the use of synthons, which contain a perfluoroalkyl group at a multiple bond, in syntheses of organic compounds of more complex structure modified by perfluoroalkyl groups.[1] Direct analogy with reactions of unfluorinated unsaturated compounds usually fails since the presence of a perfluoroalkyl group at a multiple bond significantly affects reactivity. The present review considers the features of the chemical behaviour of perfluoroalkyl-substituted dicyanoethylenes in traditional conversions of organic synthesis.

Perfluoroalkyl-substituted dicyanoethylenes combine the properties of perfluoro-olefins,[2] polyfluorocarbonyl compounds[3,4] and their acylimines,[5] and also unfluorinated polycyanoethylenes,[6,7] the chemistry of which is widely represented in appropriate reviews. The chemistry of fluorine-containing dicyanoethylenes has not been reviewed. By filling this gap the authors hope that their work will enable bridges to be built between organofluorine chemistry and classical organic synthesis.

II. Methods of synthesis of perfluoroalkyl-substituted dicyanoethylenes

Three basic methods exist for the synthesis of fluorine-containing dicyanoethylenes. The first method described for obtaining 1,2-dicyano-1,2-bis(trifluoromethyl)ethylenes (Ia, b) and their analogues was the pyrolysis of chlorosulphite derivatives of perfluoroalkyl- and fluorohaloalkyl-cyanomethanes in the presence of sulphur.[8]

$$R_F(NC)CH-OSOCl \xrightarrow{200-800^\circ C} R_F(NC)C{=}C(R_F)CN \quad (Ia, b)$$

This method is similar to the preparation of tetracyanoethylene by chlorination–dehydrochlorination of dicyanomethane.[9] The mechanism probably includes the formation of appropriate intermediates of the carbene type in both cases. Dimerisation of these intermediates leads to the ethylene derivative. In the pyrolysis of the chlorosulphite derivative of (trifluoromethyl)cyanomethane a mixture is formed of the *cis*- and *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylenes (Ia, b), the quantitative ratio of which is not reported. The isomeric mixture may be separated by GLC. The *cis*-isomer (Ia) is transformed readily into *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene (Ib) by treatment with triethylamine.[10]

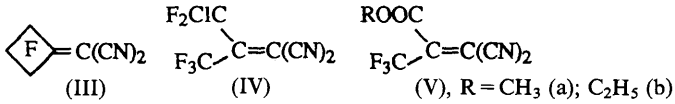
The synthesis of the initial chlorosulphite derivatives[8,10] was effected in the following way:

$$CF_3CH(OH)_2 \xrightarrow{P_2O_5/H_2SO_4} CF_3CHO \xrightarrow[C_5H_5N]{HCN} CF_3CH(CN)-OH \xrightarrow{SOCl_2} CF_3CH(CN)-OSOCl$$

The second method is based on the use of the Knoevenagel reaction under somehat modified conditions. Dicyanomethane and perfluoro- or fluorohaloketones are condensed in the presence of catalytic quantities of zinc chloride. The resulting alcohol is dehydrated with phosphorous pentoxide in the liquid phase or by passing the vapour over silica gel at 100–300 °C.[11–16] For example, the condensation of dicyanomethane and hexafluoroacetone with subsequent dehydration of the adduct with P_2O_5 leads to 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) in 50% yield.[14]

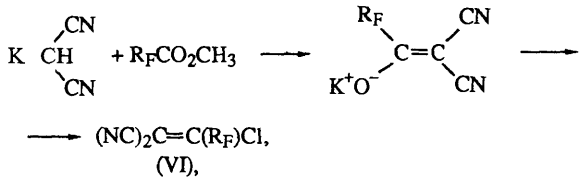
$$CH_2(CN)_2 + F_3CC(O)CF_3 \xrightarrow{ZnCl_2} H-C(CN)_2-C(CF_3)_2-OH \xrightarrow{P_2O_5} (NC)_2C{=}C(CF_3)_2 \quad (II)$$

The corresponding fluorine-containing ylidenedicyanomethanes were obtained in a similar manner from perfluorocyclobutanone[13] and chloropentafluoroacetone,[15,16] and from the methyl (Va) and ethyl (Vb) esters of trifluoropyruvic acid (III, IV, Va, b).[17]



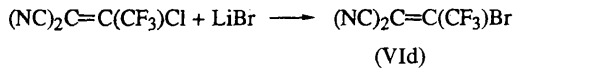
(III) (IV) (V), R = CH_3 (a); C_2H_5 (b)

At the beginning of the eighties a method was proposed for the synthesis of fluorine-containing ylidenedicyanomethanes by condensing the potassium or sodium salts of dicyanomethane with esters of perfluorocarboxylic acids with subsequent treatment of the salts of β,β-dicyano-α-(perfluoroalkyl)vinyl alcohol with phosphorus pentachloride.[13,18,19]



$R_F = CF_3$ (a), C_2F_5 (b), n-C_3H_7 (c)

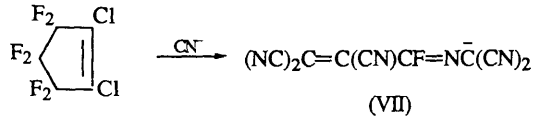
The yield of olefins (VIa–c) is increased on using $PhPCl_4$ as chlorinating agent.[19] The corresponding bromoolefin (VId) was obtained from 2-chloro-1,1-dicyano-2-(trifluoromethyl)ethylene by heating with anhydrous lithium bromide to 120 °C.[16]



(VId)

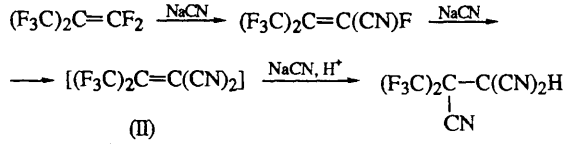
The method described for obtaining fluorine-containing ylidenedicyanomethanes has been used successfully to synthesise analogues of them containing CO_2R or CF_3 groups.[19]

While considering methods of synthesising fluorine-containing dicyanoethylenes it is impossible not to mention reactions involving the substitution of vinylic halogen atoms in perfluoroolefins and fluorohaloolefins by cyano groups. Thus the reaction of 1,2-dichloropentafluorocyclopentene with sodium cyanide leads to the formation of the 1,1,4,5,5-pentacyano-3-fluoro-2-azapentadiene anion (VII).[20]



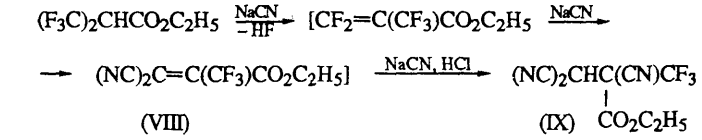
(VII)

Replacement of a vinylic fluorine by a cyano group is readily achieved in the reaction of perfluoroisobutene with sodium cyanide, though the resulting nitrile is able to react further with NaCN. It is suggested that the intermediate is 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II).[2,21]



(II)

The reaction of NaCN with hexafluoro-2-hydroisobutyric acid ethyl ester leads to 2,3,3-tricyano-2-(trifluoromethyl)propionic acid ethyl ester (IX). In this case 3,3-dicyano-2-trifluoromethyl)acrylic acid ethyl ester (VIII) is probably one of the intermediates.[21]



(VIII) (IX)

III. π-Complexes of perfluoroalkyl-substituted dicyanoethylenes with aromatic compounds

All the olefins considered form intensely coloured solutions on mixing with aromatic compounds or other π-bases. This colour indicates the formation of π-complexes which are characterised by intense absorption in the visible or near ultraviolet regions. The absorption maxima of complexes do not belong to either of the reactants and are attributed to a new molecular form. Several complexes, their absorption maxima and extinction coefficients (ε) are shown in Table 1.[14]

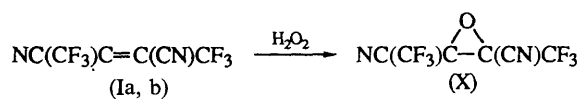
Table 1. π-Complexes of dicyanoolefins (II, III)

π-Base	π-Acid			
	(II)		(III)	
	λ, nm	ε	λ, nm	ε
Pyrene	500	3670	580	1930
Durene	386	2520	423	2430
Hexamethylbenzene	445	1060	497	1040
Benzene	316	1950	334	2170
Toluene	327	1720	358	1720

Footnote. Solvent CH_2Cl_2, temperature 24 °C.

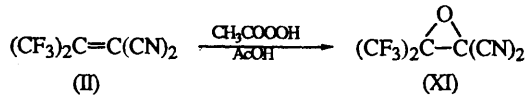
IV. Oxidation–reduction reactions of perfluoroalkyl-substituted dicyanoethylenes

1,2-Dicyano-1,2-bis(trifluoromethyl)ethylene (Ia, b) react with hydrogen peroxide with the formation of the 2,3-dicyano-2,3-bis(trifluoromethyl)oxiranes (X).[10]



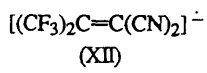
(Ia, b) (X)

Like alkenes (Ia, b), 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) and its analogues are oxidised by hydrogen peroxide or peracids to 2,2-dicyano-3,3-bis(trifluoromethyl)oxirane (XI) and its perhaloalkyl derivatives.[12,13]



(II) (XI)

Alkene (II) forms the anion radical of 1,1,-dicyano-2,2-bis(trifluoromethyl)ethylene (XII) on electrochemical reduction in dimethylformamide at 20 °C.

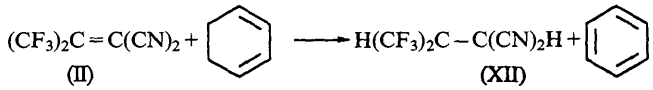


(XII)

The ESR spectrum of this anion-radical has been investigated.[22,23]

The corresponding anion-radical was obtained from *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene (Ib).[22,23] The electron affinities of (Ia, b) have been estimated on the basis of experimental ionisation potentials and their photoelectron spectra were studied.[24]

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene (II) may be reduced with cyclohexadiene to the corresponding ethane derivative (XIII).[16] No traces of the [4 + 2] cyclic adduct were detected.



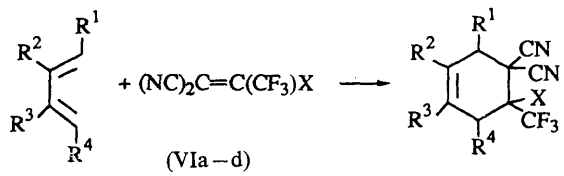
(II) (XII)

Hydrazobenzene is oxidised by alkene (II) to azobenzene.[25] Probably 1,1-dicyano-2,2-bis(trifluoromethyl)ethane (XIII) is formed in this case however it was not isolated from the reaction mixture. The dicyanoethylenes (Va, b), like the alkene (II), react with hydrazobenzene.[17]

V. Cycloaddition reactions of perfluoroalkyl-substituted dicyanoethylenes

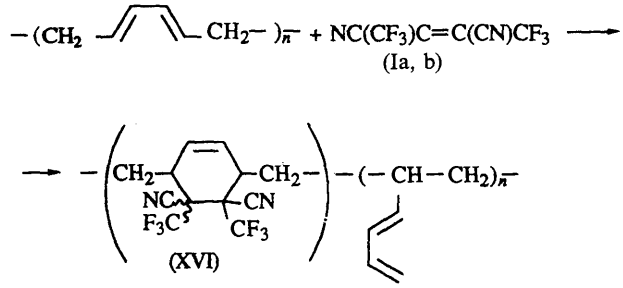
1. The Diels–Alder reaction ([4 + 2] cycloaddition)

Fluorine-containing dicyanoethylenes are reactive dienophiles in the Diels–Alder reaction. 1,1-Dicyano-2,2-bis(trifluoromethyl)-ethylene (II), 1,1-dicyano-2-(trifluoromethyl)-2-(chlorodifluoromethyl)ethylene (IV) and 1,1-dicyano-2-halo-(perfluoroalkyl)-ethylenes (VIa–d) react with 1,3-butadiene, 2,3-dimethylbutadiene, isoprene and several other linear dienes at 0–25 °C with or without a solvent giving [4 + 2] cycloaddition products (XV) in high yield.[14,16,26,27]

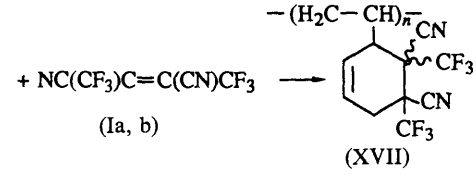


(VIa–d) (XV)

This reaction was used for the modification of various polymers of trienes. For example, polymers of 1,3,5-hexatriene, 1,3,5-heptatriene and 2,4,6-octatriene containing conjugated diene groups were modified using the Diels–Alder reaction with 1,2-dicyano-1,2-bis(trifluoromethyl)ethylene) Ia, b) at 25–80 °C in solution in benzene, toluene or tetrahydrofuran.[28,29] It was established that cyclic structures were formed in the main chain (XVI) or in the side chains (XVII) of the polymers. The conversion was from 10 to 75%.

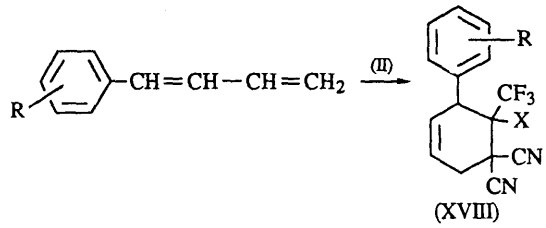


(Ia, b) (XVI)



(Ia, b) (XVII)

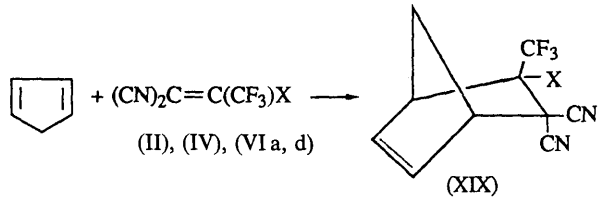
A systematic study has been made of the [4 + 2] cycloaddition reactions of alkene (II) and *trans*-1-arylbutadienes leading to the cyclohexane derivatives (XVIII).[26,27]



(XVIII)

R = *p*-$N(CH_3)_2$, *p*-OCH_3, *p*-CH_3, H, *m*-F, *m*-Cl, *m*-CF_3, *m*-NO_2

A comparison has been carried out of the relative reaction rates of various fluorine-containing dicyanoethylenes with cyclopentadiene leading to a [4 + 2] cycloaddition product (XIX).[16]

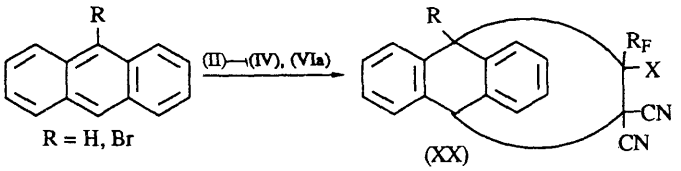


(II), (IV), (VI a, d) (XIX)

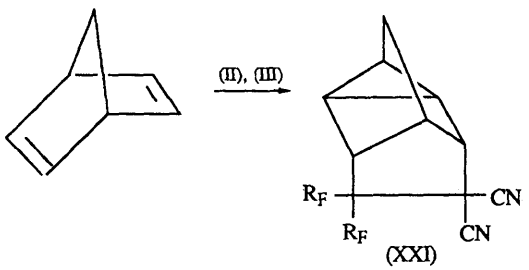
The reactivity decreases in the series $(CF_3)_2C{=}C(CN)_2$ (II) > $(CF_3)(CF_2Cl)C{=}C(CN)_2$ (IV) > $(CF_3)ClC{=}C(CN)_2$ (VIa) > $(CF_3)BrC{=}C(CN)_2$ (VId). All the alkenes considered are less reactive than tetracyanoethylene.[30]

Anthracene and certain of its derivatives may act as dienes. Dicyanomethylenehexafluorocyclobutane (III) reacts with anthracene in benzene at room temperature forming the adduct (XX) after a few minutes.[14] The reaction conditions are more forcing for alkenes (II),

(IV) and (VIa).[14,16] A temperature of 100 °C is required to form cyclic adducts with 9-bromoanthracene.[16]

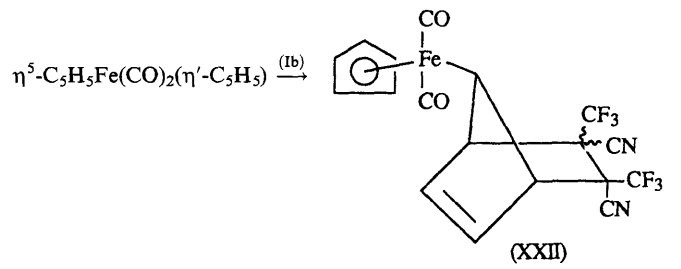


The alkenes (II) and (III) are reactive dienophiles in homo-Diels–Alder reactions.[14] Thus 1,1-dicyano-2,2-bis(trifluoromethyl)-ethylene (II) gives the cyclic adduct (XXI) with norbornadiene even at room temperature. The reaction is complete in approximately three hours, which is significantly less than for the analogous reaction of tetracyanoethylene.[31]

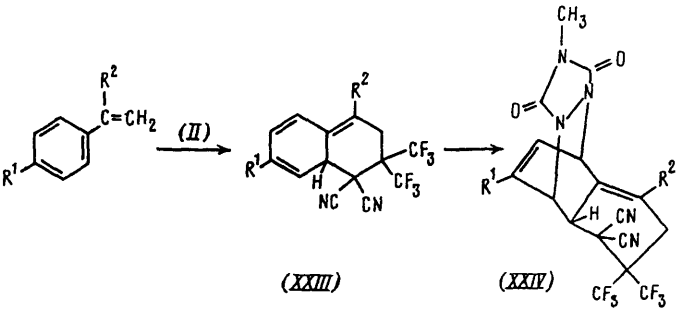


The high reactivity of the alkenes (II) and (III) compared with tetracyanoethylene in the reaction with norbornadiene is explained by their more readily polarisability and the possibility of forming an intermediate or transition state with a larger charge separation.[14]

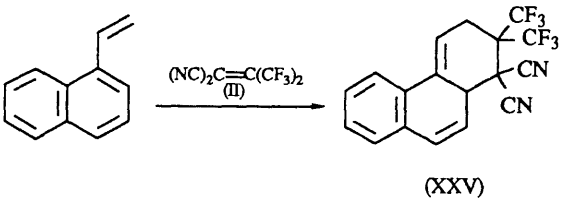
The diene system may be part of an unsaturated hydrocarbon ligand in a transition metal complex. The reaction of η^5-$C_5H_5Fe(CO_2)(\eta'$-$C_5H_5)$ with *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene (Ib) leads to the 1:1 adduct (XXII) containing a norbornyl ring.[32]



Reactions of [4 + 2] cycloaddition have been reported in which the aromatic benzene nucleus acts as part of a diene system.[33,34] Derivatives of styrene and 1,1-dicyano-2,2-bis(trifluoromethyl)-ethylene (II) are subject to a reversible Diels–Alder reaction. The nonaromatic adduct (XXIII) was isolated and was in its turn the substrate in a [4 + 2] cycloaddition reaction with *N*-methyl-triazolinedione leading to the tricyclic product (XXIV).



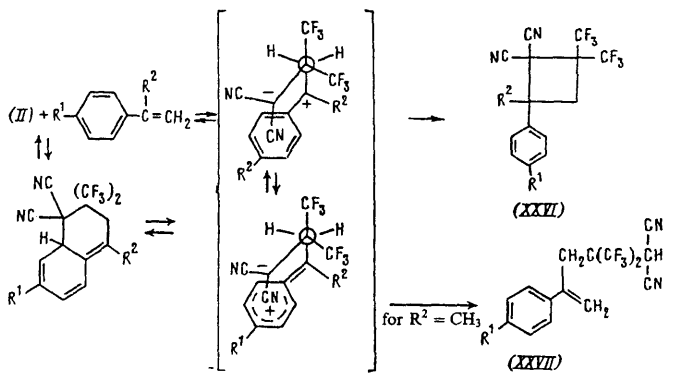
The effects of substituents R^1 and R^2 and the influence of solvent polarity on the reaction rate are in agreement with a synchronous reaction mechanism.[34] It was noted that if part of the initial diene is a naphthalene system then the cycloaddition product (XXV) is stable and the Diels–Alder reaction is irreversible.[34]



(XXV)

This phenomenon is due to the lower loss of resonance energy by the naphthalene system compared with benzene.

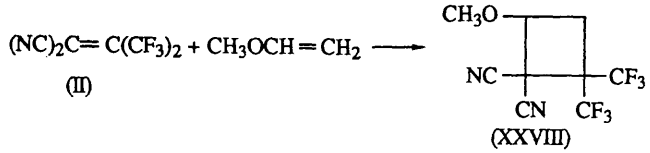
In a detailed study of the conversions occurring in the styrene—1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) system it was shown that at 20 °C a slow irreversible reaction forming the cyclobutane derivatives (XXVI), i.e. a [2 + 2] cycloaddition, competes with the rapid reversible Diels–Alder cycloaddition. Products (XXVII) of the ene reaction were also detected. The overall scheme of these conversions is as follows.[33]



2. [2 + 2] Cycloaddition reactions

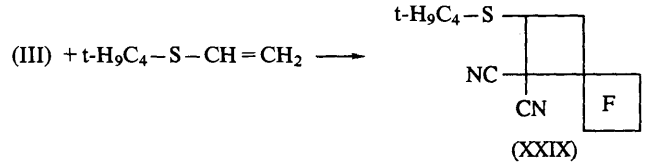
The formation of cyclobutane derivatives together with Diels–Alder reaction products was recorded on reacting the alkene (II) with 1-chloro-1,3-butadiene,[16] 1,1-diarylbutadiene[26] and 1-aryl-1,3-butadiene.[26,27] In the case of 1,1-diarylbutadiene the [2 + 2]

cycloaddition product was the main product.[35] The [2 + 2] cycloaddition reaction with olefins occupies a special place in the chemistry of fluorine-containing dicyanoethylenes as they are often effected under exceptionally mild conditions.[14] Thus 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) reacts practically instantaneously with methyl vinyl ether even at −78 °C forming 1,1-dicyano-2,2-bis-(trifluoromethyl)-4-methoxycyclobutane (XXVIII) in 87% yield.



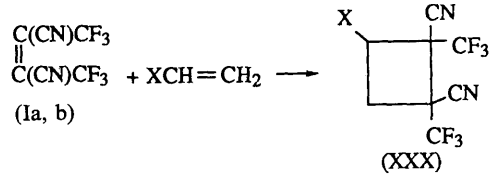
(XXVIII)

The alkene (II) gives a cyclic adduct of type (XXVI) after a few minutes with styrene, 4-methoxystyrene and α-methylstyrene at 0 °C in solvents such as pentane or carbon tetrachloride. No formation of Diels–Alder reaction products is observed at reduced temperatures.[11–14] Under the same conditions t-butyl vinyl sulphide and α-methylstyrene react with dicyanomethylenehexafluorocyclobutane (III) forming the corresponding spiro derivatives of cyclobutane, such as (XXIX).



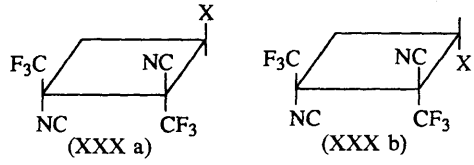
(XXIX)

The stereochemistry of the [2 + 2] cycloadditions of *cis*- and *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylenes (Ia) and (Ib) has been studied.[36] It was found that these alkenes react at room temperature with alkyl vinyl ethers, alkyl vinyl sulphides and 4-alkoxystyrenes forming the cyclobutanes (XXX). The solvent polarity exerts a strong effect on the reaction rate.

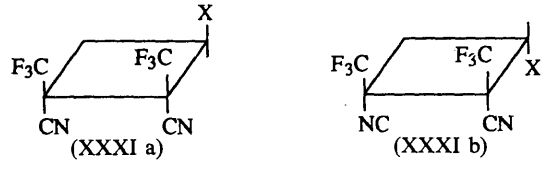


(XXX)

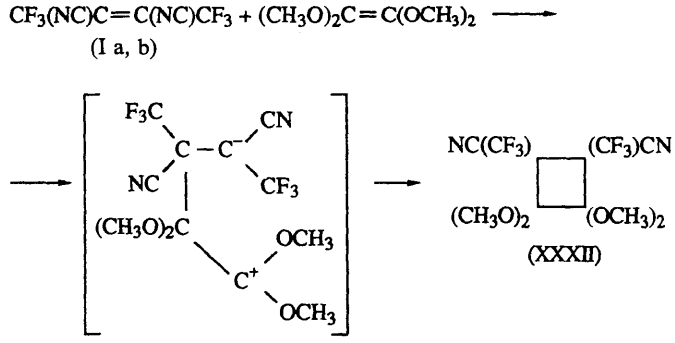
The reaction of (Ib) with the above olefins is stereoselective in the absence of solvent and gives exclusively the cyclobutane diastereomers (XXXa, b).



The corresponding reaction of the *cis* isomer (Ia) leads to the diastereomers (XXXIa, b).

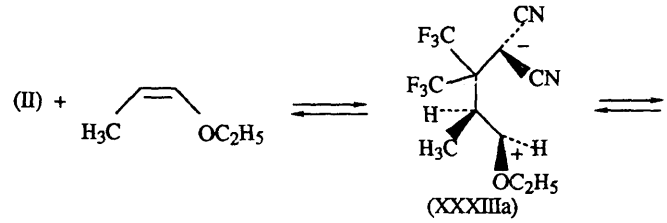


The [2 + 2] cycloaddition of 1,2-dicyano-1,2-bis(trifluoromethyl)-ethylenes (Ia, b) with tetramethoxyethylene has been studied and a zwitterionic mechanism has been proposed for the formation of the adducts (XXXII).[37]

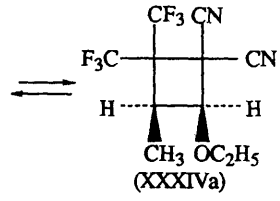


(XXXII)

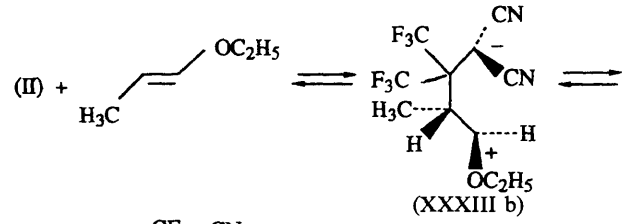
The features and mechanism of the [2 + 2] cycloaddition of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) and alkyl vinyl ethers has been studied in detail by Huisgen and Bruckner.[38] It was found that the cyclobutane derivatives (XXXIV) are formed through a 1,4-dipolar intermediate which was trapped by reaction with ethanol or acetic acid. No regioisomer (XXXIV) was recorded on NMR investigation of the reaction products. Since the cyano groups stabilise the negative charge better than the trifluoromethyl groups in the 1,4-dipolar intermediate (XXXIII) and the reaction of *cis*- and *trans*-1-ethoxypropene with (II) is not stereospecific, the following [2 + 2] cycloaddition mechanism is proposed.



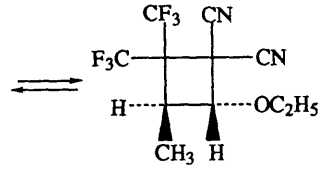
(XXXIIIa)



(XXXIVa)



(XXXIII b)



(XXXIV b)

The reaction of the cyclobutanes (XXIVa, b) with ethanol (2 d, 20 °C) leads to the acetal (XXXV).[38,39]

$$\text{(XXXIV a or b)} \xrightarrow{C_2H_5OH} H(CN)_2C-C(CF_3)_2-CH_2CH(OC_2H_5)_2$$

(XXXV)

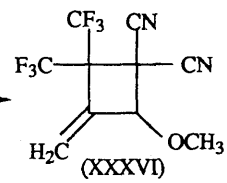
This result is a consequence of the equilibrium (XXXIII) ⇄ (XXXIV). A similar trapping of the 1,4-dipole also occurs on reaction with acetic acid.

A study of the kinetics of the reaction of (II) with ethyl vinyl ether showed the marked effect of solvent polarity on the reaction rate.[35] The rate constants are increased on introducing donor substituents into the α-position of the ethyl vinyl ether while a β-methyl group leads to the opposite effect, probably due to the increased role of steric factors.

Olefins having a cumulative diene system also readily undergo [2 + 2] cycloaddition. For example, 1-methoxy-1,2-propadiene reacts with the alkene (II) leading to the adduct (XXXVI) with an exocyclic double bond.[35]

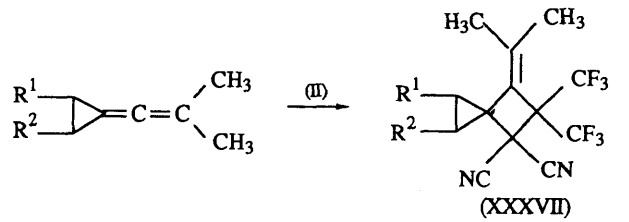
$$H_2C{=}C{=}CHOCH_3 + (NC)_2C{=}C(CF_3)_2 \longrightarrow$$

(II)



(XXXVI)

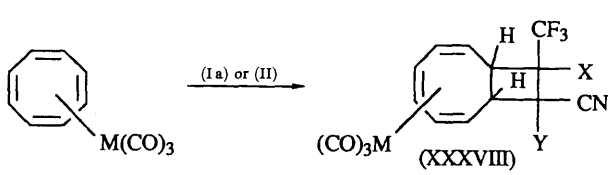
Similar results were obtained for the reaction of 1-(2-methylpropylidene)-2-phenylcyclopropane and 7-(2-methylpropenylidene)-bicyclo[4,1,0]heptane with 1,1-dicyano-2,2-bis(trifluoromethyl)-ethylene (II). In the first case (R^1 = C_6H_5, R^2 = H) an isomeric mixture of the cyclic adducts (XXXVII) is formed.[40]



(XXXVII)

A radical mechanism has been proposed for cycloaddition reactions of cumulene systems with the dicyanoethylene (II).[41] The retention of the cyclopropane ring, indicating the formation of a phenylcyclopropenyl radical which undergoes ring fission with more difficulty than a phenylcyclopropenyl cation, points in favour of this mechanism.

As with the Diels–Alder reaction the [2 + 2] cycloaddition of fluorine-containing dicyanoethylenes may occur with an unsaturated hydrocarbon ligand in a transition metal complex. Thus alkanes (Ib) and (II) react with tricarbonylcyclooctatetraeneruthenium and iron forming adducts of composition 1 : 1 which are assigned the structure (XXXVIII) on the basis of ^1H and ^{19}F NMR spectral data.[41]

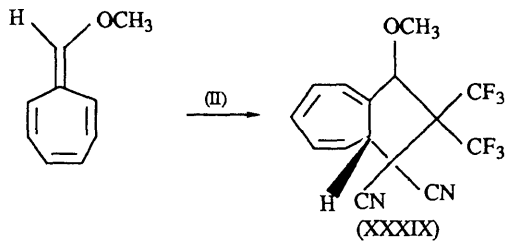


(XXXVIII)

By comparing the reactivity of the alkanes (Ia, b) and (II), (III) with the reactivity of tetracyanoethylene (TCE)[42,43] in reactions occurring by the zwitterionic mechanism, it may be concluded that reactivity decreases in the series (III) > (II) > (TCE) > (Ia, b). Middleton[14] explains the higher reactivity of (II) and (III) compared to TCE and (Ia, b) by their higher polarisability and greater inclination towards the formation of polar intermediates.

3. Other cycloaddition reactions of perfluoroalkyl substituted dicyanoethylenes

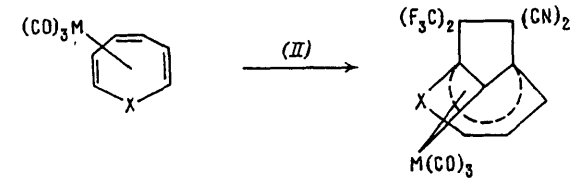
It is known that heptafulvenes with electron-donating substituents may react with fluorine-containing dicyanoethylenes according to an [8 + 2] cycloaddtion. For example, 8-methoxyfulvene and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) give the cyclic adduct (XXXIX).[44]



(XXXIX)

The reaction is regiospecific and leads to a diastereomeric mixture of hydroazulenes (XXXIX).[44]

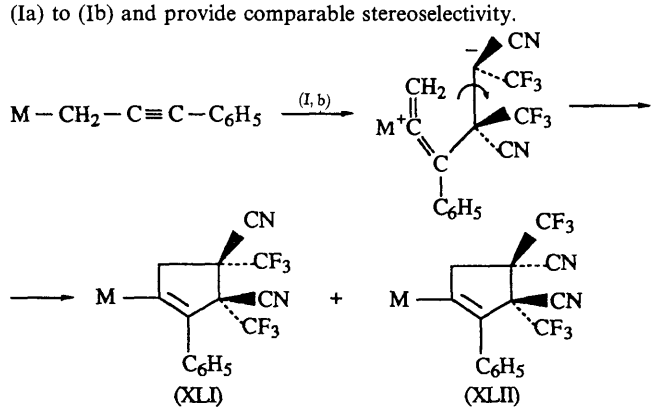
The *exo*-1,3-cyclic adducts (XL) of alkene (II) and tricarbonyl-(η-cycloheptа-2,4,6-trien-1-one) iron and tricarbonyl(η-*N*-methoxy-carbonyl-1H-azepines) iron or ruthenium have been described.[45]



M = Ru, Fe; X = CH_2, NCO_2CH_3 (XL)

A zwitterionic mechanism is proposed for this reaction.

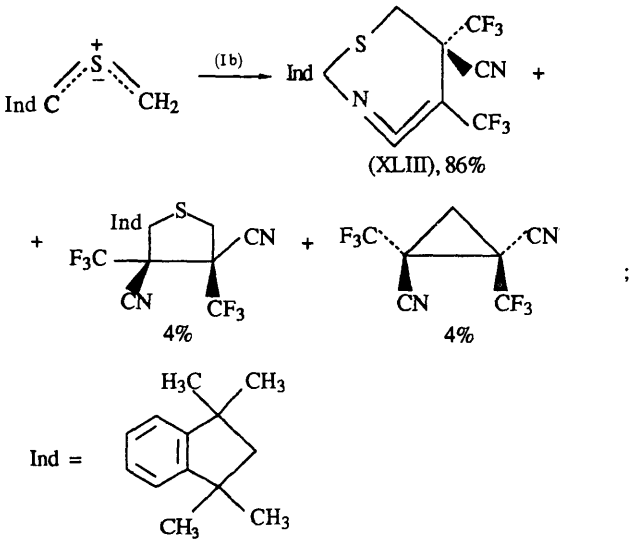
Another example of the cycloaddition of the alkenes (Ia, b) to the unsaturated hydrocarbon ligand of a transition metal complex is the reaction of η^5-$C_6H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ with (Ib) in benzene at 20 °C. This leads to compounds (XLI) and (XLII) with 75% regioselectivity.[46] The analogous reactions for the *cis*-isomer (Ia), at least partially if not completely, occur through the isomerisation of (Ia) to (Ib) and provide comparable stereoselectivity.



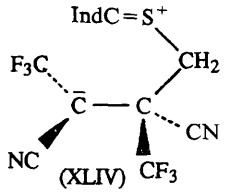
(XLI) (XLII)

M = η^5-$C_5H_5Fe(CO)_2$, $Mn(CO)_5$, $Re(CO)_5$

The [3 + 4] cycloaddition of 1,1,3,3-tetramethylindane-2-thione *S*-methylide and 2,3-bis(trifluoromethyl)fumaronitrile leading to the ketenimine (XLIII) has been studied by Huisgen and collaborators.[47]

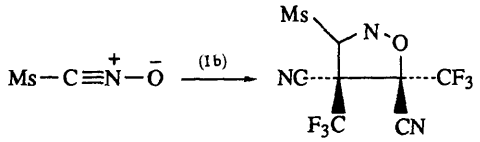


The zwitterion (XLIV) is the probable intermediate.



Similar results are obtained for the cycloadditions of (Ia) and other sulphur methylides.[48]

The mechanism of the 1,3-dipolar cycloaddition of nitrile oxides to the *trans* isomer of alkene (Ib) was studied.[49]

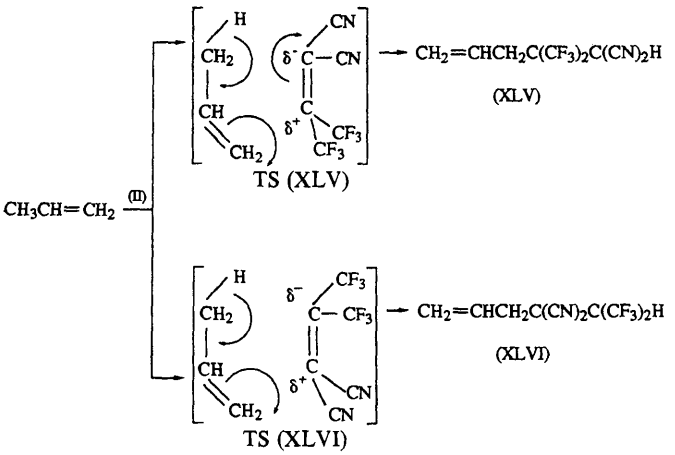


This reaction occurs stereospecifically according to a synchronous cycloaddition mechanism.

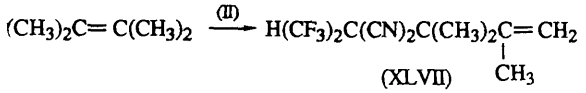
In concluding this section mention must be made of the attempts at computer prediction of the spatial structure of the products of the six-electron cycloaddition of electron-deficient alkenes, such as (Ib), to various olefins.[50]

VI. Reactions of perfluoroalkyl-substituted dicyanoethylenes with olefins involving the allylic hydrogen

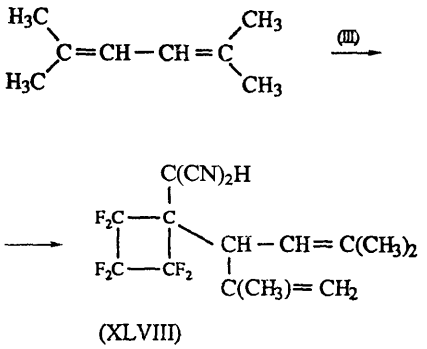
Unactivated olefins which contain an allylic hydrogen atom enter into ene reactions with alkenes (II) and (III). For example, 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) gives a mixture of isomeric adducts (XLVI) and (XLVII) on reaction with propylene at 150 °C.[14]



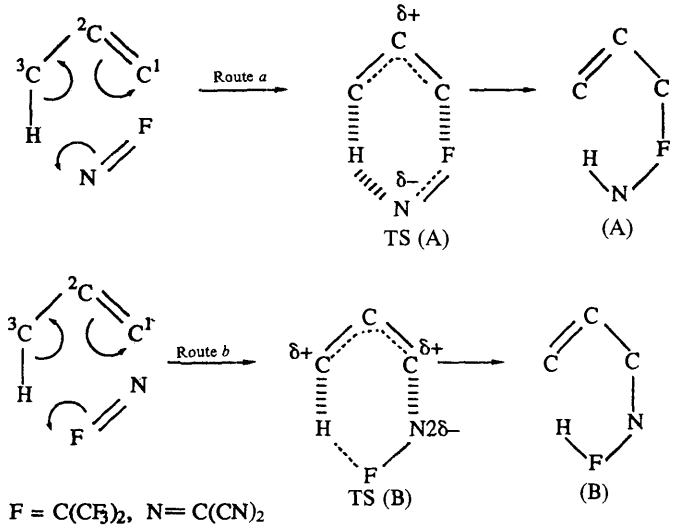
The product (XLV) is formed in good yield which is explained by the high probability of implementing the transition state [TS (XLV)].[14] The formation of the isomer (XLVI) is more favoured. This conclusion is in accordance with the fact that the sterically hindered tetramethylethylene gives a single product (XLVII) at room temperature.[14]



The reaction of alkene (II) with 1,1,4,4-tetramethylbutadiene at 20 °C also leads to the product of the ene reaction (XLVIII).[14]

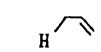
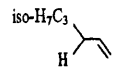
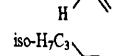
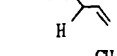
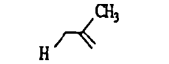
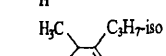


A detailed study of the reaction of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) with various olefins has been carried out.[51] The reaction mechanism may be represented as follows using the symbols taken from the original work.



The usual enophiles (maleic anhydride, azodicarboxylic ester, formaldehyde, etc.) are carbophilic, i.e. the new C–C bond is more developed in the transition state than X–H (X = C, N, O ...). The charge distribution for the alkene (II) is determined by the ability of the cyano groups to stabilise the negative charge. Reaction of the F portion of the alkene (II) with C(1) leads to a zwitterion with simultaneous transfer of hydride ion reducing the ionic character of the TS (A). A terminal CH(CN) group appears in the reaction product in this case. On implementing TS (B) the hydride transfer and the formation of the $(CF_3)_2C-H$ bond precede the formation of the C–C bond. The negative charge of the carbanion formed from alkene (II) is better stabilised by the CN groups than by the trifluoromethyl groups in TS (A). In this case the reaction product will contain a terminal $H(CF_3)_2C$ group.

Table 2. Products of the ene reactions of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene with olefins at 20 °C.[51]

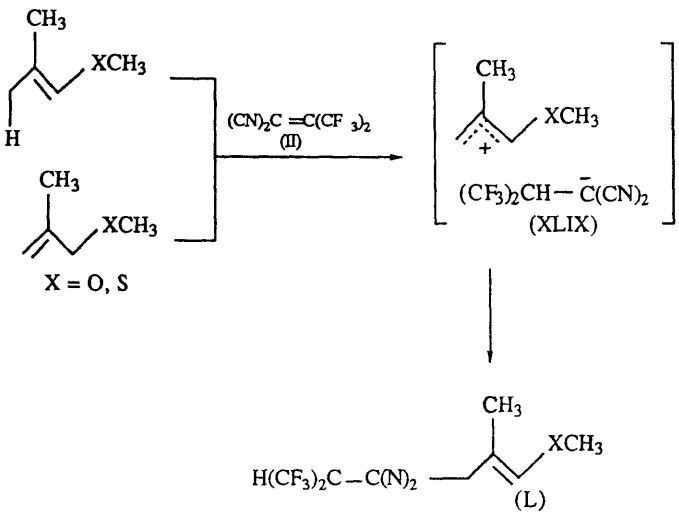
Olefin	Reaction time	Relative amount of products, %	
		(A)	(B)
	12 h	93	7
	18 d	67	33
	141 d	0	100
	18 d	100	0
	40 h	61	39
	29 d	100	0

Both one-stage reactions (*a*) and (*b*) occur with a compulsory shift of the double bond. Recognition of the terminal group of the ene reaction product suggests the implementation of TS (A) or TS (B).[51]

The results of some reactions of alkene (II) with olefins are shown in Table 2.

The introduction of an isopropyl or phenyl group into the C(3) position enables stabilisation of the quasi-allylic cation TS (B). Route *b* is effected in these cases by 33 and 100% respectively. Substituents at C(2) make the quasi-carbocation RS (A) tertiary and consequently aid the formation of the product (A).

The reaction of isobutenyl or methylallyl ethers and thioethers with 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) involving the allylic hydrogen atom has been investigated systematically.[52] In this the ion pair (XLIX) generated in the hydride transfer is the intermediate in the main reaction pathway.



The better stabilisation of the negative charge of (XLIX) by the cyano groups leads to the formation of adducts with terminal $(CF_3)_2CH$ groups. Allyl ethers and thioethers react similarly.

Although the dimethylacetal of dimethylketene is subject only to a [2 + 2] cycloaddition with the alkene (II),[35] the corresponding slow reaction of the dithioacetal gives the product (LI).[52]

$$(CH_3)_2C{=}\,C(SCH_3)_2 + (NC)_2C{=}C(CF_3)_2 \longrightarrow$$

$$\longrightarrow H(CF_3)_2C(CN)_2CH_2C{=}\,C(SCH_3)_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad (LI)$$

It may be concluded from the above that 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) and dicyanomethylenehexafluorocyclobutane (III) are unique enophiles with a marked ability to split off hydride ion from the allyl carbon atom. The alkene (II) is the sole known representative of the ethylene series reacting with unactivated olefins at room temperature without a catalyst.

VII. Reactions of perfluoroalkyl-substituted dicyanoethylenes with nucleophiles

The fluorine-containing dicyanoethylenes readily react with nucleophiles due to their electrophilic nature.

1. Reaction with water and alcohols

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene (II) readily adds water without a catalyst forming 2,2-dicyano-1,1-bis(trifluoromethyl)ethanol (LII).[14]

$$\underset{\text{(II)}}{(NC)_2C{=}\,C(CF_3)_2} + H_2O \longrightarrow \underset{\text{(LII)}}{H(NC)_2C{-}\,C(CF_3)_2OH}$$

In strongly acidic medium (II) may be hydrolysed to the diamide (LIII).[14]

$$\underset{\text{(II)}}{(NC)_2C{=}\,C(CF_3)_2} \xrightarrow{H_2SO_4/H_2O} \underset{\text{(LIII)}}{(CF_3)_2C{=}\,C(CONH_2)_2}$$

The reaction of adding alcohols to the alkene (II) is reversible and leads to the unstable adduct (LIV) which decomposes to the starting materials even on vacuum distillation. The position of the equilibrium depends on the size of the hydrocarbon group of the alcohol. The equilibrium is shifted to the right in the reaction of (II) with methanol and ethanol. The opposite picture is seen with t-butyl alcohol. Isopropanol and the alkene (II) give approximately equal quantities of the product (LVI) and the starting materials of equilibrium.[14]

$$\text{(II)} + ROH \rightleftharpoons \underset{\text{(LIV)}}{H(CN)_2C{-}\,C(CF_3)_2OR}$$

The reaction of 2-chloro-1,1-dicyano-2-(trifluoromethyl)ethylene (VIa) with alcohols is irreversible and leads, probably according to an addition–elimination mechanism, to 2-alkoxy-1,1-dicyano-2-(trifluoromethyl)ethylenes (LV).[18]

$$\underset{\text{(VIa)}}{(NC)_2C{=}\,C(CF_3)Cl} + ROH \longrightarrow \underset{\text{(LV)}}{(NC)_2C{=}\,C(CF_3)OR}$$

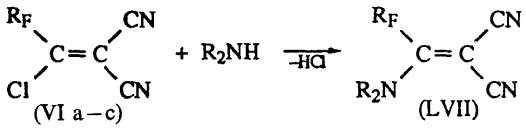
$R = CH_3,\ C_2H_5$

2. Reaction with nitrogen-containing nucleophiles

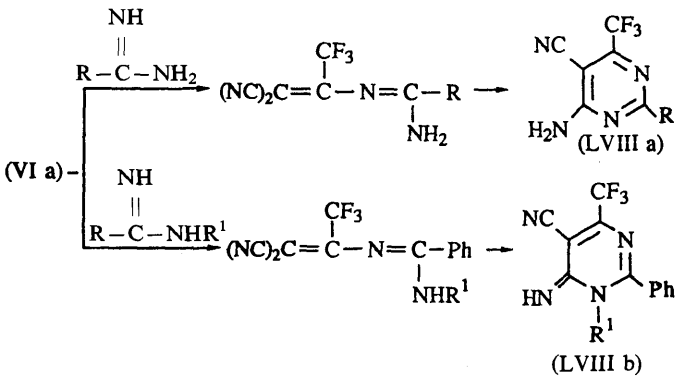
The alkene (II) adds ammonia at the double bond forming an amphoteric amine which was isolated as the tetraethylammonium salt (LVI).[14]

$$\underset{\text{(II)}}{(CF_3)_2C{=}\,C(CN)_2} + NH_3 \xrightarrow[-HCl]{N(C_2H_5)_4Cl} \underset{\text{(LVI)}}{H_2N{-}\overset{CF_3}{\overset{|}{C}}{-}\overset{CN}{\overset{/}{C}}{}^{+}N(C_2H_5)_4 \;\; {}^{CF_3}_{CN}}$$

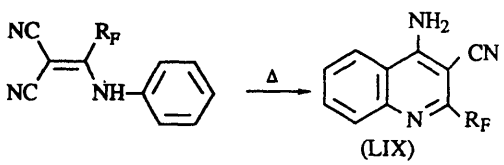
The 1,1-dicyano-2-chloro-2-(perfluoroalkyl)ethylenes (VIa–c) react with primary and secondary aliphatic, primary aromatic amines and amidines with the formation of *N*-vinylation products (LVII).[18,19]



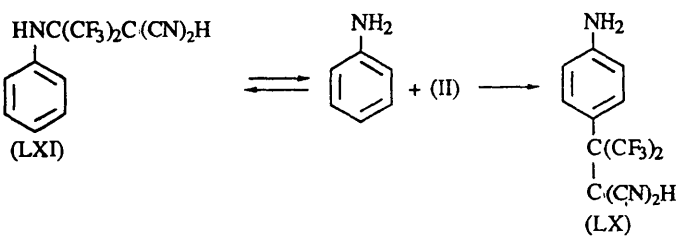
In several cases the resulting *N*-vinyl derivatives undergo further intramolecular cyclisation with the participation of the cyano group. Thus the products of the *N*-vinylation of amidines are cyclised into 5-cyano-4-trifluoromethylpyrimidines (LVIIIa, b).[53]



The *N*-vinyl derivatives of aniline are converted on heating into 4-amino-3-cyano-2-(perfluoroalkyl)quinolines (LIX).[19]

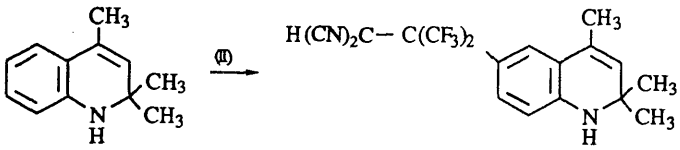


In contrast to dicyanoethylenes containing vinylic halogen atoms 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) reacts with aniline to give the C(4) alkylation product (LX).[11,14,25] It was shown recently that the reaction is complex. The unstable *N*-alkylation product (LXI) is formed first and is in equilibrium with the initial aniline and alkene under the reaction conditions (20 °C, Freon 113). A competing slow irreversible reaction leads to the 4-substituted aniline derivative (LX).[25]



The presence of a substituent in the 2 position to the amino group in *o*-toluidine generates steric hindrance to the formation of an *N*-alkylation product shifting the equilibrium in the *N*-alkylation

product—[arylamine + (II)] system to the right. An increase in the concentrations of the starting materials increases the overall rate of formation of the *C*(4)-alkylation product. The same effect assists rapid *C*(4)-alkylation of the *N*-alkylanilines by the alkene (II). The reaction of alkene (II) with 2,2,4-trimethyl-1,2-dihydroisoquinoline, representing secondary arylamines, also leads to the product of alkylation in the *para* position to the amino group (LXII).[25]

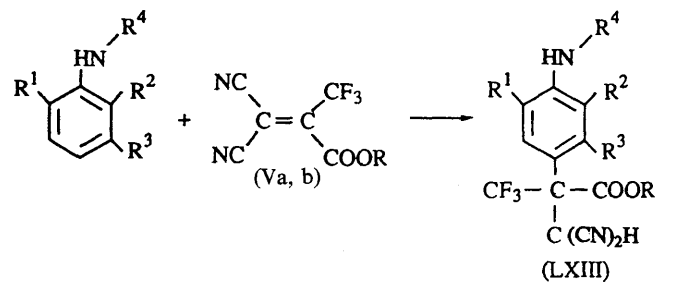


(LXII)

Diphenylamine, in spite of significant steric hindrance to *N*-alkylation, is substituted significantly more slowly which is linked with the reduced nucleophilicity of the benzene nuclei compared with the *N*-alkylanilines. 4-Substituted anilines do not form stable products with the alkene (II).[25]

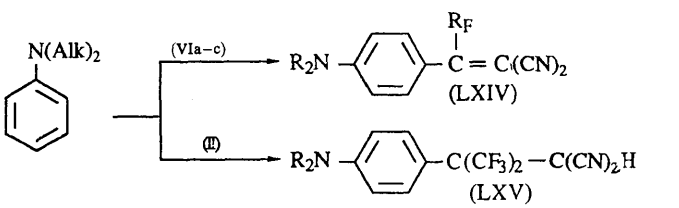
The features of the reaction of anilines with alkene (II) correspond mainly with the results of the tricyanovinylation of aniline with tetracyanoethylene.[54–56]

The reaction of primary and secondary arylamines with the esters of 3,3-dicyano-2-(trifluoromethyl)acrylic acid (Va, b) has also been studied systematically. It was noted that the range of anilines clearly subject to C(4) alkylation by the alkenes (Va, b) was reduced compared to the alkene (II). Positive results were obtained for 2,6-dimethyl- and 2,5-dimethoxyanilines and for diphenylamine. The corresponding derivatives of 4-[2,2-dicyano-1-alkoxycarbonyl-1-(trifluoromethyl)ethyl]aniline (LXIII) were isolated.[17]



(LXIII)

N,N-Dialkylanilines are alkylated at C(4) under mild conditions by the alkenes (VIa–c) and (II) with the formation of the products (LXIV) and (LXV).[16,18,25,27]

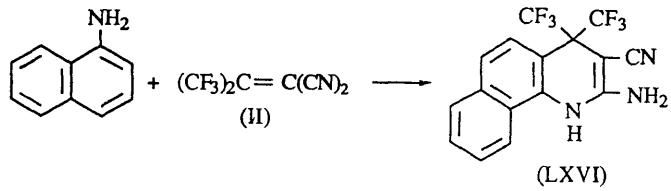


(LXIV)

(LXV)

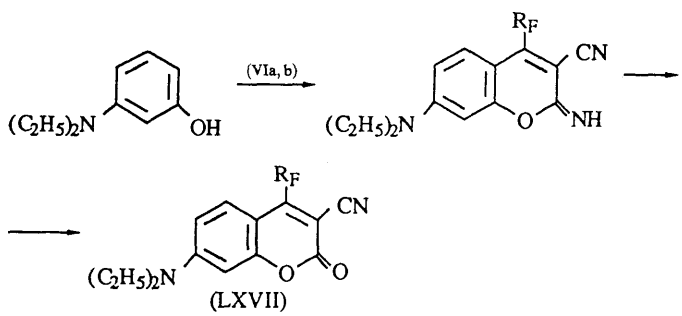
N,N-Dimethylaniline was successfully alkylated at C(4) by esters of 3,3-dicyano-2-(trifluoromethyl)acrylic acid (Va, b) in acetic acid solution.[17]

Cases when the *C*-alkylation of the aromatic nucleus is accompanied by heterocyclisation involving the cyano or some other functional group of the electrophilic alkene are of particular interest. Stable heterocyclic compounds modified by perfluoroalkyl groups are formed. For example, the regiospecific alkylation of 1-aminonaphthalene at C(2) by alkene (II) is accompanied by an intramolecular cyclisation involving a cyano and the amino group leading to the benzoquinoline derivative (LXVII).[25,58]



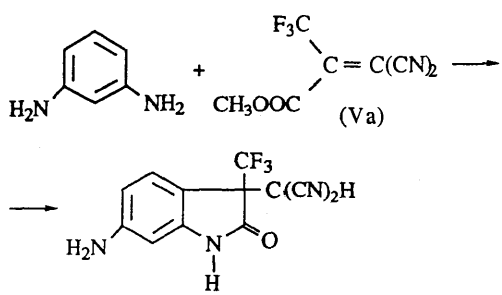
(LXVI)

Cyclisation involving the hydroxyl group of the nucleophile and a cyano group of 2-chloro-1,1-dicyano-2-(trifluoroalkyl)ethylenes (VIa, b) was used in the synthesis of the perfluoroalkyl substituted coumarin derivatives (LXVII).[57]



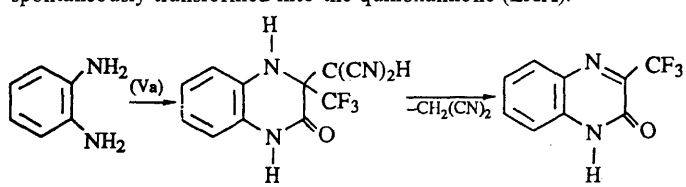
(LXVII)

On reacting the acrylic acid derivative (Va) with *m*-phenylenediamine the *C*-alkylation is accompanied by the formation of a lactam (LXVIII).[17]



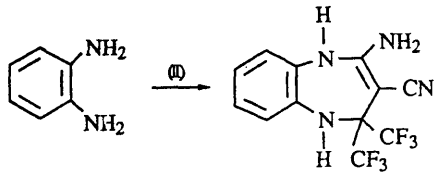
(LXVIII)

Lactamisation reaches *N*-alkylation in the case of *o*-phenylenediamine. The dihydroquinoxaline (LXIX) is formed which is spontaneously transformed into the quinoxalinone (LXX).[17]



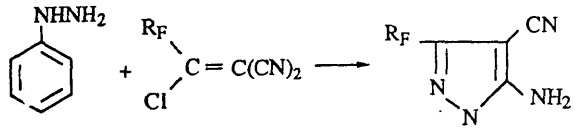
(LXIX) (LXX)

The reacton of *o*-phenylenediamine with 1,1-dicyano-2,2-bis-(trifluoromethyl)ethylene (II) terminates with the formation of the dihydro-1,5-benzodiazepine (LXXI).[17,59]



(LXXI)

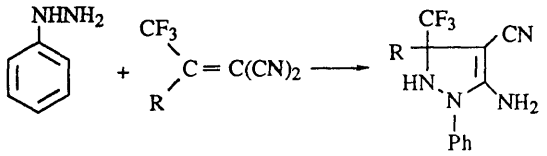
Phenylhydrazine reacts with the dicyanoethylenes (VIa–c) with the formation of the pyrazole derivatives (LXXII).[18,19]



(VIa–c)

(LXXII)

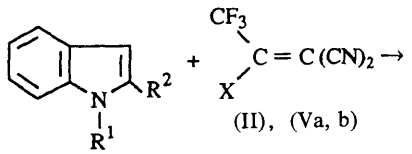
The analogous reaction with 1,1-dicyano-2-(trifluoromethyl)ethylenes (II) and (Va) leads to the pyrazoline derivative (LXXIII).[17,25,60]



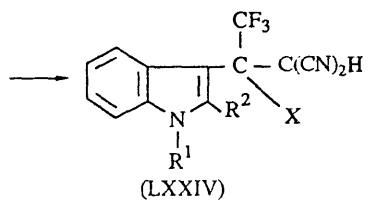
(LXXIII)

R = CF_3 (II); COOMe (Va)

There are only limited data on the *C*-alkylation reactions of nitrogen-containing heteroaromatic compounds with perfluoroalkyl substituted dicyanoethylenes. In addition it is known that indole, 2-methylindole and *N*-methyl-2-phenylindole react under mild conditions with 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) and with esters of 3,3-dicyano-2-(trifluoromethyl)acrylic acid (Va, b) with the formation of products (LXXIV) of substitution of the indole nucleus of C(3).[61]



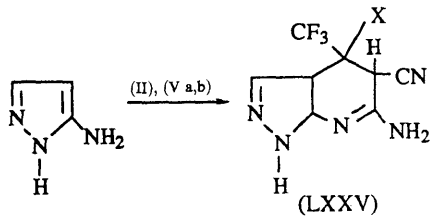
(II), (Va, b)



(LXXIV)

X = CF_3, $COOCH_3$, $COOC_2H_5$

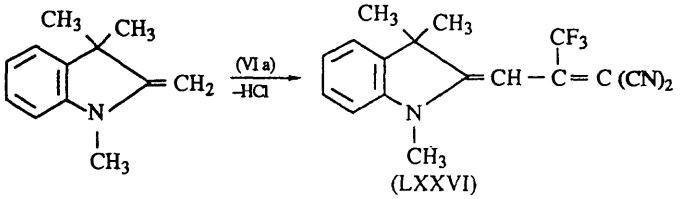
The *C*-alkylation of 3-aminopyrazole is accompanied by heterocyclisation leading to the dihydropyrazolopyridine (LXXV).[17,25]



(LXXV)

X = CF_3, $COOCH_3$, $COOC_2H_5$

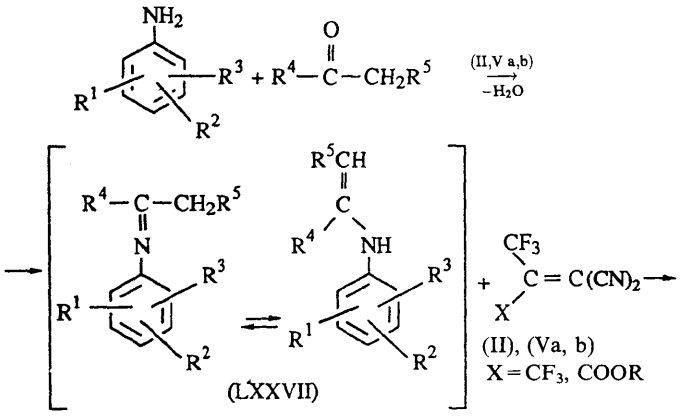
The *C*-alkenylation of 1,3,3-trimethyl-2-methyleneindoline with 2-chloro-1,1-dicyano-2-(trifluoromethyl)ethylene (VIa) is an example of the reaction of perfluoroalkyl substituted dicyanoethylenes with enamines. The strongly coloured compound (LXXVI) is formed.[18]



(LXXVI)

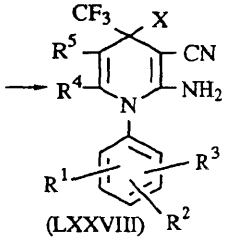
It has been suggested that certain acyclic enamines may react with 1,1-dicyano-2-(trifluoromethyl)ethylenes (II) and (Va, b) with the formation of dihydrobenzene derivatives.[62] The product of β-*C*-alkylation in this case is stabilised by cyclisation involving the nitrile group and the β′-CH fragment of the enamine.

A nonstandard example of the use of compounds existing in a state of imine–enamine equilibrium is the three component reaction of anilines, ketones and 1,1-dicyano-2-(trifluoromethyl)ethylenes (II) and (Va, b) leading to the *N*-phenyl-1,4-dihydropyridine derivative (LXXVII).[62]



(LXXVII)

(II), (Va, b)
X = CF_3, COOR



(LXXVIII)

The key stage of the process is the formation of the Schiff's bases (LXXVII) which are subject to β-*C*-alkylation in their enamine form with subsequent intramolecular cyclisation. A similar heterocyclisation is also effected on reacting alkenes (II) and (Va, b) with anils obtained from aldehydes.[62]

3. Reactions with salts of CH-acids

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene (II) reacts with sodium cyanide in acetonitrile forming the adduct (LXXIX) which is stable below 300 °C.[14]

$$(NC)_2C=C(CF_3)_2 + NaCN \longrightarrow Na(NC)_2C-C(CF_3)_2CN$$

(II) (LXXIX)

The reaction of alkene (VIa) with the sodium salt of dicyanomethane is known. The tetramethylammonium salt (LXXX) is formed in the presence of tetramethylammonium chloride.[16]

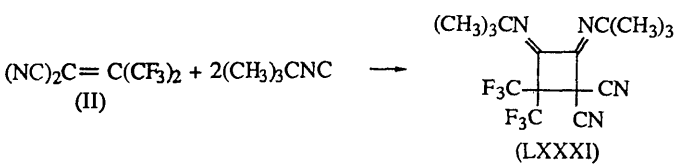
$$(NC)_2C=C(CF_3)CL + (NC)_2CHNa \xrightarrow{N(CH_3)_4Cl} (NC)_2C=C(CF_3)\overline{C}(CN)_2.\overset{+}{N}(CH_3)_4$$

(VIa) (LXXX)

VIII. Other reactions of perfluoroalkyl substituted dicyanoethylenes

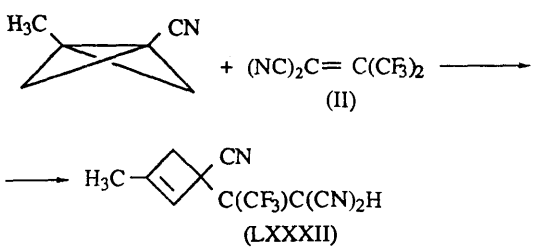
Data are included in this section on chemical conversions of fluorine-containing dicyanoethylenes which have not been systematically covered in the literature or belong to a special area of heteroorganic chemistry but are sufficiently important when creating a more complete picture of the chemical properties of the alkenes under consideration.

The first type includes the reaction of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) with t-butyl isocyanide at 0 °C. The resulting crystalline adduct of composition 1 : 2 was assigned the structure (LXXXI).[14]



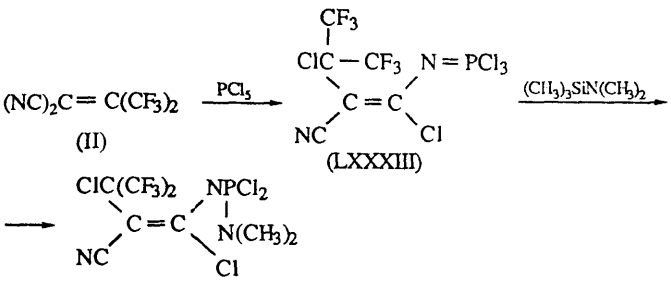
(LXXXI)

The reaction of (II) with bicyclo[1,1,0]butane is an example of an electrophilic addition leading to the cyclobutane derivative (LXXXII).[63]



(LXXXII)

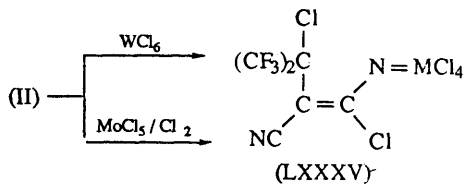
The reaction of the alkene (II) with phosphorus pentachloride leads to the (phosphoranilidenamino)ethylene (LXXXIII), treatment of which with $(CH_3)_3SiN(CH_3)_2$ gives the compound (LXXXIV).[64]



(LXXXIII)

(LXXXIV)

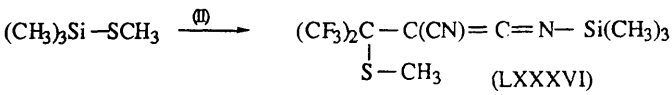
The acyclic nitrenes (LXXXV) may be obtained by the reaction of tungsten hexachloride or molybdenum pentachloride with the alkene (II).[65]



(LXXXV)

M = W, Mo

The olefin (II) reacts under mild conditions by insertion into Si–Si, Si–As, B–S or B–N bonds forming ketenimino derivatives such as compound (LXXXVI).[15,65]



(LXXXVI)

The reactions of alkenes (Ia, b) and (II) with transition metal complexes have been studied fairly widely.[66–70]

IX. Applications of perfluoroalkyl-substituted dicyanoethylenes and compounds obtained from them

1,2-Dicyano-1,2-bis(trifluoromethyl)ethylenes (Ia, b) are patented as stabilising additives for chlorinated hydrocarbons.[71]

The electron-accepting properties of fluorine-containing dicyanoethylenes were used in a study of the photo-dimerisation of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*endo*, *endo*-dimethanonaphthalene.[72]

Polymers of conjugated trienes, modified with the alkenes (Ia, b) by the Diels–Alder reaction,[28] acquire a high stability towards various actions and also improved electrical insulating properties.

Dicyano-*S*-diaminomethylenesulphilidenes, obtained from 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene oxide and thiourea derivatives, have been proposed for bleaching paper.[12]

The reaction of alkene (II) with aniline gives 4-[2,2-dicyano-1,1-bis(trifluoromethyl)ethyl]aniline (LX) which after diazotisation and coupling with β-naphthol gives an orange dye for wool.[11] Compounds (LXIV) and (LXXIV), which are intensely coloured, may also be used as dyes.[18]

The purpose-directed synthesis of 2,2-dicyanonorbornene derivatives (XIX) from the alkenes (II) and (VIa–d) and study of their biological activity has been carried out by Dupont.[16] It turned out these these compounds are exceptionally toxic (LD50 < 4 mg kg^{-1}) but 2,2-dicyano-3,3-bis(trifluoromethyl)norbornene has an absolutely lethal dose on oral administration to rats of the order of 1.5 mg kg^{-1}, i.e. it is more toxic than sodium cyanide. In addition

the heterocyclic compounds synthesised from trifluoromethyl substituted dicyanoethylenes are obviously interesting from the point of view of searching for new biologically active compounds.

References

1. K Tanaka (N Ishikawa, Editor) *Preparation and Function of Fluorine Compounds* (Translated into Russian), Mir, Moscow, 1990, p. 265
2. Yu V Zeifman, E G Ter-Gabrielyan, N P Gambaryan, et al. *Usp. Khim.*, 1984, **43**(3) 431 [English translation in *Russ. Chem. Rev.*, 1984(3)]
3. C G Krespan, W J Middleton *Fluorine Chem. Rev.*, 1967, **1** 145
4. V I Saloutin, K I Pashkevich, I Ya Postovskii *Usp. Khim.*, 1982, **51**(8) 1287 [English translation in *Russ. Chem. Rev.*, 1982(8)]
5. A V Fokin, A F Kolomiets, N V Vasil'ev *Usp. Khim.*, 1984, **53**(3) 398 [English translation in *Russ. Chem. Rev.*, 1984(3)]
6. A J Fatiadi *Synthesis*, 1986, (4) 249
7. F Freeman *Chem. Rev.*, 1980, **80** 329
8. US P. 3 133 115; *Ref. Zh. Khim.*, 1965, 18N45P
9. T L Cairns, R A Carloni, D D Coffman, et al. *J. Am. Chem. Soc.*, 1958, **80** 2755
10. US P. 3 238 228; *Ref. Zh. Khim.*, 1967, 14N1100P
11. US P. 3 162 674; *Ref. Zh. Khim.*, 1965, 21N109P
12. US P. 3 185 700; *Ref. Zh. Khim.*, 1966, 21N114P
13. US P. 3 194 819; *Ref. Zh. Khim.*, 1966, 17N94P
14. W J Middleton *J. Org. Chem.*, 1965, **30** 1402
15. E M Abel, J P Crow, J N Wingfield *J. Chem. Soc., Dalton Trans.*, 1972, (7) 787
16. W J Middleton, E M Bingham *J. Fluorine Chem.*, 1982, **20** 397
17. V Yu Tyutin, N D Chkanikov, A F Kolomietz, et al. *J. Fluorine Chem.*, 1991, **54** 272
18. V I Krokhtyak, A Ya Il'chenko *Zh. Org. Khim.*, 1980, **16** 1694
19. V I Krokhtyak, A Ya Il'chenko, L M Yagupol'skii *Zh. Org. Khim.*, 1981, **17** 268
20. W R Carpenter, G J Palenik *J. Org. Chem.*, 1967, **32** 1219
21. B L Dyatkin, S R Sterlin, L G Zhurabkoba, et al. *Zh. Org. Khim*, 1973, **9** 1786
22. E A Polenov, S R Sterlin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 704
23. B I Shapiro, Yu N Afanas'ev, E A Polenov, et al. *Khimiya i Khimicheskaya Tekhnologiya* (Chemistry and Chemical Technology), Moscow, 1972, p. 106
24. K N Houk, L L Munchausen *J. Am. Chem. Soc.*, 1976, **98** 937
25. K V Komarov, N D Chkanikov, M V Galakhov, et al. *J. Fluorine Chem.*, 1990, **47** 59
26. J Drexler, R Lindermayer, M A Hassan, et al. *Tetrahedron Lett.*, 1985, **26** 2555
27. J Drexler, R Lindermayer, M A Hassan, et al. *Tetrahedron Lett.*, 1985, **26** 2559
28. US P. 3 278 641; Chem. Abs., 1967, 29388f
29. V L Bell *J. Polymer Sci., Part A*, 1964, **2** 5305
30. W J Middleton, R E Heckert, E L Litte *J. Am. Chem. Soc.*, 1958, **80** 2783
31. A T Blomquist, Y C Meinwald *J. Am. Chem. Soc.*, 1959, **81** 667
32. J P Williams, A Wojcicki *Inorg. Chem.*, 1977, **16** 3116
33. R Bruckner, R Huisgen *Tetrahedron Lett.*, 1990, **31** 7133
34. R Bruckner, R Huisgen, J Schmid *Tetrahedron Lett.*, 1990, **31** 7129
35. R Bruckner, R Huisgen *Tetrahedron Lett.*, 1990, **31** 2557
36. S Proskow, H E Simmons, T L Cairns *J. Am. Chem. Soc.*, 1963, **85** 2341
37. R W Hoffman, U Bressel, J Gehlhans, et al. *Chem. Ber.*, 1974, **104** 873
38. R Huisgen, R Bruckner *Tetrahedron Lett.*, 1990, **31** 2553
39. R Bruckner, R Huisgen *Tetrahedron Lett.*, 1990, **31** 2561
40. R Gompper, D Lach *Tetrahedron Lett.*, 1973, **29** 2687
41. M Green, D C Wood *J. Chem. Soc. A*, 1969, (7) 1172
42. H Graf, R Huisgen *J. Org. Chem.*, 1979, **44** 2594
43. R Huisgen, G Steiner *Tetrahedron Lett.*, 1974, (39) 3763
44. A Bäumler, J Daub, W Pickl, et al. *Chem. Ber.*, 1985, **118** 1857
45. M Green, S M Heathcock, T W Turney, et al. *J. Chem. Soc., Dalton Trans.*, 1977, (2) 204
46. J P Williams, A Wojcicki *Inorg. Chem.*, 1977, **16** 2506
47. R Huisgen, E Langhals, H Nöth *J. Org. Chem.*, 1990, **55** 1412
48. R Huisgen, E Langhals, T Oshima *Heterocycles*, 1989, **29** 2075
49. Y M Chang, J Sims, K N Houk *Tetrahedron Lett.*, 1975, (50) 4445
50. J S Burnier, W L Jorgensen *J. Org. Chem.*, 1983, **48** 3923
51. R Huisgen, R Bruckner *J. Org. Chem.*, 1991, **56** 1679
52. R Bruckner, R Huisgen *J. Org. Chem.*, 1991, **56** 1677
53. A Ya Il'chenko, V I Krokhtyak, L M Yagupol'skii *Khim. Geterotsikl. Soedin.*, 1981, 1680
54. D D R Gompper *Angew. Chem., Int. Ed. Engl.*, 1964, **3** 560
55. P G Farrell, P N Ngo *J. Chem. Soc., Perkin Trans. 2*, 1973, 974
56. B C McKusick, R E Heckert, T L Cairns, et al. *J. Am. Chem. Soc.*, 1958, **80** 2806
57. A Ya Il'chenko, R E Koval'chuk, V I Krokhtyak, et al. *Zh. Org. Khim.*, 1981, **17** 2630
58. K V Komarov, N D Chkanikov, S V Sereda, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1917
59. K V Komarov, N D Chkanikov, S V Sereda, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1920
60. K V Komarov, N D Chkanikov, S V Sereda, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2417
61. N D Chkanikov, K V Komarov, V Yu Tyutin, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1193
62. V Yu Tyutin, N D Chkanikov, A F Kolomietz, et al. *J. Fluorine Chem.*, 1991, **54** 272
63. E P Blanchard, A Cairncross *J. Am. Chem. Soc.*, 1966, **88** 487
64. H W Roesky, H Penio, K Keller, et al. *Chem. Ber.*, 1986, **119** 3150
65. E W Abel, J P Crown, J N Wingfield *J. Chem. Soc., Chem. Commun.*, 1969, 967
66. M Cooke, M Green *J. Chem. Soc. A*, 1969, 651
67. T Blackmore, M I Bruce, F G A Stone *J. Chem. Soc., Dalton Trans.*, 1974, 106
68. B Clarke, M Green, R B L Osborn, et al. *J. Chem. Soc. A*, 1986, 167
69. V A Mukhedkar, A J Mukhedkar *J. Inorg. Nucl. Chem.*, 1981, **43** 2801
70. A Christofides *J. Organomet. Chem.*, 1983, **253** 355
71. US P. 3 277 193; *Chem. Abs.*, 1966, 20005e
72. G Jones, W G Becker, S H Chiang *J. Am. Chem. Soc.*, 1983, **105** 1269

Received 15th April 1992

Translated from *Uspekhi Khimii* **61** 1422–1456 (1992) U.D.C. 541.128:542.953:547.484.23'261:547.315.3

Reactions of polyfluoroketones with unsaturated compounds

A S Golubev, A F Kolomiets, A V Fokin
The A N Nesmeyanov Institute of Elementoorganic Compounds of the Russian Academy of Sciences

ABSTRACT. A review is presented on the reactions of polyfluoroketones with alkenes, alkynes, 1,2- and 1,3-dienes, and certain other unsaturated compounds. The reactivity of polyfluoroketones has been compared with that of diethyl oxomalonate. The characteristic dienophilic, enophilic and 1,2-dipolar properties of polyfluoroketones have been discussed.

The bibliography contains 156 references.

Contents

I. Introduction 779
II. [4 + 2]-Cycloaddition 779
III. Ene reactions 783
IV. [2 + 2]-Addition 789

I. Introduction

Among unsaturated organofluorine compounds, polyfluoroketones are second only to fluoroolefins in order of importance. The electrophilicity of ketones increases with introduction of fluorine atoms at the α-position, and such activity is at a maximum in polyfluoroketones and derivatives thereof in which one of the fluorine atoms in the α-position is replaced by an electron-accepting group: an alkoxy, carbonyl, nitro, sulphonic acid or fluorosulphonyl group. These are among the most powerful electrophilic agents known, possessing an extraordinary affinity for nucleophiles and towards π-systems with donor properties. Thus, depending on structural features, polyfluoroketones possess a wide range of chemical properties, exhibiting both the classical reactivity of aliphatic ketones.[1–3] and 'anomalous' behaviour specific to this class of functionalised ketone.

The unusual chemistry of polyfluoroketones and their derivatives is due, in part, to their extremely high electrophilicity and, in part, to the ability of perfluoroalkyl residues, especially the trifluoromethyl group, to stabilise adjacent δ-bonds. This explains the facile conversion of polyfluoroketones to stable hemiketals, hemiaminals, aldols, thermodynamically stable enols, α-fluoro-substituted alkoxides, oxetenes and other compounds with a small ring. The high electrophilicity and stabilising effect of polyfluoroalkyl groups is notably manifested in the reactions of polyfluoroketones with alkenes, alkynes, 1,2- and 1,3-dienes, and with a large number of other unsaturated compounds—the subject matter of the present review.

Up to now, there have been no review articles covering general aspects of the reactions of polyfluoroketones with unsaturated compounds; nor have the latter been examined in a critical sense. Previous reviews[4,5] and a monograph[6] in the field of organofluorine chemistry have included this aspect in part, as also has a more recent review.[7] In the authoritative survey of Witt et al.,[8] the authors collected and analysed information on the reactions of hexafluoroacetone with unsaturated elementoorganic and organometallic compounds.

In this article, we have compared the reactivity of highly electrophilic polyfluoroketones towards alkenes, cycloalkenes, alkynes, 1,3-dienes, cumulenes and a number of other unsaturated compounds. We have examined, in particular, the reactions of these unsaturated compounds with perfluorocyclobutanone, nitropentafluoroacetone, hexafluoroacetone (HFA), methyltrifluoropyruvate (MTFP), and with chloropentafluoro- and 1,3-dichlorotetrafluoroacetone. For comparison, information has also been gathered on the dienophilic, enophilic, and 1,2-dipolar properties of diethyl oxomalonate (DEOM)—an activated carbonyl compound with properties very similar to those of polyfluoroketones.

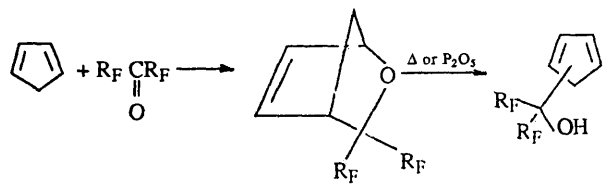
In an analysis of the collected information, an attempt has been made to assess the effect of the polyfluoroketone structure on the ability of these ketones to participate in Diels–Alder reactions, ene reactions, and in [2 + 2]-cycloaddition; the influence of the CF_3 group on these reactions has been examined by comparing the reactivity of hexafluoroacetone, methyltrifluoropyruvate, and diethyloxomalonate.

II. [4 + 2]-Cycloaddition

Among the vast array of available heterodienophiles,[9] including activated carbonyl compounds, polyfluoroketones are particularly noteworthy in that they possess unusually high reactivity in Diels–Alder cycloaddition. Thus, [4 + 2]-cycloadducts are formed between polyfluoroketones and donor-type 1,3-dienes under mild conditions in the absence of a catalyst (Table 1). Furthermore, high reactivity is manifested towards certain 1,3-heterodienes.

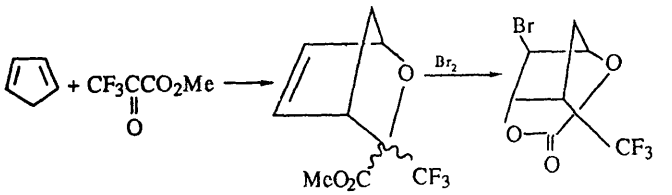
Perfluorocyclobutanone[10] and HFA [12,13] interact with cyclopentadiene even on mixing in the cold. The 2-oxabicyclo[2.2.1]hept-5-ene derivative obtained from perfluorocyclobutanone is relatively stable, and may be isolated pure by distillation under reduced pressure. However, fractionation under the normal conditions results in its conversion to 2-(α-hydroxyperfluorocyclobutyl)cyclopentadiene which readily polymerises. A similar

cycloadduct is formed from HFA, but undergoes retrodiene scission on heating above 20 °C. It is converted into a regioisomeric mixture of α-hydroxyhexafluoroisopropylcyclopentadienes in the presence of P_2O_5.[13]

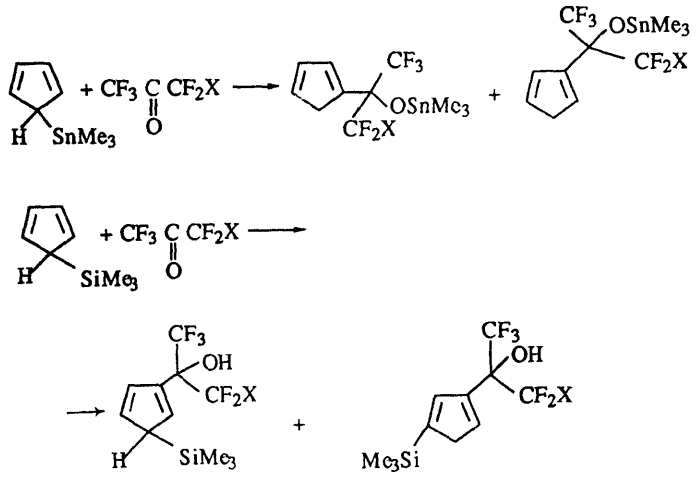


$R_F = CF_3$; R_F, $R_F = -(CF_2)_3-$

Methyl trifluoropyruvate (MTFP) has the same reactivity as HFA towards cyclopentadiene, affording a 2.5:1 mixture of *endo*- and *exo*-2-oxabicyclo[2.2.1]hept-5-enes.[21] The latter cycloadducts revert to the starting materials on heating, and are converted predominantly to a bromolactone on bromination.



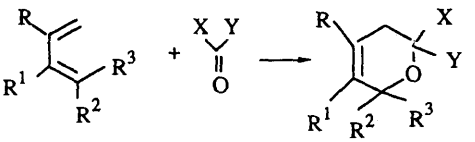
No cycloadduct is formed on reaction of HFA or chloropentafluoroacetone with cyclopentadienyltrimethyl-stannane or -silane. Instead, reaction of the cyclopentadienylstannane with these polyfluoroketones at 20 °C leads to insertion of the latter into a C–Sn bond, while reaction with the silyl analogue results in a mixture of 1,2-adducts.[23]



X = F, Cl.

Unlike polyfluoroketones, diethyl oxomalonate does not afford cycloadducts with cyclopentadiene in the temperature range −20 to 135 °C.[24]

Polyfluoroketones interact as readily with 1,3-butadiene and its alkyl and alkoxy derivatives as they do with cyclopentadiene (Table 1). The resulting 5,6-dihydro-2*H*-pyrans are stable and isolable in high yield. No information is available on the conditions required for retrodiene scission, nor on the manner of their decomposition.



$R = R^1 = R_2 = R^3 = H$; $R = CH_3$, $R^1 = R^2 = R^3 = H$;
$R = R^1 = CH_3$, $R^2 = R^3 = H$;
$R = R^1 = R^3 = H$, $R^2 = CH_3$; $R = R^1 = R^3 = H$; $R^2 = OMe$;
$R = Cl$, $R^1 = R^2 = R^3 = H$; $R = R^2 = R^3 = CH_3$, $R^1 = H$.
X, Y = $-(CF_2)_3-$; X = Y = CF_3; X = Y = CF_2Cl; X = CF_3,
Y = CF_2NO_2; X = CF_3, Y = CO_2Me.

Table 1. Reaction conditions for the cycloaddition of polyfluoroketones to 1,3-dienes and the yield of 5,6-dihydro-2*H*-pyrans.

Polyfluoroketone	1,3-Diene	*T*, °C	Time*, h	Yield, %	Refs.
	1,3-Butadiene	0	24	100	[10]
	Cyclopentadiene	20	–	93	[11]
CF_3CCF_3	" "	20	–	54	[12, 13]
	1,3-Butadiene	20	24	78	[14]
	Isoprene	20	16	75	[15]
	" "	100	16	83	[12]
	Piperylene	20	16	82	[15]
	2,3-Dimethyl-1,3-butadiene	100	–	92	[12]
	1-Ethoxy-1,3-butadiene	20	24	87	[16]
	2,4-Dimethyl-1,3-pentadiene	170	24	86	[17]
	2-Methyl-6-methylene-,2-7-octadiene (myrcene)	170	3	80	[18]
CF_3ClCCF_2Cl	1,3-Butadiene	100	–	87.5	[12]
	Isoprene	200	48	95	[19]
	2,3-Dimethyl-1,3-butadiene	20	16	55	[12]
$CF_3CCF_2NO_2$		200	10	76	[12]
	1,3-Butadiene	20	24	90	[15]
	Isoprene	−15 to −10	–	95.6	[20]
	2,3-Dimethyl-1,3-butadiene	−15 to −10	–	54.7	[20]
	Chloroprene	100	4	75.8	[20]
CF_3CCO_2Me	Cyclopentadiene	20	12	66.4	[21]
	1,3-Butadiene	20	16	94	[15]
	Isoprene	20	24	84; 83	[15, 22]
	2,3-Dimethyl-1,3-butadiene	20	24	88; 75	[15, 22]
	Piperylene	20	24	85	[15]
	Chloroprene	60	8	86	[15]

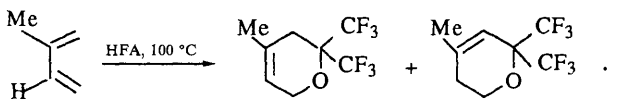
Footnote. A dash means that the reaction time has not been given.

Of the examined polyfluoroketones, perfluorocyclobutanone[10,11] and nitropentafluoroacetone[14,20] are the most reactive, the corresponding cycloadducts with 1,3-butadiene being formed in the cold or at 20 °C. Hexalfuoroacetone is slightly less reactive than nitropentafluoroacetone, interacting with 1,3-dienes at 20 °C.[14,15,20] The assertion of Ishihara et al.[25] that "HFA exhibits low reactivity towards the more familiar 1,3-dienes" is without foundation.

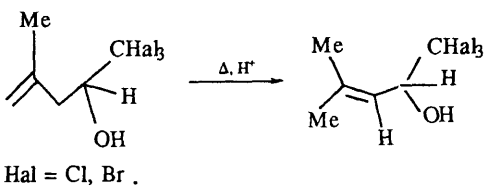
It should also be pointed out that it is not necessary to use harsh conditions for the cycloaddition of HFA or 1,3-dichlorotetrafluoroacetone with 1,3-dienes, as has been reported.[17,19] According to Linn,[12] [4 + 2]-cycloaddition with 1,3-dichlorotetrafluoroacetone at 20 °C is less facile than with HFA. It has recently been reported that MTFP is as reactive as HFA in such cycloaddition.[15]

A comparison of the reactivity of MTFP towards a number of 1,3-dienes has provided some interesting results.[15] Thus, it has been shown that cyclopentadiene, 1,3-butadiene, isoprene, piperylene (as a *cis/trans* mixture) and 2,3-dimethyl-1,3-butadiene interact with MTFP effectively under the same conditions (0–20 °C). It therefore follows that [4 + 2]-cycloaddition of these dienes with MTFP is little affected by structural variation within the dienes, by any variation in the transitional energy from transoid to cisoid form, or by the energy coefficients and degree of localisation of the frontier orbitals. As similar results are obtained with other polyfluoroketones (see Table 1), it is evident that such behaviour is characteristic of this family of dienophile.

The regioselectivity of the cycloaddition of polyfluoroketones with unsymmetrical 1,3-dienes is another characteristic feature. Thus, under all conditions, cycloaddition of the ketone proceeds in such a way that the carbon atom of the carbonyl group attacks the carbon atom of the conjugated system possessing the highest electron density. This is true under both mild and harsh conditions. The assertion that the thermal cycloaddition of polyfluoroketones with isoprene displays low regioselectivity[22] would appear to be unfounded since in the original work of Linn[12] it was shown that HFA affords only the *para*-isomer [sic] (85%) together with an isomer (15%) arising by prototropic shift:



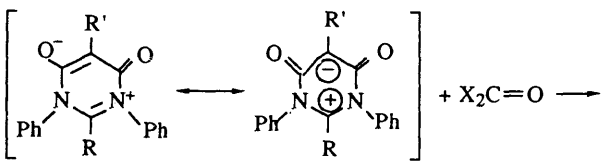
The latter product would be anticipated if traces of acid were present in the medium. Such acid-catalysed prototropic shfits, in fact, are characteristic of structures of the type:[26]

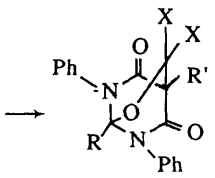


Hal = Cl, Br.

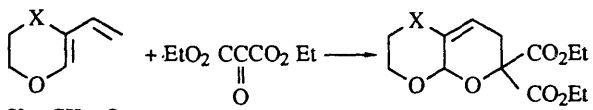
The somewhat anomalous cycloaddition of polyfluoroketones to 1,3-dienes is probably due to the electronic configuration of the carbonyl group and associated charged residues which make a large contribution to the formation of the pericyclic transition state. The high electronegativity of the carbonyl oxygen of the dienophile and the high electron-accepting ability of the perfluoroalkyl group leads to a significant decrease in the level of the LUMO and to its localisation primarily on the carbon atom of the carbonyl group, as has been demonstated with perfluorocyclobutanone.[27]

In this context, it is interesting to note that DEOM is noticeably more reluctant to participate in [4 + 2]-cycloaddition with 1,3-dienes than polyfluoroketones.[9] In fact, cycloaddition of DEOM with 1,3-butadiene and its alkyl derivatives can only be achieved at high temperatures (130–140 °C).[24,28–31] Cycloaddition at a lower temperature (50 °C) is only possible with electron-rich 1,3-dienes, such as 1-alkoxy-3-alkyl-1,3-butadienes,[32] 5-vinyl-3,4-dihydro-2*H*-pyran and 5-vinyl-2,3-dihydro-1,4-dioxin.[33] The notable difference in dienophilic reactivity between HFA and DEOM is apparent from the relative ease of cycloaddition of these compounds with 6-oxo-2,6-dihydro-1-pyrimidinium-4-olates [...3,6-dihydro? (Ed. of Translation)], involving a synchronous [$4\pi_s$ + $2\pi_s$]-mechanism: the former dienophile reacts at 0 °C, whereas cycloaddition with DEOM requires heating at 110 °C.[34] Oxadiazabicyclooctanediones are obtained as the reaction product:



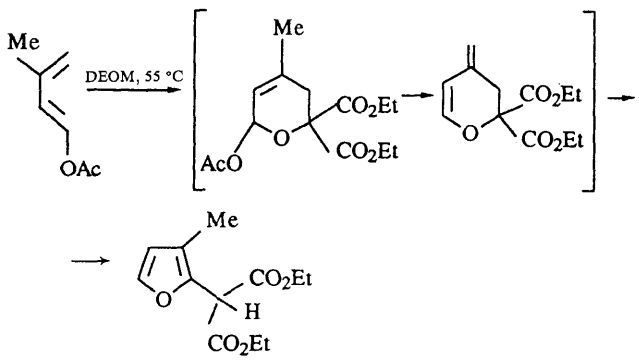


X = CF_3, CO_2Et.



X = CH_2; O.

1-Methoxy-3-methyl-1,3-butadiene forms an intermediate [4 + 2]-cycloadduct with DEOM on heating in THF. This subsequently eliminates acetic acid and rearranges to give a substituted furan.[35]

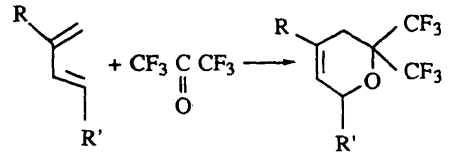


Coupled with the lower activity of DEOM is the somewhat reduced regioselectivity in its [4 + 2]-cycloaddition with unsymmetrical 1,3-dienes.[24] With isoprene, the para-isomer is formed predominantly together with around 10% of the meta-isomer. The regioselectivity of cycloaddition with piperylene is higher, the proportion of ortho- and meta-cycloadducts being 19 : 1.

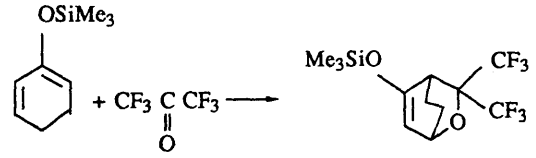
Further differences in the dienophilic activity of polyfluoroketones and DEOM are apparent in their reactions with siloxy-1,3-dienes, which have been extensively studied in the field of natural product synthesis,[36,37] notably in the context of asymemtric diene syntheses based on chiral organoaluminium catalysts.[38,39]

Hexafluoroacetone interacts regiospecifically with a variety of siloxy-1,3-dienes in the absence of catalysts at –40 to –45 °C. The sole regioisomer is that anticipated by considering the polarisation of

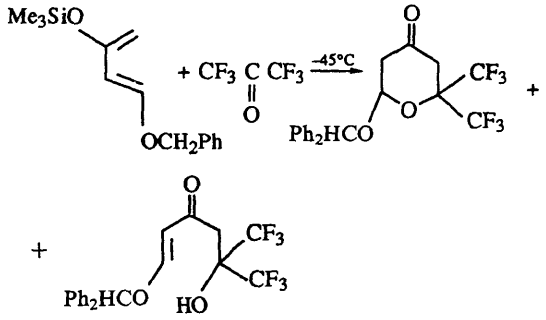
the carbonyl group and the 1,3-conjugated system.[25]



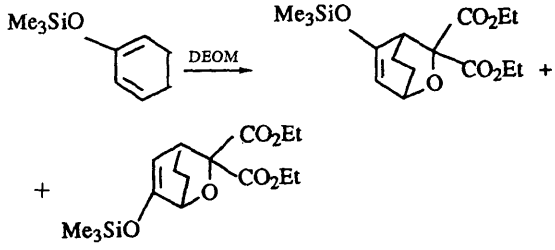
R = H, R' = $OSiMe_3$; R = $OSiMe_3$, R' = H.



However, the reaction of HFA with (*E*)-1-benzyloxy-3-trimethylsiloxy-1,3-butadiene yields both [4 + 2]-cycloadduct and an aldol-type by-product.[40]

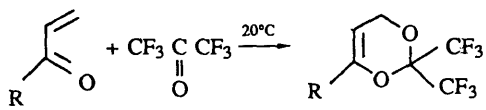


Diethyl oxamalonate (DEOM) normally participates in such reactions at 130–140 °C,[41] although a [4 + 2]-cycloadduct is obtainable on heating this dienophile with the electron-rich 1-methoxy-3-trimethylsiloxy-1,3-butadiene in refluxing THF over several hours.[35] However, the cycloaddition of DEOM with 1,3-dienes displays low regioselectivity. Thus, a 55 : 45 mixture of para- and meta-adducts is formed from 2-trimethylsiloxy-1,3-cyclohexadiene.[41]



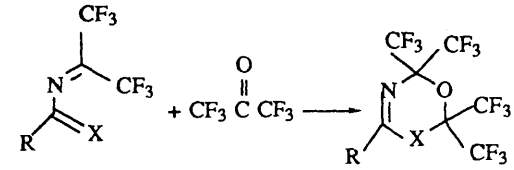
Low regioselectivity was also noted for the reaction of DEOM with 1-methyl-2-trimethylsiloxy-1,3-butadiene.

Dieles–Alder reactions with polyfluoroketones may also be performed with 1,3-heterodienes. Thus, mixing HFA with acrolein or methyl vinyl ketone at low temperature, followed by warming to 20 °C, leads to the corresponding [4 + 2]-adduct in quantitative yield.[42]



R = H, Me

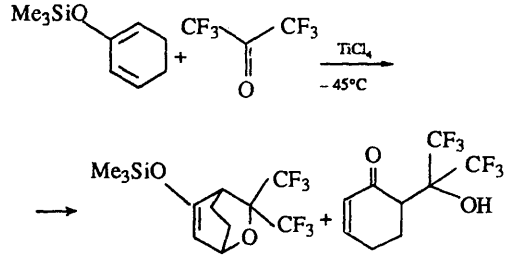
Heating HFA with highly electrophilic acylimine derivatives of HFA affords the corresponding 1,3,5-dioxazine,[43] while thioacylimine and iminoacylimine derivatives give the corresponding 1,3,5-oxathiazine and 1,3,5-oxadiazine derivatives.[44]



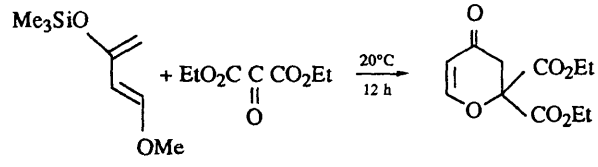
X = O, S, NR^1; R = Ph, 4–ClC_6H_4, Bu^t.

In all such heterodiene syntheses, reaction proceeds by attack of the carbonyl carbon of HFA at the most electron-rich atom of the 1,3-heterodiene component. It should be noted that such Diels–Alder reactions of HFA acylimine derivatives with non-fluorinated carbonyl compounds may be undertaken under milder conditions.[45]

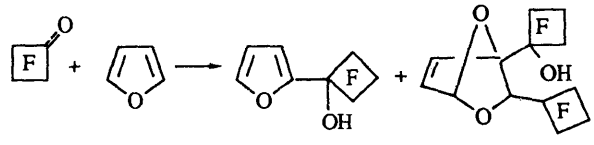
Little information is available on Lewis acid-catalysed cycloaddition of polyfluoroketones with 1,3-dienes. It is reported that the cycloaddition of HFA with 1-trimethylsiloxy-1,3-cyclohexadiene in the presence of $TiCl_4$ is accompanied by the formation of an aldol derivative as by-product.[25]



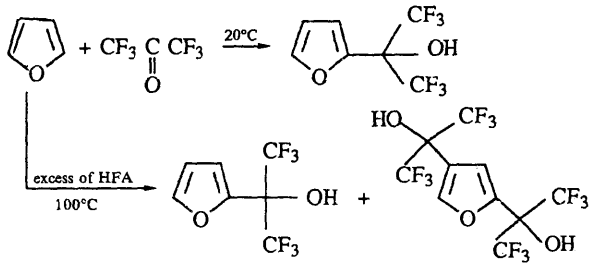
In the $SnCl_4$-catalysed reaction of isoprene with MTFP at –50 °C, an ene adduct is formed together with a [4 + 2]-cycloadduct (see below). The cycloaddition of DEOM with 1-ethoxy-3-alkyl-1,3-butadienes can be successfully carried out at 20 °C in the presence of tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)-europium(III).[46] Zinc chloride (250 mol%) activates the cycloaddition of DEOM with 1-methoxy-3-trimethylsiloxy-1,3-butadiene.[47] This reaction is accompanied by removal of the silyl protective group and elimination of methanol.



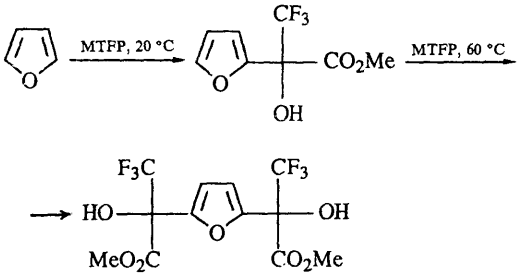
Normally, the interaction of polyfluoroketones with heterocyclic 1,3-dienes leads to 1,2-adducts rather than [4 + 2]-cycloadducts. However, in the reaction of perfluorocyclobutanone with furan, both 1,2- and [4 + 2]-adducts have been isolated.[48]



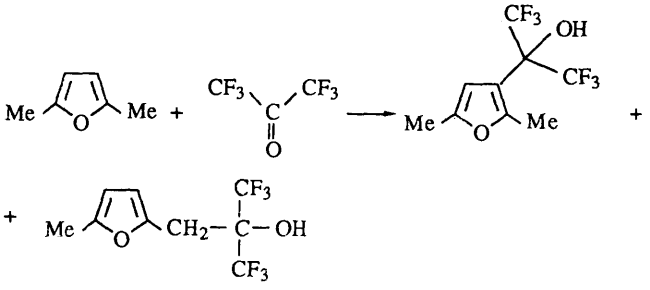
Depending on the temperature and ratio of the reactants, the interaction of HFA with furan leads to either a 2-substituted furan or a mixture of 2-substituted and 2,4-disubstituted furan.[48–50]



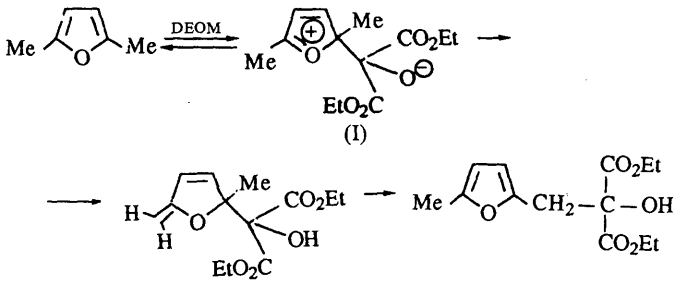
The reaction of furan with MTFP proceeds in a step-wise manner to give the corresponding 2,5-disubstituted furan via mono-substitution.[51,52]



The interaction of 2,5-dimethylfuran with HFA leads to a 3:1 mixture of side chain-substituted and ring-substituted derivatives.[49]



The reaction of DEOM with 2,5-dimethylfuran can only be conducted at elevated pressure.[53] In this instance, side-chain substitution is exclusive. It is thought that a zwitter-ion (I) is formed initially, and subsequently stabilised by a 1,5-sigmatropic shift.[54]

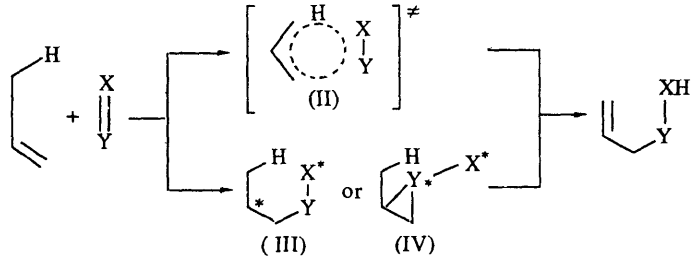


The reactions of *N*-methylpyrrole and thiophene with polyfluoroketones proceed by C-alkylation only.[48,49,51]

III. Ene reactions

An ene reaction is defined as the addition of an electron-rich olefin (the ene component) having a allylic hydrogen to an electron-deficient double bond (the enophile), as a result of which the double bond of the olefin undergoes migration with transfer of the allylic hydrogen atom to the enophile.[55,56]

In his review, Hoffmann alludes to the possibility of there being a broad spectrum of transition states for an ene reaction.[55] One extreme is a symmetry-allowed concerted $[2\pi_s + 2\pi_s + 2\delta_s]$-process, as represented by transition state (II) (see below). However, the symmetry of the transition state is such that the other extreme, namely a step-wise pathway, is also possible. Here, the transition state could be represented by either a zwitter-ionic structure or a biradical having free (III) or restricted (IV) rotation.[56] A study of the several by-products formed during such ene reactions would tend to suggest that a step-wise mechanism is operative.[57,58]

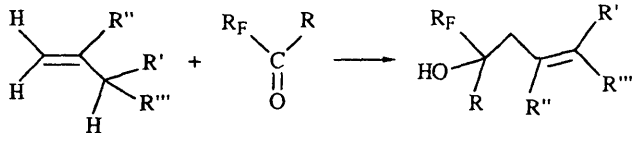


Synthetic applications of ene reactions have been legion in recent years. This is particularly true in the field of asymmetric synthesis in the presence of chiral catalysts.[59]

Polyfluoroketones are among the more interesting enophiles. In view of their high activity in ene reactions, they have sometimes been called "superenophiles",[62,63] as also have trifluoronitrosomethane,[60] DEOM,[62] and thionylimines with electron-accepting substituents.[61]

1. Ene reactions of polyfluoroketones with alkenes

Polyfluoroketones undergo ene reaction with terminal alkenes under mild conditions to give exclusively or predominantly homoallyl alcohols.[10,21,64,65]



R, R_F = — $(CF_2)_3$ —, CF_3, CF_2Cl; $R_F = CF_3$, $R = CF_2Cl$; $R_F = CF_3$, $R = CF_2NO_2$; $R_F = CF_3$, $R = CO_2Me$.

Literature data on these reactions are summarised in Table 2. It should be noted that, contrasting with classical enophiles, polyfluoroketones participate in ene syntheses under mild conditions. Normally, the reaction can be conducted in the temprature range 20–100 °C, and in certain instances below 0 °C. For example, the following reactions can be carried out at 20–25 °C: polyfluorocyclobutanone with propene and 2-phenylpropene;[10,11] nitropentafluoroacetone with 2-methylpropene;[64] HFA with 2-methyl-, 2-methoxy- and 2-phenyl-propene;[64,65] and MTFP with 2-methylpropene and its homologues.[21] 1,3-Dichlorotetrafluoroacetone, HFA and MTFP each undergo ene reaction with active ene components, such as β-pinene and 3,7-dimethylenedicyclo[3.3.1]-nonane.[65,69]

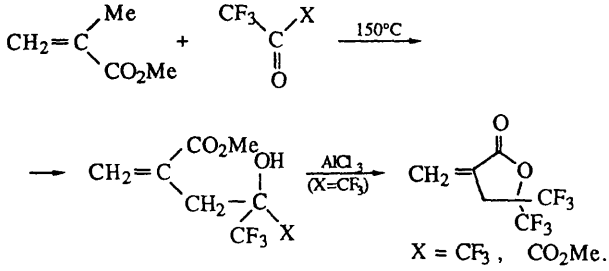
Table 2. Reaction conditions and yields of homoallyl alcohols obtained by reaction of polyfluoroketones with terminal alkenes.

Polyfluoroketone	Alkene	T, °C	Time*, h	Yield, %	Refs.
O F	Propene	20	–	88	[10]
	–	175	12	87	[11]
	2-Phenylpropene	20	1440	79	[11]
CF_3CCF_3 O	Propene	145	12	7.6	[66]
	" "	150	2.5	17	[65]
	" "	150	9	67	[64]
	2-Methylpropene	20	24	97	[64]
	" "	35–40	12	62.1	[66]
	" "	50	3	36	[67]
	" "	25–30	78	60	[68]
	3,7-Dimethylene-bicyclo[3.3.1]nonane	20	–	95.6	[69]
	β-Pinene	35	2	80	[65]
	2-Methoxypropene	0–35	1	85	[65]
	2-Phenylpropene	40	4	80	[65]
	2-Methyl-3-phenylpropene	25–30	65	82	[68]
	3-(Triphenylsilyl)propene	60	28	65	[23]
	3-(Trimethylsilyl)propene	100	48	86	[23]
	1-Butene	20	12	52	[66]
	" "	25	72	40	[68]
	1-Octene	100	2	75	[65]
	2-Chloropropene	165	4	10–20	[65]
	3-Chloropropene	165	4	3	[65]
	2-Acetoxypropene	25	56	–	[66]
	4-Allylanisole	100	3	82.5	[70]
	Allylbenzene	120	5	80.7	[70]
	Ally phenyl ether	150	–	16.2	[70]
	Allyl phenyl sulphide	150	15	67.7	[70]
	Methyl methacrylate	165	6	16	[65]
CF_2ClCCF_3 O	Methacrylonitrile	165	4	3	[65]
	Allybenzene	25	72	53	[68]
	3-(Triphenylsilyl)propene	80	24	53	[23]
	3-(Trimethylsilyl)propene	100	24	89	[23]
CF_2ClCCF_2Cl O	2-Phenylpropene	45–100	72	93	[71]
	–	60	60	62	[65]
	β-Pinene	−70–0	24	62	[67]
	2,4,4-Trimethylpent-1-ene	66–71	5	50	[67]
	1,5-Hexadiene	100	24	90	[66]
	3-(Triphenylsilyl)propene	100	24	49	[23]
	3-(Trimethylsilyl)propene	100	24	83	[23]
$CF_3CCF_2NO_2$ O	Propene	100	6	66	[64]
	3-Methylpropene	20	24	96	[64]
	3-Methylpropene	−20	288	73.6	[21]
CF_3CCO_2Me O	3,7-Dimethyl-ene-bicyclo[3.3.1] nonane	20	0.5	94.6	[69]
	2-Methyl-1-pentene	20	24	84	[22]
	1-Butene	100	48	83	[72]
	1-Hexene	100	5	90	[72]
	–	80–100	40–50	91	[22]
	1-Octene	80–100	40–50	96	[22]
	1-Hexadecane	80–100	40–50	79	[22]
	Vinylcyclohexane	80–100	40–50	74	[22]
	Allylbenzene	100	14	84	[72]
	2-Chloropropene	120	12	61.4	[72]
	2-Methyl-3-chloropropene	100	48	70	[72]
	3-Iodopropene	150	48	21	[72]
	Methyl methacrylate	160	48	15	[72]

Footnote. A dash means that data are unavailable.

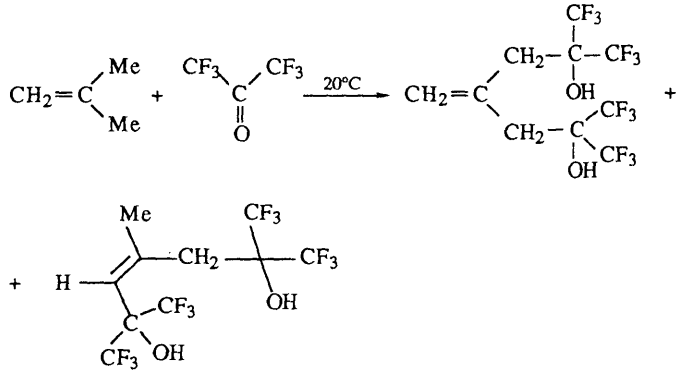
A further feature of polyfluoroketone chemistry is that their enophilic activity towards active ene components is as high as their dienophilic activity towards 1,3-dienes. This distinguishes polyfluoroketones from classical enophiles[55] which participate in ene reactions much less easily than in diene syntheses. It should be noted also that, in the family of highly electrophilic polyfluoroketones, the most active enophile (and dienophile) is perfluorocyclobutanone. This is evident from the reactivity of polyfluoroketones towards propene.[10] Hexafluoroacetone and methyl trifluoropyruvate display similar ene reactivity, while that of chloropentafluoro- and 1,3-dichlorotetrafluoro-acetone is lower and that of nitropentafluoro-acetone is somewhat higher.

It is also significant that polyfluoroketones participate in an unusually wide spectrum of ene reactions. For example, they react not only with classical ene components (differing in their donor properties and polarisation of the C=C bond but also with terminal 2-chloroalkenes, the unsaturation of which is deactivated by conjugation with the chlorine atom.[72] Ene reaction also takes place by interaction of polyfluoroketones with such 3-substituted propenes as 3-aryloxy- and 3-arylthio-propenes,[70] 3-iodopropene,[72] and 3-chloropropene,[65] which are normally unreactive as ene components or only weakly active. Even methyl methacrylate undergoes ene reaction with HFA [65] and MTFP.[72]



The ene adduct obtained with HFA is further converted to a λ-lactone on treatment with $AlCl_3$.[67] Bulky allylic substituents, such as trimethyl- and triphenyl-silyl, in the alkene component do not inhibit ene reaction with HFA or with chloropentafluoro- and 1,3-dichlorotetrafluoro-acetone.[23]

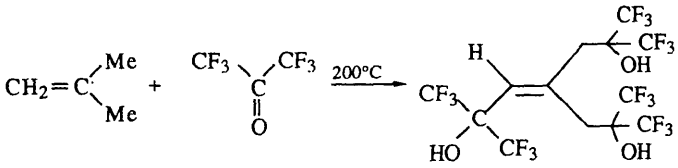
In certain instances the selectivity of the ene reaction between polyfluoroketones and alkenes is lower than normal because the initially formed homoallyl alcohol is itself a highly active ene component and undergoes a subsequent ene reaction to give a 2:1 adduct. The effect of the reaction conditions on such adduct formation has been studied in detail,[68] with particular reference to the reaction of HFA with 2-methylpropene.[66,68,73,74]



Similar products have also been observed on interaction of 2-methylpropene with 1,3-dichlorotetrafluoroacetone.[68,75] and MTFP.[21] In the latter instance, 2:1 adducts are even formed at −20 C.[72] The formation of such adducts also takes place on

reaction of HFA with propene,[68,76,77] 1-butene,2-phenylpropene, 2-methyl-1-pentene, 2-methyl-1-undecene, and 2-methyl-3-phenylpropene,[68] as well as on reaction of 1,3-dichlorotetrafluoroacetone with 2-phenylpropene and 1,5-hexadiene.[66]

A 3:1 adduct has been isolated by reacting 2-methylpropene with a four-fold excess of HFA.[68,78]

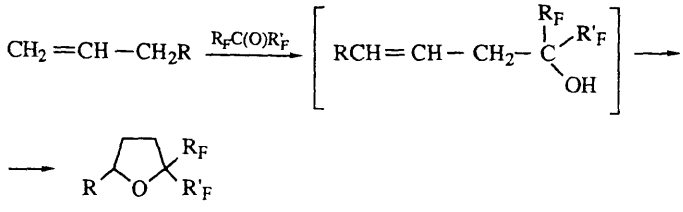


The ene reactions of polyfluoroketones with propenes having electron-donating allylic functionality afford tetrahydrofuran derivatives as by-product[64,70–72] the yield of which depends on the temperature and the reaction time. Under certain conditions such tetrahydrofurans are the main product (see Table 3).

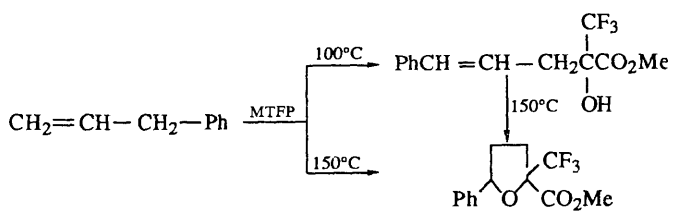
Table 3. Reaction conditions and yields of tetrahydrofurans obtained by reaction of polyfluoroketones with terminal alkenes.

Polyfluoroketone	Alkene	*T*, °C	Time*, h	Yield, %	Refs.
CF_3CCF_3 ‖ O	Allyl methyl ether	100	20	18	[64]
	4-Allylanisole	150	–	79	[70]
	Allyl phenyl sulphide	150	15	17.8	[70]
$CF_3CCF_2NO_2$ ‖ O	Allyl methyl ether	100	10	30	[64]
CF_3CCO_2Me ‖ O	Allyl methyl ether	110	30	57	[72]
	Allylbenzene	150	14	32.3	[72]
CF_2ClCCF_2Cl ‖ O	4-Allylanisole	45–100	144	91	[71]
	Allyl phenyl ether	45–100	310	67	[71]
	Diallyl ether	45–100	144	97	[71]

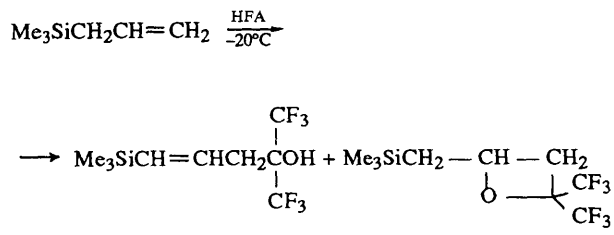
The formation of these products can be explained by cycloisomerisation of the initially formed homoallyl alcohols.



This was confirmed in a study of the reaction of HFA with 4-allylanisole[70] and of MTFP with allylbenzene.[72]

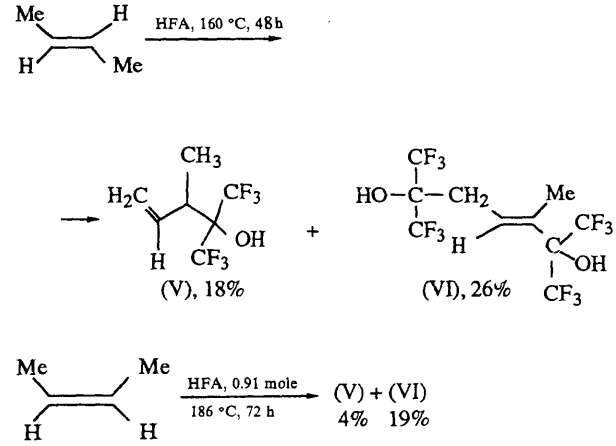


Only one example is known of a thermal reaction between a polyfluoroketone and a terminal alkene wherein by-product formation is kinetically independent of the primary ene reaction. Thus, it has been shown that HFA interacts with 3-(trimethylsilyl)propene to give a mixture of the corresponding homoallyl alcohol and an oxetane.[23]

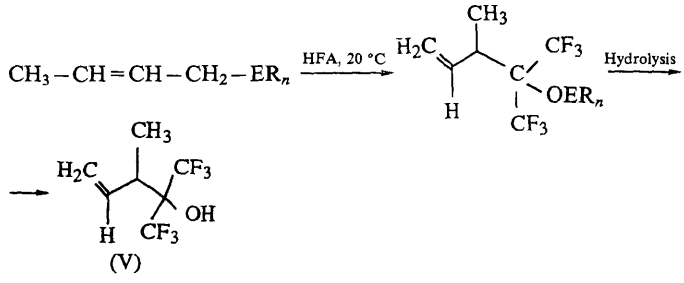


Here, [2 + 2]-cycloaddition coexists with ene reaction as a quite independent pathway.

Contrasting with terminal alkenes, internal alkenes interact with polyfluoroketones only under harsh conditions. For example, the reactions of *trans*- and *cis*-2-butene with HFA require heating at 160 and 180 °C, respectively. The resulting homoallyl alcohols, having a terminal vinyl group, readily participate in a subsequent ene reaction.[68]

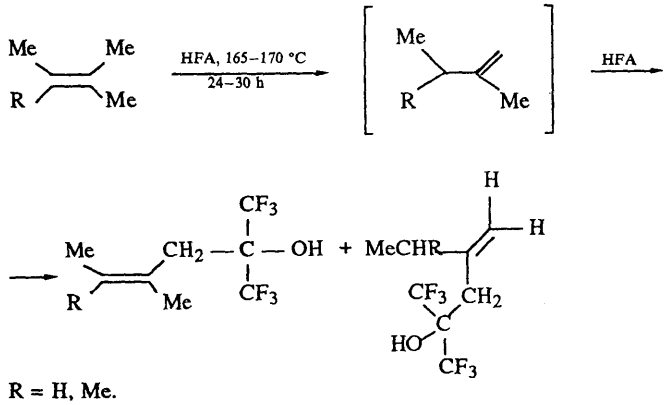


The homoallyl alcohols (V) and chloropolyfluoro analogues have also been prepared by reaction of the corresponding polyfluoroketones with crotyldibutylborane, tricrotylborane,[79] crotyltrimethylstannane or crotyltriphenylstannane.[23] The initial ene reaction proceeds regiospecifically at 20 °C with transfer of the organometallic residue to the oxygen atom of the carbonyl group.



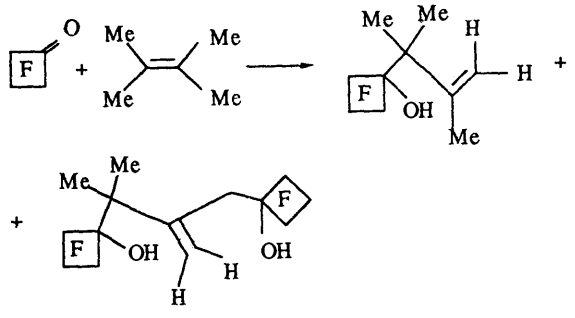
$ER_n = B(n\text{-}Bu)_2$, $B(CH_2{-}CH{=}CH{-}CH_3)_2$, $SnMe_3$, $SnPh_3$.

Treatment of HFA with trimethyl- or tetramethyl-ethene under harsh conditions initially produces a terminal alkene which then reacts with the ketone to give a mixture of two isomeric homoallyl alcohols.[68]

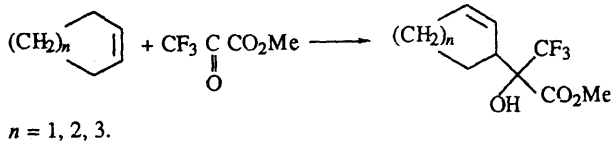


R = H, Me.

Perfluorocyclobutanone, however, reacts at 100 °C with tetramethylethene as a typical internal alkene, i.e. by formation of the corresponding homoallyl alcohol and a 2:1 adduct.[11]



Ene reactions of polyfluoroketones with cycloalkenes require the same forcing conditions as with internal acyclic alkenes. Thus, the interaction of MTFP with cyclohexene affords a preparatively useful yield of ene adduct at 170 °C, while cyclopentene and cycloheptene require heating at 150–160 °C.[21,72]

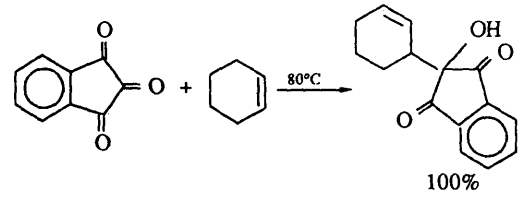


n = 1, 2, 3.

However, only a small yield of ene adduct (up to 5%) is obtained on heating HFA with cyclohexene at 160 °C for 5 h.[65] It is worth noting that ene reactions of the pro-chiral MTFP with cycloalkenes afford a mixture of diastereoisomeric ene adducts. The ratio of diastereoisomers is quite high (up to 85% of one diastereoisomer in the mixture), so that these thermal ene reactions are stereoselective.[72]

The enophilic properties of DEOM are quite different from those of polyfluoroketones. Thus, DEOM reacts with terminal ene components to give the anticipated homoallyl alcohols but under noticeably more forcing conditions.[80–85] More to the point, 3-substituted propenes do not react at all with DEOM even under harsh conditions.[71]

In a comparative study of the reactions of DEOM, HFA and MTFP with 3,7-dimethylenebicyclo[3.3.1]nonane, it was found that DEOM is significantly less reactive than the two polyfluoroketones.[69] However, where ene reactions with internal alkenes and cycloalkenes are subject to steric control, there is little difference in the reactivity of polyfluoroketones[21,65] and DEOM.[30,80,85] From this it follows that ene reactions with polyfluoroketones (HFA and MTFP) and DEOM are equally affected by steric forces, and that the enophilicity of these ketones is less important with bulky ene components. In fact, where the carbonyl group is relatively unhindered, as in 1,2,3-indantrione, ene reaction proceeds under fairly mild conditions, even with cycloalkenes.[62]

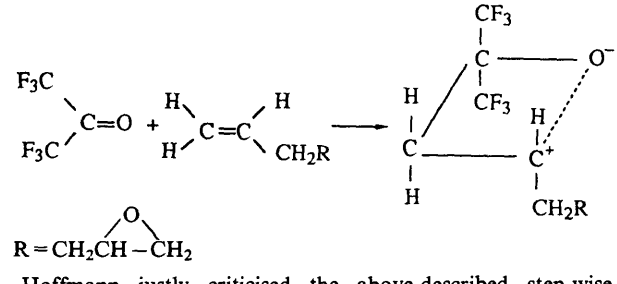


100%

It is evident that differences in the electronic state of the carbonyl group in polyfluoroketones and DEOM are more important. A molecular orbital study of ene reactions indicates that the energy and asymmetry of the LUMO of the enophile has a critical effect on the formation of a pseudoaromatic transition state.[86] It is very significant that, unlike DEOM, polyfluoroketones are characterised by a noticeably lower level for their LUMO which is predominantly localised on the carbon atom of the carbonyl group.[27]

Given the unusual electronic state of polyfluoroketones, one would not anticipate a concerted mechanism for their ene reactions, but rather the formation of a transition state wherein carbon–carbon bond formation has developed to a greater extent than hydrogen migration to the carbonyl group. However, from initial studies, it is evident that such ene reactions do involve a typical concerted pathway with the suprafacial formation of a pseudoaromatic six-membered transition state.[8,64] Gordon arrived at the same conclusion as a result of studying the kinetics of the reaction of HFA with propene in the gas phase.[87] At the same time, it was found that reaction is profoundly affected by steric hindrance, as reflected in the unusually low value for the kinetically derived pseudoexponential factor. It should be noted that thermal ene reactions with DEOM, which have been studied in more detail,[56,83–85,88,89] are also assumed to involve a concerted mechanism, wherein the six-membered transition state takes due account of the non-linear and aymmetric transfer of hydrogen.[56]

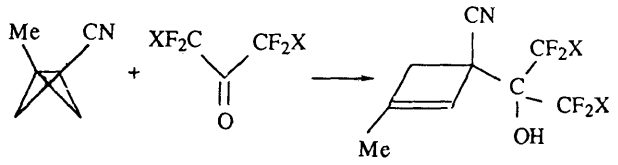
A step-wise mechanism has been proposed in one instance to explain the unexpected reaction of allyl glycidyl ether with HFA.[65] Here, it is thought that a four-centred bipolar ion is formed initially.



Later, Hoffmann justly criticised the above-described step-wise mechanism.[55] Nevertheless, the possibility still exists[56] that thermal ene reactions with polyfluoroketones may deviate from a concerted pathway, given that these enophiles are more reactive than DEOM towards classical ene components and that their behaviour towards 3-substituted propenes is distinctly different. The formation of a

[2 + 2]-cycloadduct from HFA and 3-(trimethylsilyl)propene under mild conditions would also lend weight to a non-concerted mechanism.

Only two examples are known to us where ene products are formed by interaction of polyfluoroketones with a strained δ-bonded system. This involves the reaction of HFA and 1,3-dichlorotetrafluoroacetone with 1-cyano-3-methylbicyclo[1.1.0]butane, as was outlined in Hoffmann's review.[55]



X = F, Cl.

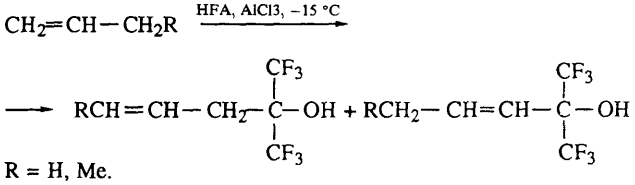
2. Reactions of polyfluoroketones with ene components in the presence of a Lewis acid

Like Diels–Alder cycloaddition, ene reactions are catalysed by Lewis acids.[55]

It has been shown that the lone pair-donating properties of the carbonyl oxygen atom of polyfluoroketones are largely nullified. This is evident from the fact that HFA is virtually unreactive towards electrophilic agents[4] and that the oxygen atom of HFA is not protonated by superacids.[90] It is also evident that no alternative sites in the polyfluoroketone molecule are available for interaction with Lewis acids. Hence only strong Lewis acids coordinate with polyfluoroketones, as is evident in the $AlCl_3$-catalysed reactions of nitropentafluoroacetone, HFA and chloropentafluoroacetone with unsaturated substrates, including ene components.[4,5]

Thus, HFA interacts with cyclohexene in the presence of $AlCl_3$ at −10 °C to give an ene adduct in 56% yield.[91] 1,1,1-Trifluoroacetone reacts similarly with cyclic olefins in the presence of $AlCl_3$ at −78 °C.[92] The $AlCl_3$-catalysed reaction of HFA or chloropentafluoroacetone with propene or 1-butene takes place at −15 °C.[93–95]

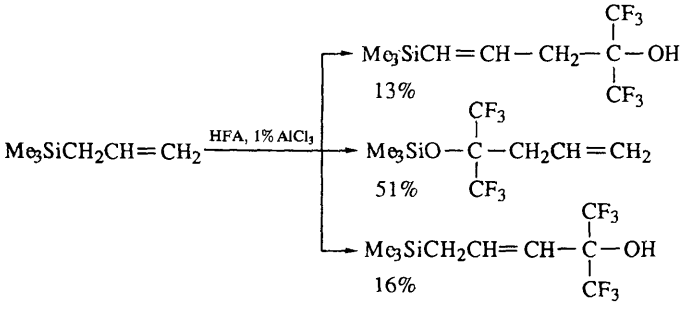
In these reactions, allyl alcohols are formed to a much greater extent than homoallyl alcohols.



R = H, Me.

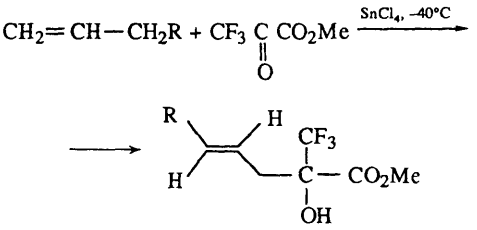
It has also been shown that the resulting allyl and homoallyl alcohols are formed in kinetically independent pathways.

The reaction of HFA with 3-(trimethylsilyl)propene can also be achieved in the presence of $AlCl_3$, but here the ene adduct predominates.[23]



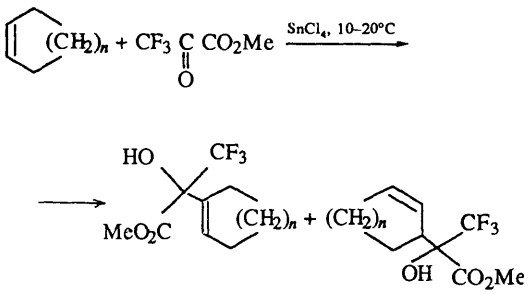
It is thought that the $AlCl_3$-catalysed reactions of polyfluoroketones with terminal alkenes involves the same activation as takes place in Friedel–Crafts reactions.[23,93] Thus, the donor–acceptor complex formed between the ketone and $AlCl_3$ attacks the terminal carbon atom of the unsaturation to give a carbocation, which is stabilised by elimination of a proton from an adjacent carbon atom.

The methoxycarbonyl group in MTFP provides a second site for complexation with the Lewis acid, so that ene reactions with this polyfluoroketone may be performed with $SnCl_4$. In fact, the $SnCl_4$ catalysed ene reactions of MTFP with propene and 1-butene afford exclusively ene adducts even at −40 °C.[21]



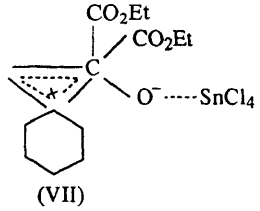
R = H, Me.

The $SnCl_4$-catalysed reactions of MTFP with cyclopentene and cyclohexene take place at 10–20 °C under steric control.[21] Here, the corresponding allyl alcohols are formed predominantly (60–65%), while the yield of ene adducts does not exceed 15%.



n = 1,2.

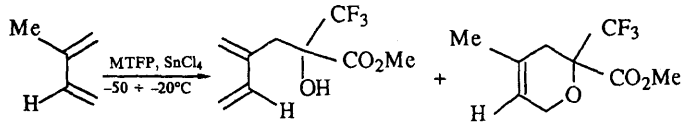
It should be noted that DEOM also reacts readily with terminal and internal alkenes in the presence of $SnCl_4$.[56,83,84] The mechanism of these processes has been studied in detail. A kinetic model has been proposed to explain the observed intramolecular and intermolecular isotope effects. This involves a three-membered intermediate having restricted rotation, exemplified below (VII) for the reaction of DEOM with methylenecyclohexane in the presence of $SnCl_4$.



(VII)

Although $SnCl_4$-catalysed reactions of DEOM and MTFP are apparently similar, one cannot assume that the rules and mechanism applicable to ene reactions with DEOM also hold true for ene reactions with MTFP.

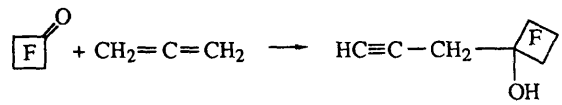
As mentioned above, $SnCl_4$ changes the course of the reaction of MTFP with isoprene in such a way that a 4:1 mixture of ene and Diels–Alder adducts is formed.[15]



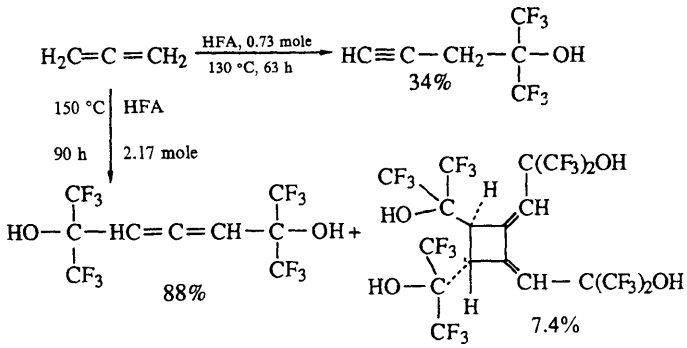
Similar results have been obtained previously for the reactions of chloral and *n*-butyl glyoxylate with isoprene and 2,3-dimethyl-1,3-butadiene.[96]

3. Ene reactions of polyfluoroketones with 1,2-dienes

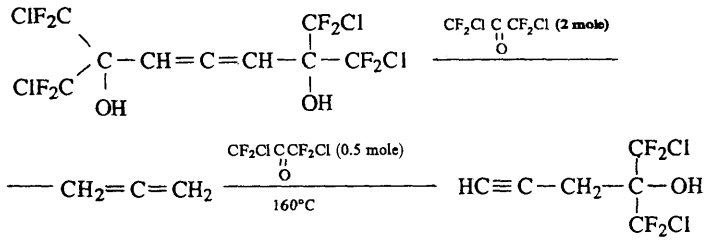
By analogy with the ene reactions considered above,[68] polyfluoroketones might be expected to form ene adducts with 1,2-dienes by a similar step-wise mechanism, taking into account the geometrical constraints of the reacting molecules. However, studies of isotopic effects on the reaction of perfluorocyclobutanone with allene[97,98] have shown clearly that the rate-limiting stage is consistent with a concerted mechanism involving a non-linear and asymmetric transfer of hydrogen. In fact, this reaction leads to an ene adduct (47% yield) even at 20 °C.[10]



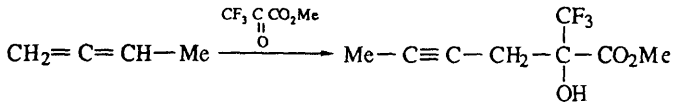
The reactions of allene with other polyfluoroketones can only be achieved on heating. Thus, heating HFA with allene at 130 °C affords an ene adduct (34% yield), which is almost completely transformed at 150 °C to a 2:1 adduct in the presence of an excess of HFA.[68]



Similarly, 1,3-dichlorotetrafluoroacetone interacts with allene at 160 °C to give 1:1 and 2:1 adducts depending on the proportion of the reactants.[99]

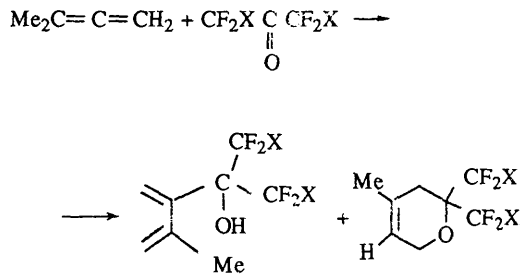


The ene reaction of MTFP with 1,2-butadiene proceeds under milder conditions (80 °C).[72]



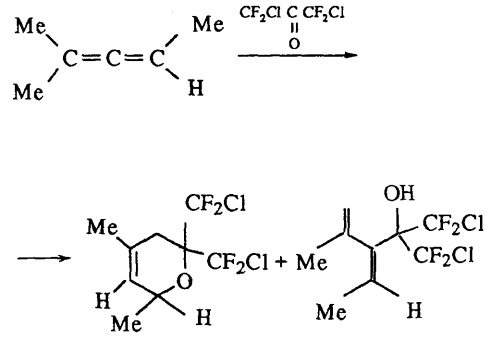
In the presence of polyfluoroketones, 3-methyl-1,2-butadiene and tri- and tetra-methylallene partly or completely isomerise into the corresponding 1,3-diene even at 20 °C. As a consequence, either Diels–Alder adducts or mixtures containing the latter and ene adducts are formed.[17,19]

Thus interaction of HFA or 1,3-dichlorotetrafluoroacetone with 3-methyl-1,2-butadiene at 175 °C affords a mixture of the corresponding hydroxy-1,3-diene and dihydropyran. Reaction is slow at 20 °C, but proceeds rapidly on heating.



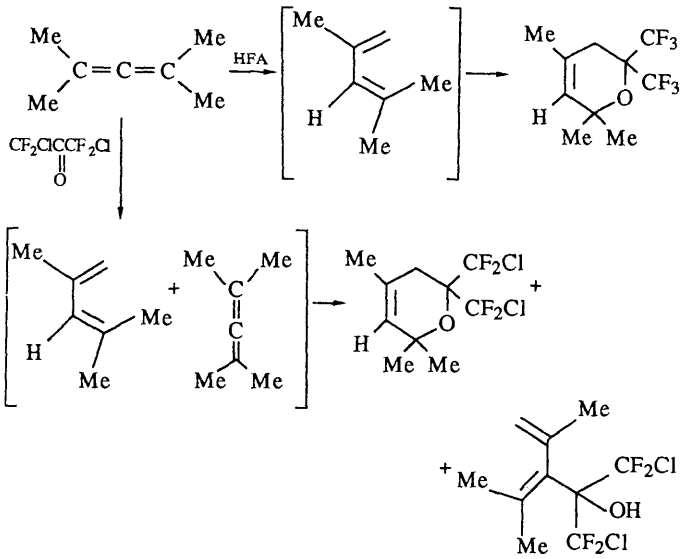
X = F or Cl.

The reason between trimethylallene and 1,3-dichlorotetrafluoroacetone affords the corresponding dihydropyran as the main product (56%) together with a 13% yield of an ene adduct.



Tetramethylallene isomerises completely in the presence of HFA at 20 °C to give 2,4-dimethyl-1,3-pentadiene which, under these conditions, readily undergoes diene synthesis. The isomerisation

proceeds more slowly in the presence of 1,3-dichlorotetrafluoroacetone to give both [4 + 2]-adduct and ene adduct (6%).

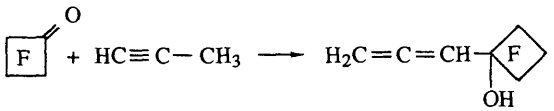


An unsuccessful attempt was made to minimise prototropic rearrangement of polymethyl-substituted allenes to conjugated dienes by carrying out the reaction in the gas phase at 100 °C.[19]

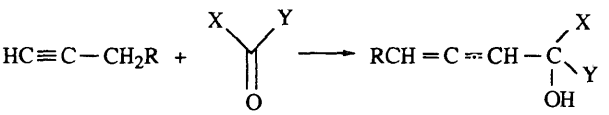
4. Ene reactions of polyfluoroketones with alkynes

Classical enophiles normally do not react with terminal alkynes as readily as they do with alkenes.[55] However, polyfluoroketones are an exception, reacting equally well with both alkynes and alkenes.

Thus, even at 20 °C, perfluorocyclobutanone reacts with propyne to give the corresponding allenealcohol in 43% yield.[10]

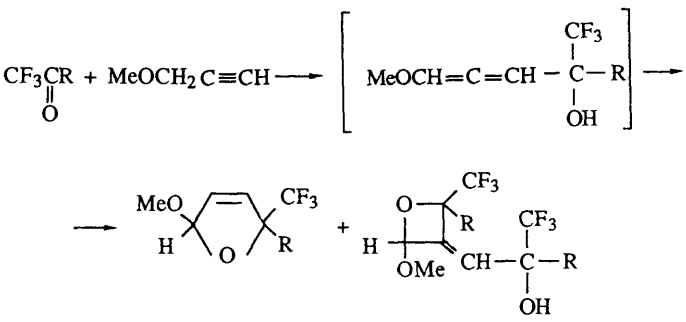


Allenealcohols are obtained similarly from the reaction of HFA with propyne,[99] from the reaction of MTFP with propyne and with 1-hexyne,[72] and from the reaction of 1,3-dichlorotetrafluoroacetone with propyne, 1-pentyne, or 1-undecyne at 50–100 °C. Ene adducts are also formed on interaction of 1,3-dichlorotetrafluoroacetone with propargyl chloride (140 °C),[99] and on interaction of MTFP with propargyl bromide (110 °C).[72]



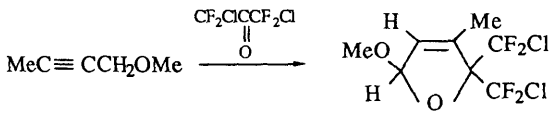
R = H, Et, Pr^n, n-C_9H_{19}, Cl, Br;
X = Y = CF_3, CF_2Cl, X = CF_3, Y = CO_2Me.

A mixture of dihydrofuran and oxetane derivatives was obtained on reaction of HFA, nitropentafluoroacetone or MTFP with methyl propargyl ether.[72,100] It is thought that an initial ene reaction affords the corresponding allenealcohol, which then undergoes cycloisomerisation or participates in [2 + 2]-cycloaddition with a second molecule of the ketone.

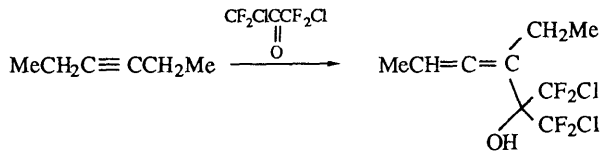


R = CF_3, CF_2NO_2, CO_2Me.

In the patent literature, it is reported that only dihydrofuran derivatives are formed on reaction of 1,3-dichlorotetrafluoroacetone with methyl propargyl ether and on reaction of HFA with ethyl propargyl ether.[101] The interaction of but-2-yn-1-yl methyl ether with 1,3-dichlorotetrafluoroacetone also affords the corresponding dihydrofuran exclusively.[101]



There are also references to ene reactions involving an internal alkyne. Thus, dichlorotetrafluoroacetone reacts with 3-hexyne during 20 h at 170 °C to give the expected allenealcohol.[99]



IV. [2 + 2]-Addition

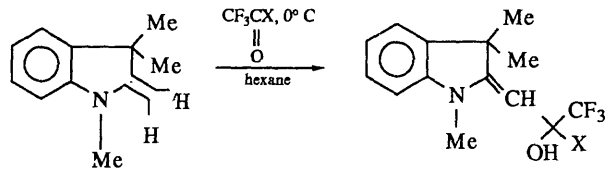
As has been mentioned previously (p. 786), it is the unusual electronic state of the C=O bond in polyfluoroketones which is responsible for their high reactivity with isolated, highly-polarised, electron-rich multiple bonds. As a consequence, several types of conversion are possible, the predominant ones being: [2 + 2]-cycloaddition; [2 + 2]-cycloaddition with subsequent ring opening or [2 + 2]-retroscission; and coupling to give an intermediate 1,4-dipolar zwitter-ion, stabilised by prototropic rearrangement or cycloaddition to the polyfluoroketone molecule. Furthermore, in certain instances, such reaction pathways are also possible with weakly polar and even polarised electron-deficient unsaturated compounds. Thus, the chemistry of [2 + 2]-addition with polyfluoroketones is far more extensive than with other 1,2-dipolarophiles.

All of the above-mentioned reaction types can be readily explained, in qualitative terms, by a step-wise [2 + 2]-addition which is consistent with molecular orbital calculations.[102–105] However, certain [2 + 2]-additions with polyfluoroketones may be interpreted in terms of a pericyclic pathway, the likelihood of which may be ascertained by the perturbation method.[106,107]

1. [2 + 2]-Addition across the C=C bond

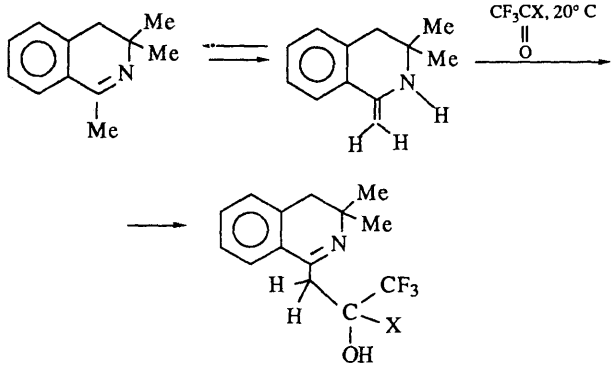
Enamines, ketene acetals, vinyl ethers, and ketenes are all highly reactive towards polyfluoroketones in [2 + 2]-addition. In certain instances, styrene and α,β-unsaturated carbonyl compounds also participate in this reaction.

Enamines interact the most smoothly with classical 1,2-dipolarophiles. Since the atom of nitrogen in the transition state is stabilised by an adjacent cationic centre, such reactions normally proceed via prototropic rearrangement of an intermediate zwitter-ion. This has been established for the reactions of HFA and MTFP with 2-methylene-1,3,3-trimethylindoline at 0 °C.[108]



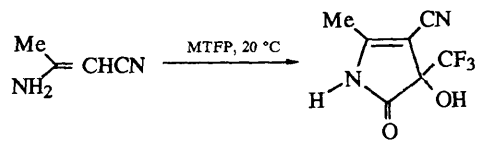
X = CF_3, CO_2Me.

Similarly, HFA and MTFP interact at 20 °C with the enamine form of 3,4-dihydro-1,3,3-trimethylisoquinoline.[109]

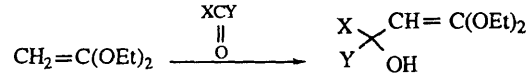


X = CF_3, CO_2Me.

MTFP reacts with 3-aminocrotononitrile in acetonitrile at 20 °C. The ketone initially interacts across the multiple bond, after which intramolecular ring closure takes place to give a lactam in 68% yield.[110]

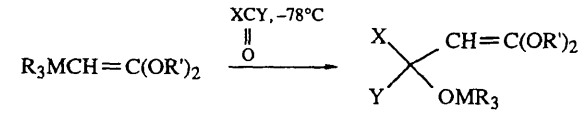


Ketene acetals react energetically with nitropentafluoroacetone, HFA and 1,1,3-trifluoro-1,3,3-trichloroacetone. However, no oxetanes were formed. Instead, reaction takes place at −30 to 20 °C to give the corresponding allylic tertiary alcohols.[111,112]



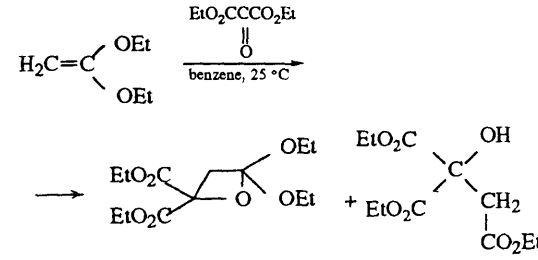
X = Y = CF_3; X = CF_3, Y = CF_2NO_2; X = CF_2Cl, Y = $CFCl_2$.

Acyclic products are also formed on reaction of silyl- and germylketene acetals with HFA, 1,3-dichlorotetrafluoroacetone and 1,1,3-trifluoro-1,3,3-trichloroacetone.[112,113]

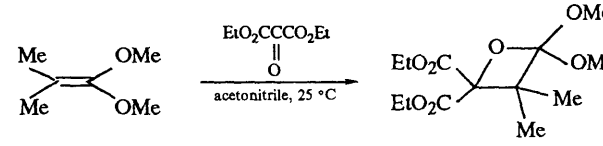


MR_3 = Me_3Si, $MeCl_2Ge$; X = Y = CF_3, CF_2Cl;
X = CF_2Cl, Y = $CFCl_2$; R' = Me, Et.

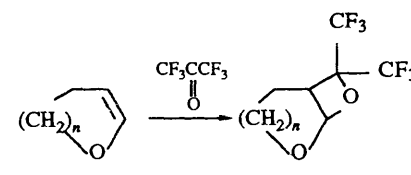
In a spectroscopic study of reactions of polyfluoroketones with 2-trimethylsilylketene acetals at −78 °C, it was shown that the initial product is the corresponding oxetane which is cleaved on raising the temperature. It is worth noting that interaction of DEOM with diethyl keteneacetal in benzene affords a mixture of the corresponding oxetane (58%) and a trace of an acyclic product.[114]



In the highly polar acetonitrile as solvent, this reaction gives a mixture of four products, none of which is the corresponding oxetane. However, the interaction of DEOM with 1,1-dimethoxy-2-methylpropene affords an oxetane exclusively, even in acetonitrile.[114]

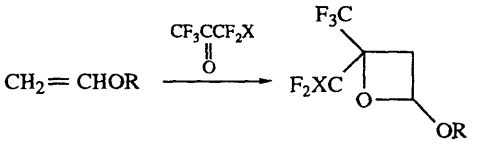


Stable oxetanes have been obtained by reaction of polyfluoroketones with a variety of vinyl ethers.[115–121] The most active of these is 2,3-dihydrofuran which yields a stable [2 + 2]-cycloadduct with HFA at −20 °C in 57% yield. With 3,4-dihydro-2*H*-pyran, however, such cycloaddition requires a higher temperature (50 – 60 °C).[121]



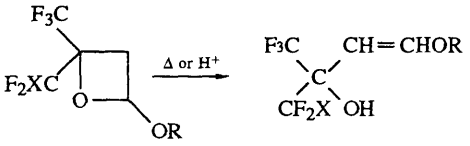
n = 1, 2

Alkyl vinyl ethers react with HFA more slowly at −20 °C. However, a preparative yield of oxetane derivatives is obtainable with HFA and nitropentafluoroacetone at 20 °C in dimethyl sulphate.[115]



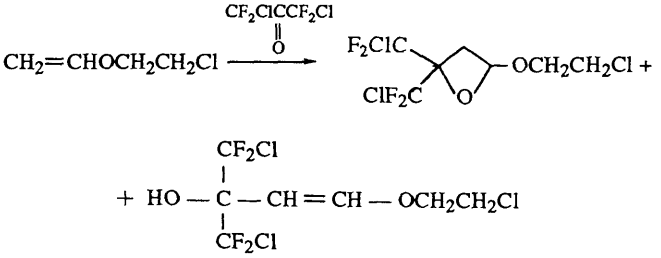
X = F, NO_2; R = Et, Bu^n.

Ring opening of the products takes place slowly at 100 °C, but noticeably faster in the presence of H_2SO_4.

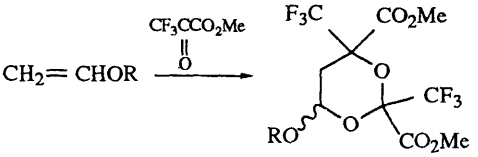


X = F, NO_2; R = Et, Bu^n.

In certain instances, e.g. on reaction of 1,3-dichlorotetrafluoroacetone with 2-chloroethyl vinyl ether, isomerisation of the oxetane takes place during the reaction.[116]

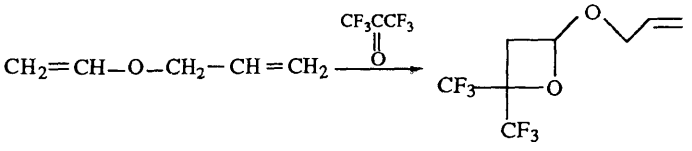


Contrasting with HFA, MTFP reacts with alkyl vinyl ethers in polar media to give products derived by 1,4-dipolar cycloaddition to an initially-formed zwitter-ion.[110] The course of the reaction is not affected by the proportion of the reactants.



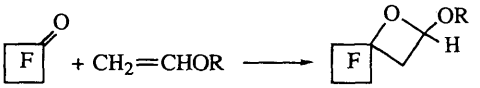
R = Et, Bu^n.

An interesting result was reported on studying the reaction of HFA with allyl vinyl ether.[120] Here, the sole product at 0 °C is an oxetane derivative, formed by exclusive attack of the vinylic unsaturation.



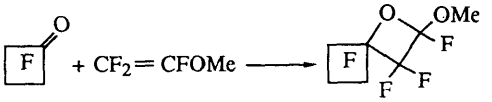
In such instances, polyfluoroketones undergo [2 + 2]-cycloaddition far more smoothly than ene reaction. Evidently, more information is required in order to elucidate the structures of the 2:1 and 3:1 adducts obtained on ene reaction of HFA and nitropentafluoroacetone with methyl allyl ether[64] and on reaction of *N*-methyl-*N*-allylaniline with HFA.[70]

Vinyl esters only participate in [2 + 2]-cycloaddition with perfluorocyclobutanone.[119] Thus, reaction with vinyl acetate and benzoate at 20 °C affords the corresponding oxetane in 54 and 45% yield, respectively.

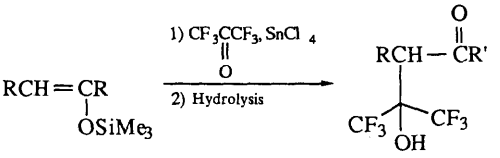


R = COMe, COPh.

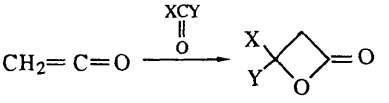
Perfluorocyclobutanone reacts similarly with methyl trifluorovinyl ether.[10]



A study has been made of the catalytic effect of Lewis acids on the reaction of HFA with trimethylsilyl enolethers. Reaction takes place at −45 °C in the presence of $SnCl_4$ or $TiCl_4$. The corresponding ketones were isolated on hydrolysis of the reaction mixture.[25]

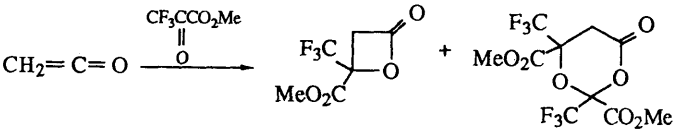


Contrasting with ketene acetals, ketenes form stable [2 + 2]-cycloadducts with polyfluoroketones. Thus 2-oxetanones are obtained in preparative yield by reaction of ketene itself with perfluorocyclobutanone,[119] nitropentafluoroacetone,[122] HFA [123] and with 1,3-dichlorotetrafluoroacetone.[124]

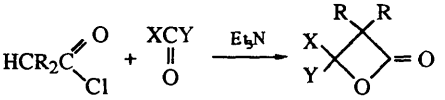


X = Y = −$(CF_2)_3$−, CF_3, CF_2Cl; X = CF_3, Y = CF_2NO_2.

A mixture of 2-oxetanone and 1,3-dioxan-4-one derivatives was obtained on passing ketene into a solution of MTFP in ether.[125]

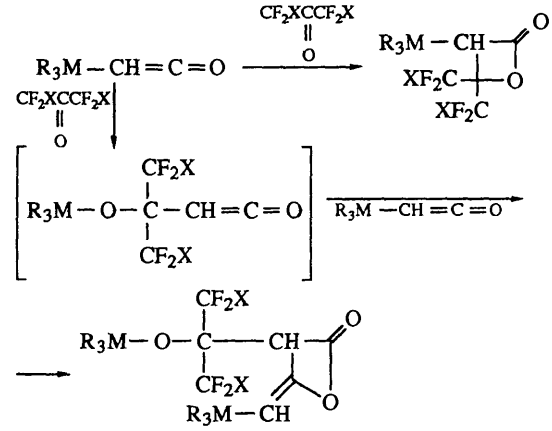


The isolation of 2-oxetanones on reaction of 1,1,3-trifluoro-1,3,3-trichloroacetone and MTFP with acetyl chloride[126] and dichloroacetyl chloride,[110] respectively, confirmed that ketenes are formed *in situ* [in the presence of base].



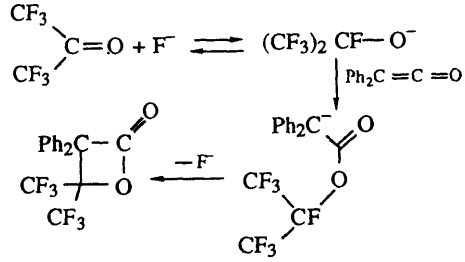
R = H, X = CF_2Cl, Y = $CFCl_2$; R = Cl, X = CF_3, Y = CO_2Me.

Silyl-, germyl- and stannyl-ketenes also interact with HFA and 1,3-dichlorotetrafluoroacetone to give 2-oxetanones.[127] An ionic [2 + 2]-addition takes place simultaneously to give an intermediate ketene which reacts with a second molecule of the starting ketene to give a 4-ene-2-oxetanone as by-product.

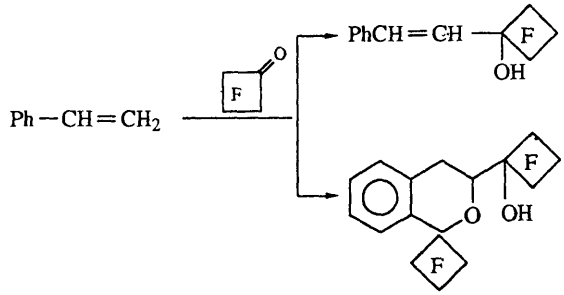


X = F, Cl; R_3M = $SiMe_3$, $GeCl_2Me$, $SnBu^n_3$.

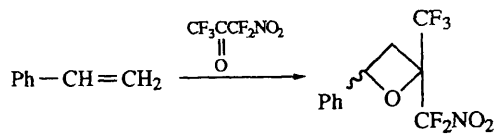
The steric effect of the phenyl groups in diphenylketene prevents reaction with HFA even at 100 °C. However, a 2-oxetanone derivative is obtained in preparative yield under nucleophilic catalysis.[128]



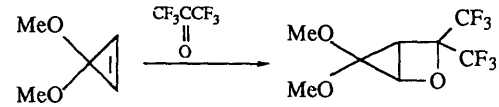
Only the most electrophilic polyfluoroketones react with weakly polarised alkenes. Thus, interaction of perfluorocyclobutanone with styrene at 20 °C yields an ionic [2 + 2]-adduct,[11] while an isochroman is formed in the presence of an excess of the ketone.



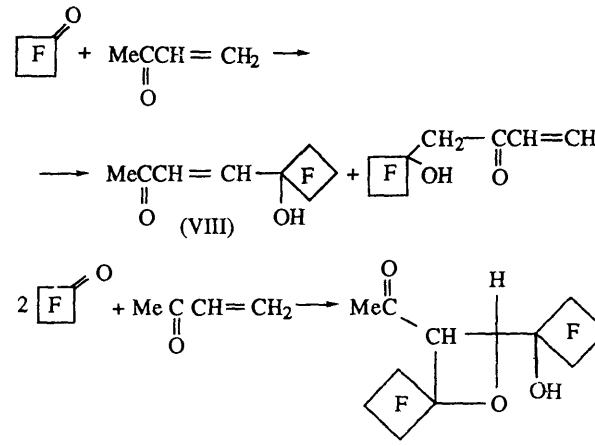
Heating a mixture of nitropentafluoroacetone and styrene at 100 °C for 10 h affords the corresponding oxetane in 37% yield.[129]



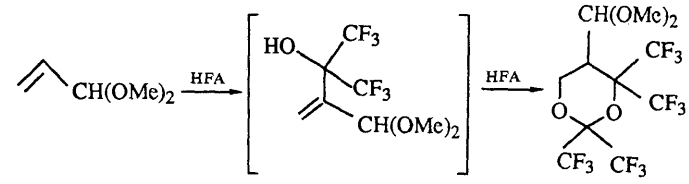
Under similar conditions, HFA initiates polymeristion of the alkene.[65] However, a [2 + 2]-cycloadduct is formed with the strained dimethyl ketal of cyclopropenone at 20 °C.[130]



Electron deficient α,β-unsaturated aldehydes, ketones, esters and nitriles react with polyfluoroketones under forcing conditions in the presence of a catalyst. Thus, treatment of methyl vinyl ketone with perfluorocyclobutanone at 100 °C affords a mixture of compounds, among which a ketol and the anomalous [2 + 2]-adduct (VIII) have been identified. An oxetane is obtained, however, in the presence of an excess of perfluorocyclobutanone. This has been shown to arise by cycloaddition of intermediate (VIII) with a second molecule of the ketone.[11]

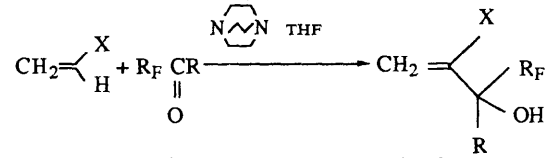


Reaction of acrolein dimethyl acetal with HFA at 150 °C produces a 1,3-dioxane (9%), which is thought to arise by the scheme shown below.[131]



The initial [2 + 2]-addition takes place in accordance with the polarisation of the C=C bond.

The same polarisation factors are at play in the reactions of HFA, MTFP, 1,3-dichlorotetrafluoroacetone and bromopentafluoroacetone with methyl acrylate, acrylonitrile, and acrolein in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO).[132]

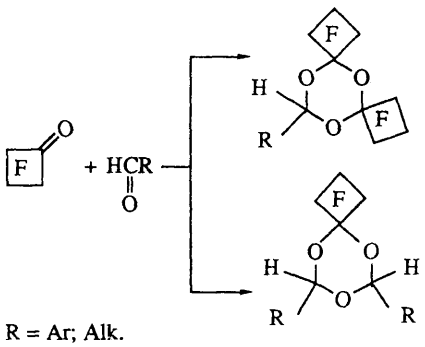


R = R_F = CF_3, CF_2Cl; R_F = CF_3, R = CO_2Me;
R_F = CF_3, R = CF_2Br; X = CO_2Et, CN, CHO, COMe.

Among non-fluorinated carbonyl compounds, only DEOM participates readily in this conversion (known as the Baylis–Hillman reaction).[133] The addition of aliphatic and aromatic aldehydes requires more forcing conditions.[134] The mechanism of the Baylis–Hillman reaction involves addition of DABCO at the β-position of the α,β-unsaturated system, followed by interaction of the carbonyl compound with the generated anionic centre at the adjacent α-site.[135]

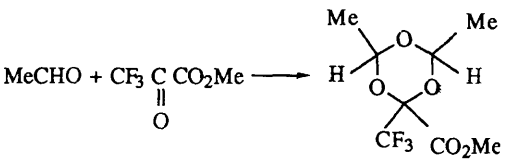
2. [2 + 2]-Addition across hetero-unsaturations, C=Y and X=Y

Polyfluoroketones interact with aliphatic and aromatic carbonyl compounds at room temperature or below. A zwitter-ion is formed initially, this being stabilised by 1,4-dipolar addition either to a second molecule of the polyfluoroketone or to the non-fluorinated component to give the corresponding 1,3,5-trixane. Thus, perfluorocyclobutanone reacts with aromatic aldehydes and certain ketones to give predominantly a 2:1 cycloadduct; a 1:2-cycloadduct, however, is formed with aliphatic aldehydes.[136]



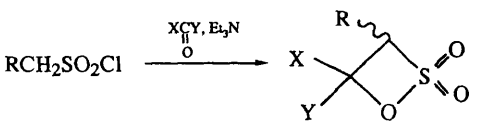
R = Ar; Alk.

Acetaldehyde interacts with MTFP at 20 °C to give a 1:2 cycloadduct exclusively.[110]



In the reactions of polyfluoroketones with aliphatic aldehydes, stable aldols are formed as by-products. The proportion of the latter increases with the length of the aliphatic chain. Enolisable ketones afford predominantly stable ketols with perfluorocyclobutanone,[11] while ketols are formed exclusively with HFA and MTFP.[137–140] The former initiates polymerisation of an acetone/formaldehyde mixture even at −78 °C.[141]

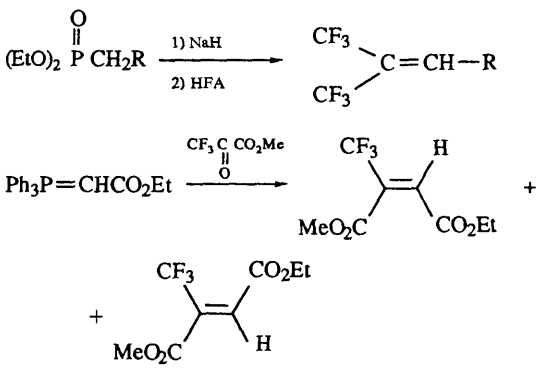
Chloropentafluoroacetone, 1,3-dichlorotetrafluoroacetone and MTFP yield β-sultones on reaction with sulphenes, generated *in situ* by treatment of the corresponding alkanesulphonyl chlorides with Et_3N at 20 °C.[110,142–145]



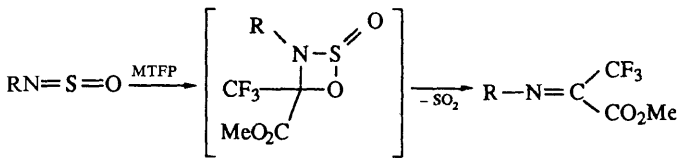
R = H, Cl; X = Y = CF_2Cl; R = H, X = CF_3, Y = CF_2Cl; R = H, X = CF_3, Y = CO_2Me.

A complex mixture of products was obtained with HFA, primarily because this ketone serves as a powerful dehydrogenating agent towards Et_3N.[146,147]

Witt's survey[8] provides extensive data on the reactions of HFA with unsaturated elementoorganic and organometallic compounds. Recently, new information on the use of polyfluoroketones in the Wittig and Horner–Emmons reactions has been made available.[148–150]



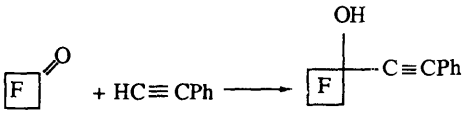
[2 + 2]-Cycloaddition-cycloreversion of polyfluoroketones with isocyanates and thionylimines has already been reviewed in the context of perfluoroketimine chemistry.[43,45] It is worth noting that, contrasting with HFA,[151] MTFP reacts with thionylimines in the absence of catalyst on warming.[152]



R = Ph, COPh, COMe.

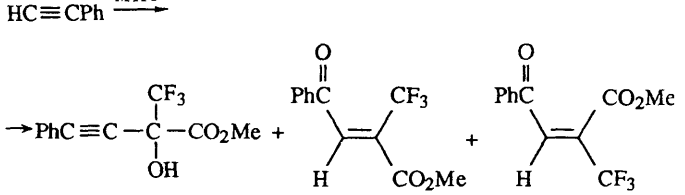
3. Addition across the C≡C bond

Terminal alkynes lacking a propargylic hydrogen atom react with polyfluoroketones to give either Favorskii products (tertiary acetylenealcohols) or [2 + 2]-cycloadducts (oxetenes), electrocyclic ring opening of which leads to α,β-unsaturated carbonyl compounds. For example, phenylacetylene reacts with perfluorocyclobutanone to give exclusively an acetylenealcohol even at 0 °C.[11]



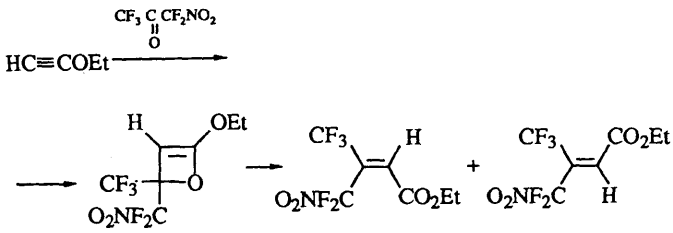
It should be noted that non-fluorinated ketones only participate in the Favorskii reaction in the presence of a strong base.[153]

Phenylacetylene reacts slowly at 20 °C with MTFP, or rapidly above 60 °C, to give a mixture of the corresponding acetylenealcohol and methyl α-trifluoromethyl-β-benzoylacrylate (as a mixture of *Z*- and *E*-isomers).[110]

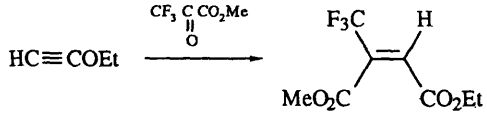


The products of this reaction were isolated pure and shown to be formed in kinetically independent pathways, i.e. no interconversions involving these products were observed, even under forcing conditions.

The reactions of ethoxyacetylene with HFA [154] and nitropentafluoroacetone[111] below room temperature lead to oxetenes, which rearrange at 20 °C to give substituted acrylates. A mixture of *Z*- and *E*-isomers was obtained from nitropentafluoroacetone.

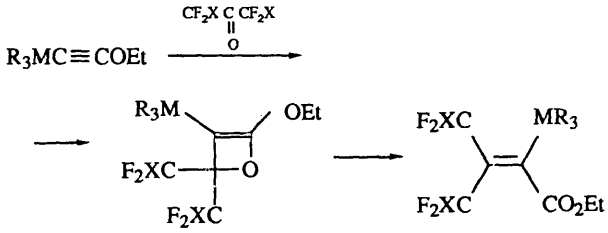


Ethoxyacetylene interacts with MTFP to give a trifluoromethylmaleic acid diester exclusively.[110]



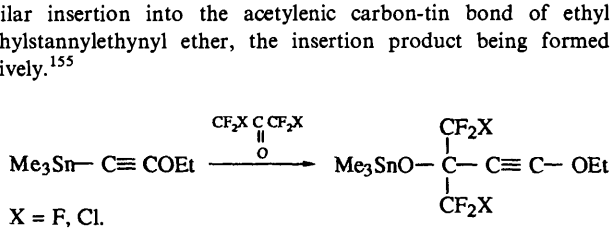
There was no intermediate formation of an extreme derivative under these conditions (20 °C).

Relatively stable oxetenes have been obtained by reaction of polyfluoroketones with trimethylsilyl and trimethylgermyl derivatives of ethoxyacetylene.[155] The resulting trimethylsilyloxete derivatives are converted to the corresponding acrylate at 20 °C over a period of 2 months or at 100 °C during 30 min.



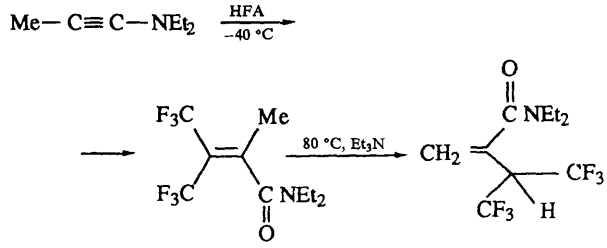
X = F, Cl; MR_3 = $SiMe_3$, $GeMe_3$, $SiEt_3$, $GeEt_3$.

Germyl-substituted acetylenealcohols are obtained as by-products on reaction of polyfluoroketones with ethyl trimethylgermylethynyl ether, i.e. the polyfluoroketones are inserted into the acetylenic carbon-germanium bond. 1,3-Dichlorotetrafluoroacetone undergoes a similar insertion into the acetylenic carbon-tin bond of ethyl trimethylstannylethynyl ether, the insertion product being formed exclusively.[155]



X = F, Cl.

1-Diethylaminoprop-1-yne reacts with HFA even at −40 °C to give an acrylamide derivative by ring opening of an intermediate oxetene. On heating in the presence of Et_3N, the product undergoes prototropic rearrangement to give α-(hexafluoroisopropyl)acrylic acid *N*,*N*-diethylamide.[156]



It was not possible to characterise the intermediate oxetene. Although there is a propargylic hydrogen atom in the starting ynamine, no simultaneous ene reaction was detected, i.e. the [2 + 2]-pathway is exclusive.

Polyfluoroketones (especially HFA) are seen as highly electrophilic ketones, which interact energetically with water, alcohols and amines to give stable hydrates, hemiketals and hemiaminals, respectively. This behaviour is typical of highly electrophilic carbonyl compounds. In fact, they are akin to certain aldehydes (formaldehyde, chloral, fluoral) and ketones with electron-accepting substituents (mesoxalates and certain 1,2-di- and 1,2,3-triketones, etc.).

***

The present review covers one particular aspect of the chemistry of polyfluoroketones—their unusually high affinity towards conjugated and unconjugated donor-type π-systems, with which they undergo uncatalysed [4 + 2]-cycloaddition, ene reaction and [2 + 2]-addition below or at room temperature. Non-fluorinated aliphatic ketones either do not participate in these reactions or do so only under forcing conditions. Even highly electrophilic, non-fluorinated ketones require heating (above 100 °C) or catalytic acitvation.

Recently, it has been shown that reactions of polyfluoroketones with unsaturated compounds are highly selective under certain circumstances. They may proceed regiospecifically with characteristically high stereoselectivity, in certain instances yielding only one stereoisomer. There is much to be gained by further studies in this area, notably with a view to designing effective routes to functionalised unsaturated compounds.

From a comparison of the reactivity of HFA, MTFP and DEOM towards unsaturated compounds, it is apparent that the characteristic properties of polyfluoroketones are a consequence of the lower level of their acceptor LUMO and its significantly higher asymmetry. The structure of the LUMO of polyfluoroketones is itself determined by interactive effects between the carbonyl oxygen atom and the CF_3 group. Thus, replacement of one of the carbalkoxy groups of DEOM by a CF_3 group leads to a qualitatively different electronic state for the C=O bond.

The anomalous electronic state of the C=O group in polyfluoroketones is responsible for the large contribution made by charged structures in the stabilisation of the transition state on reaction with unsaturated compounds. This determines the high affinity of polyfluoroketones towards polarised unsaturated compounds of a donor type. Among the many reactions discussed in this article, a number of charge-induced processes are particularly interesting from a theoretical standpoint; these proceed exothermically or with a low energy barrier, and differ in their regiospecificity and high stereoselectivity.

References

1. *The Chemistry of the Carbonyl Group, Part 1* (Edited by S Patai), Intersci. Publ., London, etc., 1966, 1027 pp
2. *The Chemistry of the Carbonyl Group, Part 2* (Edited by J Zabicky), Intersci. Publ., London, etc., 1970, 428 pp
3. H O House *Modern Synthetic Reactions,* Benjamin, Menlo Park, etc., 1972, 856 pp
4. C G Krespan, W J Middletton *Fluorine Chem. Rev.*, 1967, **1** 145
5. N P Gambaryan, E M Rokhlin, Yu V Zeifman, et al. *Angew Chem., Int. Ed. Engl.*, 1966, **5** 947
6. M Hudlicky *Chemistry of Organic Fluorine Compounds,* Halsted Press, New York, Eliss Horwood, Chichester, 1976, 903 pp
7. *The Chemistry of α-Haloketones, α-Haloaldehydes, and α-Haloimines* (Edited by S Patai), Wiley, Chichester, etc., 1988, 412 pp
8. M Witt, K S Dhattathiyan, H W Roesky *Adv. Inorg. Chem.*, 1986 **30** 223
9. S M Weinreb, R R Staib *Tetrahedron*, 1982, **38** 3087
10. D C England *J. Am. Chem. Soc.*, 1961, **83** 2205
11. US P. 3 140 298; *Chem. Abs.*, 1963, **61** P8203f
12. W J Linn *J. Org. Chem.*, 1964, **29** 3111
13. B I Martynov, L T Lantseva, B L Dyatkin *Zh. Org. Khim.*, 1975, **11** 2282
14. Yu V Zeifman, N P Gambaryan, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 1472
15. A S Golubev, M V Galakhov, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 141
16. Yu O Shermolovich, S V Pazenok, E I Slyusarenko, L N Markovskii *Zh. Org. Khim.*, 1990, **26** 2213
17. D R Taylor, D B Wright *J. Chem. Soc., Perkin Trans. 1*, 1973, 956
18. A De Smet, M Anteunis *Bull. Soc. Chim. Belg.*, 1974, **83** 467
19. Ch B Lee, R J J Newman, D R Taylor *J. Chem. Soc., Perkin Trans. 1*, 1978, 1161
20. L A Simonyan, N P Gambaryan, P V Petrovskii, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 370
21. A S Golubev, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 127
22. V A Soloshonok, A B Rozhenko, I A Butovich, V P Kukhar *Zh. Org. Khim.*, 1990, **26** 2051
23. E W Abel, R J Rowley *J. Organomet. Chem.*, 1975, **84** 199
24. R Bonjouklian, R A Ruden *J. Org. Chem.*, 1977, **42** 4095
25. T Ishihara, H Shinjo, Y Inoue, T Ando *J. Fluorine Chem.*, 1983, **22** 1
26. US P. 4 190 730; *Chem. Abs.*, 1980, **93** P25900b
27. R Gleiter, P Schang, M Block, et al. *Chem. Ber.*, 1985, **118** 2127
28. O Achmatowicz, A Zamoyski *Rocz. Chem.*, 1961, **35** 1251
29. O Achmatowicz Jr., J Jurczak, J S Pyrek *Tetrahedron*, 1976, **32** 2113
30. R G Salomon, S Roy, M F Salomon *Tetrahedron Lett.*, 1988, **29** 769
31. S Knapp, A T Levorse, J A Potenza *J. Org. Chem.*, 1988, **53** 4773
32. B Potthoff, E Breitmaier *Chem. Ber.*, 1986, **119** 2059
33. B Potthoff, E Breitmaier *Chem. Ber.*, 1986, **119** 3204
34. H Gotthardt, K-H Schenk *Angew. Chem., Int. Ed. Engl.*, 1985, **24** 608
35. J F W Keana, P E Eckler *J. Org. Chem.*, 1976, **41** 2850
36. R R Schmidt *Acc. Chem. Res.*, 1986, **19** 250
37. S J Danishefsky, M P De Ninno *Angew. Chem., Int. Ed. Engl.*, 1987, **26** 15
38. K Maruoka, T Itoh, T Shirasaka, H Yamamoto *J. Am. Chem. Soc.*, 1988, **110** 310
39. M Terada, K Mikami, T Nakai *Tetrahedron Lett.*, 1991, **32** 935
40. A J Kirby, H Ryder *J. Chem. Soc., Perkin Trans. 1*, 1990, 617
41. J Belander, N L Lardry, J R J Pare, K Jankowski *J. Org. Chem.*, 1982, **47** 3649
42. A V Fokin, A F Kolomiets, A A Krolevets *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 976
43. S N Osipov, A F Kolomiets, A V Fokin *Usp. Khim.*, 1992, **62**(1) 6 [English translation in *Russ. Chem. Rev.*, 1992(1)]
44. K Burger, E Huber, W Schoentag, H Partscht *Chem.-Ztg.*, 1986, **110** 79
45. A V Fokin, A F Kolomiets, N V Vasil'ev, Usp. Khim., 1984, **53**(3) 398 [English translation in *Russ. Chem. Rev.*, 1984(3)]
46. M Quimpere, K Jankowski *J. Chem. Soc., Chem. Commun.*, 1987, 676
47. Ph C Bulman Page, P H Williams, E W Collington, H Finch *J. Chem. Soc., Chem. Commun.*, 1987, 756
48. US P. 3 197 480; *Chem. Abs.*, 1965, **63** P13216b
49. G I Nikishin, V G Glukhovtsev, Yu V Il'in, A V Ignatenko *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 447
50. S P Gavrilova, V G Glukhovtsev, G I Nikishin, et al. *Zh. Org. Khim.*, 1990, **26** 2416
51. A S Golubev, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2369
52. V A Soloshonok, V P Kukhar *Zh. Org. Khim.*, 1990, **26** 419
53. G Jenner, M Papadopoulos, J Yurczak, T Kozluk *Tetrahedron Lett.*, 1984, **25** 5747
54. J Yurczak, S Belniak, M Chmielewski, et al. *J. Org. Chem.*, 1989, **54** 4469
55. H M R Hoffmann *Angew. Chem., Int. Ed. Engl.*, 1969, **8** 556
56. Z Song, P Beak *J. Am. Chem. Soc.*, 1990, **112** 8126
57. L M Stephenson, M J Grdina, M Orfanopoulos *Acc. Chem. Res.*, 1980, **13** 419
58. C A Seymour, F D Greene *J. Org. Chem.*, 1982, **47** 5226
59. K Mikami, M Terada, T Nakai *J. Am. Chem. Soc.*, 1990, **112** 3949
60. M G Barlow, R N Haszeldine, K W Murray *J. Chem. Soc., Perkin Trans 1*, 1980, 1960
61. H Münsterer, G Kresze, M Brechbiel, H Kwart *J. Org. Chem.*, 1982, **47** 2677
62. G B Gill, K S Kirollos *Tetrahedron Lett.*, 1982, **23** 1399
63. J P Benner, G B Gill, S J Parrott, B Wallace *J. Chem. Soc., Perkin Trans 1*, 1984, 291
64. N P Gambaryan, El M Rokhlina, Yu V Zeifman *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 1466
65. R L Adelman *J. Org. Chem.*, 1968, **33** 1400
66. Belgian P. 625 425; *Chem. Abs.*, 1963, **59** P11335g
67. US P. 3 444 148; *Chem. Abs.*, 1969, **71** P50653b
68. W H Urry, J H Y Niu, L G Lundsted *J. Org. Chem.*, 1968, **33** 2302
69. V A Soloshonok, A B Khotkevich, P A Krasutskii *Zh. Org. Khim.*, 1991, **27** 746
70. Y Kobayashi, T Nagai, I Kumadaki *Chem. Pharm. Bull.*, 1984, **32** 5031
71. E E Gilbert *Can. J. Chem.*, 1970, **48** 730
72. A S Golubev, A F Kolomiets, A V Fokin *J. Fluorine Chem.*, 1989, **45** 158

73. J C Martin, E F Perozzi *J. Am. Chem. Soc.*, 1974, **96** 3155
74. E G Howard, P B Sargeant, C G Krespan *J. Am. Chem. Soc.*, 1967, **89** 1422
75. P E Newallis, P Lombardo *J. Org. Chem.*, 1965, **30** 3834
76. A W Show, J R Griffith *J. Fluorine Chem.*, 1980, **15** 471
77. A C Tanquary, R E Burks Jr., M V Jackson *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13** 119
78. US P. 3 409 679; *Chem. Abs.*, 1969, **70** P19576j
79. B M Mikhailov, Yu N Bubnov, A V Tsyban', M Sh Grigoryan *J. Organomet. Chem.*, 1978, **154** 131
80. O Achmatowicz, O Achmatowicz Jr., *Rocz. Chem.*, 1962, **36** 1791
81. US P. 3 253 019; *Chem. Abs.*, 1966, **65** P3754e
82. O Achmatowicz Jr., J Szymoniak *J. Org. Chem.*, 1980, **45** 1228
83. O Achmatowicz Jr., J Szymoniak *J. Org. Chem.*, 1980, **45** 4774
84. L M Stephenson, M Orfanopoulos *J. Org. Chem.*, 1981, **46** 2200
85. M F Salomon, S N Pardo, R G Salomon *J. Org. Chem.*, 1984, **49** 2446
86. S Inagaki, K Fukui *J. Am. Chem. Soc.*, 1975, **97** 7480
87. A S Gordon *J. Phys. Chem.*, 1970, **74** 1357
88. H Kwart, M W Brechbiel *J. Org. Chem.*, 1982, **47** 3353
89. G Jenner, R Ben Salem, B El'yanov, E M Gonikberg *J. Chem. Soc., Perkin Trans. 2*, 1989, 1671
90. G A Olah, Ch U Pittman Jr., *J. Am. Chem. Soc.*, 1966, **88** 3310
91. I L Knunyants, B L Dyatkin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1962, 355
92. T Nagai, I Kumadaki, T Miki, et al. *Chem. Pharm. Bull.*, 1986, **34** 1546
93. V A Pattison *J. Org. Chem.*, 1969, **34** 3650
94. US P. 4 004 073; *Chem. Abs.*, 1977, **86** P122006c
95. US P. 4 041 229; *Chem. Abs.*, 1977, **87** P152882y
96. E Klimova, E Treshova, Yu Arbuzov *Dokl. Akad. Nauk SSSR*, 1968, **180** 865
97. W R Dolbier Jr., S-H Dai *J. Chem. Soc., Chem. Commun.*, 1971, 166
98. S-H Dai, W R Dolbier Jr., *J. Am. Chem. Soc.*, 1972, **94** 3953
99. US P. 3 284 516; *Chem. Abs.*, 1967, **66** P10568n
100. V K Brel, M V Dodonov, A N Pushin, I V Martynov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 933
101. US P. 3 184 481; *Chem. Abs.*, 1965, **63** P6977a
102. R Woodward, R Hoffman *Sokhranenie Orbital'noi Simmetrii* (Conservation of Orbital Symmetry), Mir, Moscow, 1971, p. 308
103. K N Houk *Acc. Chem. Res.*, 1975, **8** 361
104. R G Hofstraat, H W Scheeren, R J F Nivard *J. Chem. Soc., Perkin Trans 1*, 1985, 561
105. J W Scheeren *Recl. Trav. Chim. Pays-Bas*, 1986, **105** 71
106. N D Epiotis *J. Am. Chem. Soc.*, 1973, **95** 1191
107. N Epiotis *Strukturnaya Teoriya Organicheskoi Khimii* (Structural Theory of Organic Chemistry), Mir, Moscow, 1981, p. 65
108. S V Pazenok, V A Soloshonok, L M Yagupol'skii *Khim. Geterotsikl. Soedin.*, 1990, 132
109. V D Sviridov, N D Chkanikov, M V Galakhov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1405
110. A S Golubev, A F Kolomiets, A V Fokin *VI Vsesoyuz. Konf. po Khimii Ftororganicheskikh Soedinenii: Tez. Dokl.* (6th All-Union Conference on the Chemistry of Organofluorine Compounds: Abstracts of Reports), Novosibirsk, 1990, p. 18
111. E A Avetisyan, L A Simonyan, N P Gambaryan *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 2742
112. G S Zaitseva, L I Livantsova, O P Novikova, et al. *Zh. Obshch. Khim.*, 1991, **61** 1395
113. L I Livantsova, G S Zaitseva, Yu I Baukov *Zh. Obshch. Khim.*, 1987, **57** 708
114. J Mattay, K Buchkremer *Heterocycles*, 1988, **27** 2153
115. N P Gambaryan, L A Simonyan, P V Petrovskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, 918
116. US P. 3 164 610; *Chem. Abs.*, 1965, **62** P7727d
117. US P. 3 253 043; *Chem. Abs.*, 1966, **65** P5367b
118. US P. 3 284 509; *Chem. Abs.*, 1967, **66** P28394t
119. US P. 3 040 058; *Chem. Abs.*, 1962, **57** P15074h
120. US P. 3 417 102; *Chem. Abs.*, 1969, **70** P47280b
121. E A Karakhanov, S V Lysenko, N F Kovaleva, et al. *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1982, **23** 159
122. I L Knunyants, A V Fokin, V A Komarov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 466
123. I L Knunyants, Yu A Cheburkov *Izv. Akad. Nauk SSSR*, 1960, 466
124. US P. 3 474 164; *Chem. Abs.*, 1970, **72** P21337s
125. G S Knunyants, I L Gambaryan, N P Gambaryan, V V Tyuleneva *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, 2662
126. G S Zaitseva, L I Livantsova, N A Orlova, et al. *Zh. Obshch. Khim.*, 1982, **52** 2076
127. G S Zaitseva, L I Livantsova, R A Bekker, et al. *Zh. Obshch. Khim.*, 1983, **53** 2068
128. Z Zubovics, N Ishikawa *J. Fluorine Chem.*, 1976, **8** 43
129. I A D'yachenko, B R Livshits, N P Gambaryan, et al. *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1966, **11** 590
130. R M Albert, G B Butler *J. Org. Chem.*, 1977, **42** 674
131. R A Braun *J. Org. Chem.*, 1966, **31** 2303
132. A S Golubev, A F Kolomiets, A V Fokin *J. Fluorine Chem.*, 1991, **54** 273
133. D Basavaiah, V V L Gowriswari *Synth. Commun.*, 1989, **19** 2461
134. S E Drewes, G H P Roos *Tetrahedron*, 1988, **44** 4653
135. H M R Hoffmann, J Rabe *Angew. Chem., Int. Ed. Engl.*, 1983, **22** 795
136. US P. 2 996 518; *Chem. Abs.*, 1962, **56** P1467a
137. L A Simonyan, N P Gambaryan, I L Knunyants *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1966, 467
138. US P. 3 627 847; *Chem. Abs.*, 1972, **76** P59188q
139. US P. 3 662 071; *Chem. Abs.*, 1972, **77** P126212d
140. A S Golubev, M V Galakhov, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2127
141. H O Colomb, F E Bayley Jr., R D Lundberg *J. Polym. Sci., Polym. Lett.*, 1978, **16** 507
142. J R Norell *J. Chem. Soc., Chem. Commun.*, 1969, 1291
143. W E Truce, L K Liu *Chem. Ind.*, 1969, **14** 457
144. US P. 3 895 044; *Chem. Abs.*, 1975, **83** P131135j
145. W Hanefeld, D Kluck *Arch. Pharm.*, 1981, **314** 799
146. N P Gambaryan, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 722
147. G S Kaitmazova, N P Gambaryan, E M Rokhlin *Usp. Khim.*, 1989, **63**(12) 2011 [English translation in *Russ. Chem. Rev.*, 1989(12)]
148. H Abele, A Haas, M Lieb *Chem. Ber.*, 1986, **119** 3502
149. H Abele, A Haas, M Lieb *J. Fluorine Chem.*, 1989, **45** 123
150. V A Soloshonok, Yu L Yagupol'skii, V P Kukhar *Zh. Org. Khim.*, 1989, **25** 2523

151. Yu V Zeifman, E G Ter-Gabrielyan, D P Del'tsova, N P Gambaryan *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 396
152. A S Golubev, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2461
153. K V Vatsuro, G L Mishchenko *Imennye Reaktsii v Organicheskoi Khimii* (Name Reactions in Organic Chemistry), Khimiya, Moscow, 1976, p. 411
154. W J Middleton *J. Org. Chem.*, 1965, **30** 1307
155. Yu I Baukov, G S Zaitseva, L I Livantsova, et al. *Zh. Obshch. Khim.*, 1981, **51** 1304
156. K Burger, H Schickaneder, A Meffert *Z. Naturforsch., B*, 1975, **30**, 622

Received 15th April 1992

Translated from *Uspekhi Khimii* **61** 1457–1490 (1992) U.D.C. 547.221+547.288

Fluorine-containing ketimines

S N Osipov, A F Kolomiets, A V Fokin
A N Nesmeyanov Institute of Heteroorganic Compounds, Russian Academy of Sciences

ABSTRACT. **Data appearing in the last ten years have been correlated for the methods of synthesis of fluorine-containing imines, their reactions with N-, O-, S-, P- and C-nucleophiles, with aromatic and heteroaromatic π-donors and in cycloaddition and cyclocondensation processes involving these compounds. The principal theoretical ideas on the reactivity of fluorine-containing ketimines are discussed.**

The bibliography contains 132 references.

Contents

I.	Introduction	798
II.	Methods of synthesis	798
III.	Reactivity	802

I. Introduction

The chemistry of fluorine-containing imines may rightfully be considered as one of the most interesting areas of fluorine chemistry. The diversity of the effects of a fluorine atom and of fluoroalkyl groups is shown most completely in these compounds due to the presence of the highly polarisable C=N bond. The mutual effects of fluorine-containing and other substituents on the azomethine bond prove to be extremely prominent. This has caused compounds to appear in the fluoroimine series with contrasting properties, from the very stable chemically inert to the extremely reactive.

Of the great variety of fluorine-containing compounds with a C=N bond the *N*-fluoroimines, imidoyl halides, fluoroazomethines including aldimines and ketimines, ketenimines and acylimines have been studied fairly well. Each type of compound is characterised by special methods of preparation and by a set of specific properties which determine both the features of their chemistry and their area of use. The search for effective components of high-energy fuels and combustion accelerators is linked with *N*-fluoroimines. The fluoroazomethines have attracted attention as potential precursors of heat-transfer agents, greases, other valuable materials and additives. Imidoyl halides, ketenimines and acylimines are most interesting as synthons for fluorine-containing biologically active compounds.

The vast literature on fluorine-containing compounds with a C=N bond is correlated in a series of publications. The principal data on *N*-fluoroimines have been discussed in reviews,[1,2] the chemistry of fluorine-containing ketenimines has been illustrated in a review[3] and in a dissertation,[4] the general state of the chemistry of fluorine-containing imines up to the early eighties is described in review articles.[5–7]

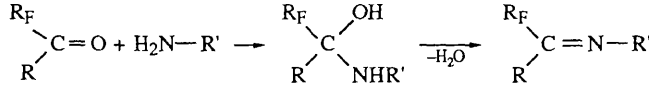
Interest in the various fluorine derivatives of the azomethines has grown during the last ten years. Particular attention has been attracted by the functionally substituted fluorine-containing ketimines, including the acylimines of polyfluoroketones, the imines of various α- and β-ketocarboxylic acids, the imines of unsaturated fluoro-carbonyl compounds and other bi- and trifunctional compounds which are interesting synthons of fluorine-containing biologically active compounds. The present paper is devoted to the correlation of this experimental material and to some of the theoretical investigations carried out in this area.

II. Methods of synthesis

From the multitude of methods developed previously for the synthesis of fluorine-containing ketimines[7] most attention has continued to be paid in the last ten years to the development of methods based on the condensation of fluorocarbonyl compounds with amino compounds. Somewhat less attention has been paid to methods based on cycloaddition–elimination reactions, including the Staudinger reaction. Interesting new approaches to the synthesis of fluorine-containing ketimines have been developed by studying the reaction of fluorine-containing nitriles and ketenimines with HCN, of geminal isocyanatohalo compounds with various nucleophilic reagents and amino compounds with fluoroalkenes and alkynes. Methods specfic for fluorine compounds have also been developed further.

1. Condensation of fluorine-containing ketones with amino compounds

The condensation of fluorine-containing ketones with amino compounds usually leads readily to geminal aminohydroxy compound (hemiaminal or hemiamidal) which is converted into a ketimine either by the elimination of water or (in the case of highly stable hydroxy compounds) by the action of strong dehydrating agents.

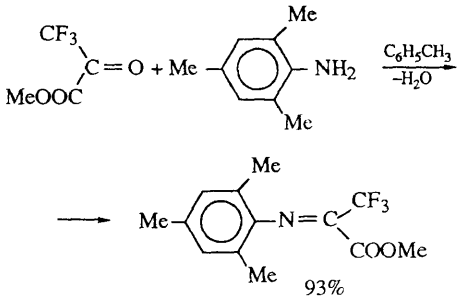


According to recent data[7] the dehydration conditions for a hemiaminal are directly dependent on the electron-accepting properties of the substituents at the ketone carbonyl carbon atom and the basicity of the amino compound. New data summarised in Table 1 define these concepts more precisely.

It turned out that aminals obtained from fluorine-containing α-ketocarboxylic acids (Table 1, No. 1–4) and alkyl(aryl) ketones (Table 1, Nos. 5–8) are readily dehydrated to imines under solvation conditions or by azeotropic distillation of the water formed.[8–18] This is in agreement with previous ideas,[7] since the carbonyl compounds listed contain only one electron-accepting group.

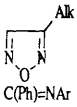
However anils are obtained from methyl trifluoropyruvate under practically the same conditions.[19,20,21] In the reaction of the latter

with mesidine the corresponding anil is formed almost quantitatively (93%).[19]



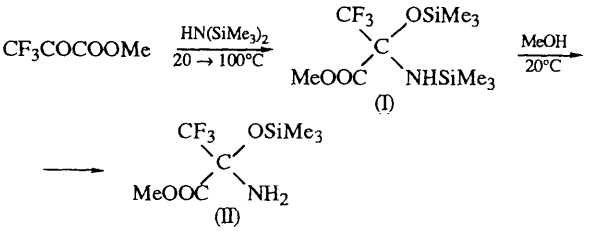
Reaction with aniline under conditions for the azeotropic distillation of water gave 35% yield. The relatively low yield of anil in this case is caused by the occurrence of several side reactions, the nature of which has been discussed.[21] Only the weakly basic nitroanilines did not give anils on reaction with methyl trifluoropyruvate. The hemiaminals formed in this case are not dehydrated even at 200 °C.[21] It must be noted that hexafluoroacetone does not form anils with either aniline[22] or with mesidine[23] under azeotropic distillation conditions. On heating, the hemiaminals are decomposed into the starting materials.

Table 1. Features of the formation of imines from fluorocarbonyl and amino compounds.

No.	R_F	R	R′	Dehydration conditions	Refs.
1	CFHCOOH	COOH	Alk	–	[8]
2	$CFAlk_2$	COOH	Alk	–	[9]
3	CFH_2	COOH	CH(Me)Ph	0–25 °C, EtOH	[10]
4	CFHAr	COOH	Alk	Δ, alcohol	[11]
5	CFH_2	Me	Alk	$K_2CO_3(MgSO_4)$, CCl_4	[12, 13]
6	CF_3	Alk	$(CH_2)OAlk$	Boiling benzene	[14]
7	C_8F_{17}	Me	Alk	Δ, $CHCl_3$	[15, 16]
8	CF_3	Ph	CH(Me)Ph	Δ, toluene *p*-TsOH	[17, 18]
9	CF_3	COOMe	Ar	Boiling benzene	[19, 20, 21]
10	$CF(CF_3)_2$	$C(O)CF(CF_3)_2$	Alk	Δ, $CHCl_3$	[24]
11	CF_3	Ph		$(CF_3CO)_2O$, Py	[25]
12	CF_3	CF_3	C(Ph)=NAr	$POCl_3$, Py	[26]
13	CF_3	COOMe	COOAlk	$(CF_3CO)_2O$, Py	[27]
14	CF_3	COOMe	$C(O)CF_3$	$POCl_3$, quinoline	[28, 29]
15	CF_3	COOMe	SO_2Me, SO_2Ph	$SOCl_2Py$	[28, 30, 31]

The adducts of perfluoro-α-diketones, for example the product of reacting diperfluoro-isobutyroyl with amines (Table 1, No. 10), are readily dehydrated under conditions of azeotropic distillation of water. Carbalkoxy and perfluoroacyl groups, in spite of their high electron-accepting properties, assist the dehydration of an adjacent hemiaminal function. The stabilisation of the intermediate carbocation and of the final azomethine bond by conjugation with the adjacent C=O group is probably decisive in this case.

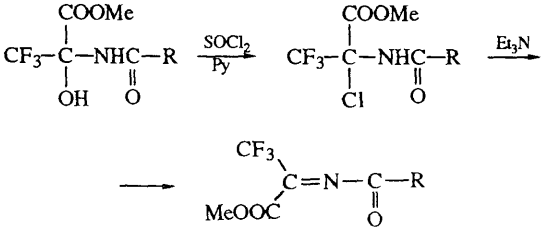
It must be noted that the positive effect of carbalkoxy groups on the dehydration of an adjacent hemiaminal function is not extended to their *N*- and/or *O*-silylated derivatives.[27–31] The silylated hemiaminals (I) and (II), obtained from methyl trifluoropyruvate and hexamethyldisilazane are not converted successfully into the imine of methyl trifluoropyruvate.[32]



The hemiaminal obtained by the desilylation of (II) is also not dehydrated. Under the conditions of its formation this compound undergoes an intramolecular condensation involving the NH_2 and COOMe groups giving oligomers.

Dehydrating agents known previously are used to obtain the new imines of hexafluoroacetone (Table 1, Nos. 11, 12) and the acylimines of methyl trifluoropyruvate (Table 1, Nos. 13, 14).[25,26] More rapid formation and high stability were recorded for the hemiamidal of methyl trifluoropyruvate compared with the hemiamidals of hexafluoroacetone together with more forcing conditions for their dehydration.[28,29]

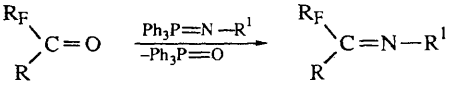
The readily formed highly stable adducts of methyl trifluoropyruvate with sulphonamides are readily dehydrated by boiling $SOCl_2$ in the presence of catalytic amounts of pyridine (Table 1, No. 15). Under these conditions the hemiaminals of methyl trifluoropyruvate are quantitatively converted into the unusually stable geminal amidochloro compounds, which turned out to be smooth precursors of methyl trifluoropyruvate acylimines.[32,33]



R = Me, OEt, CF_3.

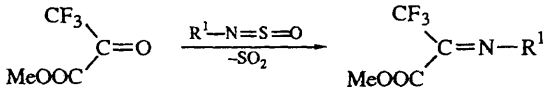
2. Cycloaddition–elimination reactions

Cycloaddition–elimination reactions have been used for obtaining new alkyl-, aryl- and acylimines using the Staudinger reaction.[17,34–38] The data obtained confirm the value of this method which enables any phosphazo compound to react with fluorine-containing aldehydes, ketones and α-ketoacid derivatives.



$R_F = CF_3$; R = H, Me, Ph, COOMe, CF_3; R^1 = Bu, Ph, CH_2Ph, CH(Me)Ph, 4-$MeOC_6H_4$, COOMe.

It is also possible to use thionyl imines for the synthesis of imines and acylimines from esters of fluorine-containing α-ketoacids.[39]

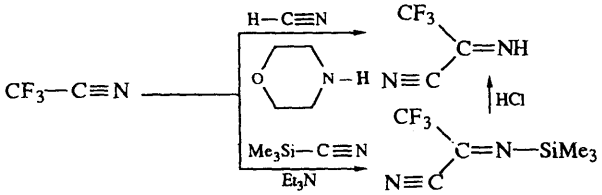


R^1 = Ph, C(O)Ph .

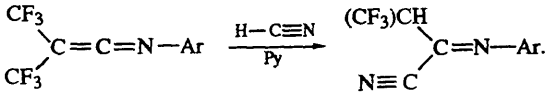
In this case the reaction occurred more readily than for hexafluoroacetone, even in the absence of a catalyst.

3. Addition of HCN to trifluoroacetonitrile

The reaction of HCN with CF_3CN has been carried out under base catalysis conditions,[5] raising the prospect of synthesising α-iminofluorocarboxylic acids. The possibility of using trimethylsilyl cyanide in place of HCN in this reaction is of particular interest,[40] since the *N*-trimethylsilylimines of α-ketoacid nitriles formed are efficienct precursors of a variety of *N*-substituted imines.



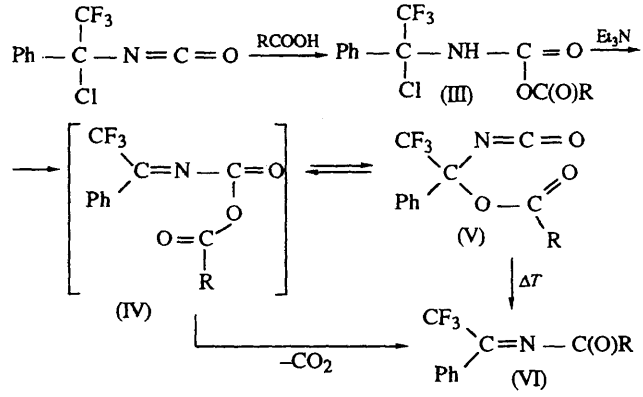
Nitriles of α-iminofluorocarboxylic acids are also formed readily by nucleophilic addition of HCN to fluorine-containing ketenimines.[41]



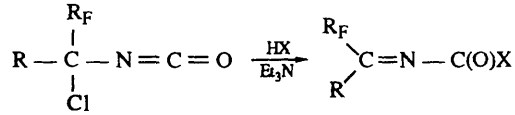
The applicability of this method is limited by the stability of the monomeric fluoroketenimines.

4. Conversion of fluorine-containing geminal chloroisocyanato compounds

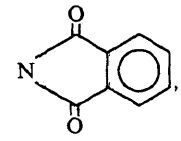
The reaction of $R_FRClCN{=}C{=}O$ with nucleophilic reagents opens broad prospects for the synthesis of various fluoroacylimines. Two types of reaction are used. Carboxylic acids are used as nucleophiles in the first reaction type and form mixed anhydrides with the chloroisocyanato compounds. These undergo rearrangement with decarboxylation on dehydrochlorination.[42] For example, 1-chloro-1-trifluoromethyl-1-phenylmethyl isocyanate reacts vigorously with carboxylic acids giving the corresponding addition products (III), which eliminate HCl above 20 °C. Compounds (III) are converted in the presence of triethylamine into the unstable mixed anhydrides (IV) which are stabilised in one of two ways. One is by decarboxylation and the formation of *N*-acylimines (VI) and the other is by a 3,3-sigmatropic shift of the acyloxy group in the C–N=C triad with the formation of 1-(acyloxy)alkyl isocyanates (V). The latter eliminates CO_2 on thermolysis (above 120 °C) giving the *N*-acylimines (VI).



The second type of reaction of chloroisocyanato compounds includes reaction with O-, N- and S-nucleophiles, such as alcohols,[43,44] imines, diphenylsulphinimine, diphenylamine,[45] potassium *O*-alkyldithiocarbonates,[46] and amides of carboxylic acids[47] in the presence of a dehydrochlorinating agent. The addition of nucleophile at the C=N bond and dehydrochlorination of the geminal chloroamino compound to the acylimines occurs under mild conditions.

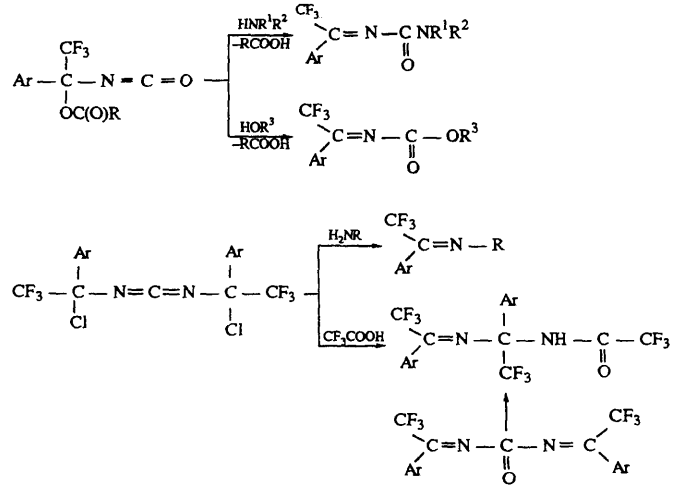


$R_F = CF_3$; R = R_F, Ar; X = OAlk, N=CAlk$_2$, N=SPh$_2$,



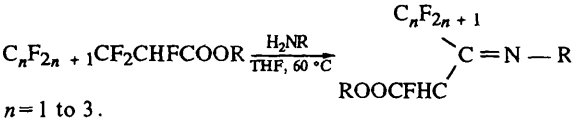
NPh_2, S — C(S)OAlk, N(Ar)C(O)Alk.

1-(Acyloxy)alkyl isocyanates,[48,49] *N,N*-bis(1-chloroalkyl)carbodiimides[42,50,51] and *N,N*-bis(alkylidene)ureas[42] react similarly to the geminal chloroisocyanato compounds. They are readily converted into the corresponding acyl- or alkylimines on reaction with alcohols, acids and amines.



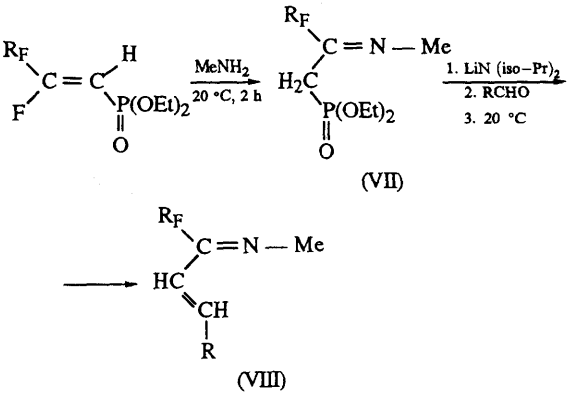
5. Reactions of fluoroalkenes and fluoroalkynes with amines

An original method has been developed for obtaining imines of β-ketofluorocarboxylic acids from esters of α-hydroperfluorocarboxylic acids and primary aliphatic amines. The reaction comprises dehydrofluorination of the initial ester, vinylic replacement of a fluorine atom by an alkylamino group and enamine–imine rearrangement. In spite of being so complex these processes lead to the corresponding imines in 70–82% yield.[52]



$n = 1$ to 3.

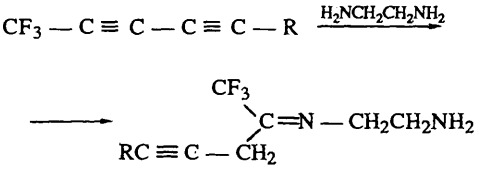
Fluoroalkenylphosphonates are used successfully to obtain fluorine-containing imines with alkenyl substituents at the carbon atom of the C=N bond.[53,54] The vinylic replacement of a fluorine atom by an alkylamino group and subsequent enamine–imine rearrangement lead to the highly reactive CH-acids (VII). Treatment of these with lithium diisopropylamine in ether at −78 °C with subsequent addition of an aldehyde leads to the *trans* isomer of (VIII) in high yield.



(VII)

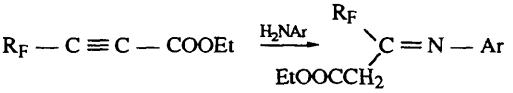
(VIII)

Fluorine-containing imines are obtained by traditional methods by reacting fluorinated diacetylenes with nitrogen-containing binucleophiles.[55]



R = iso-Pr, t-Bu, CMe_2OH.

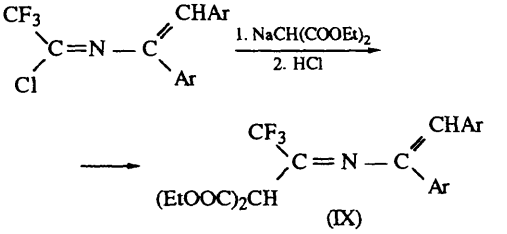
Imines of β-ketocarboxylic acids are obtained by condensing esters of fluoroalkyl substituted acetylenecarboxylic acid with substituted anilines.[56]



$R_F = C_4F_9$, C_6F_{13}, C_8F_{17}; Ar = Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$.

6. Reactions of fluorine-containing imidoyl chlorides with CH-acids

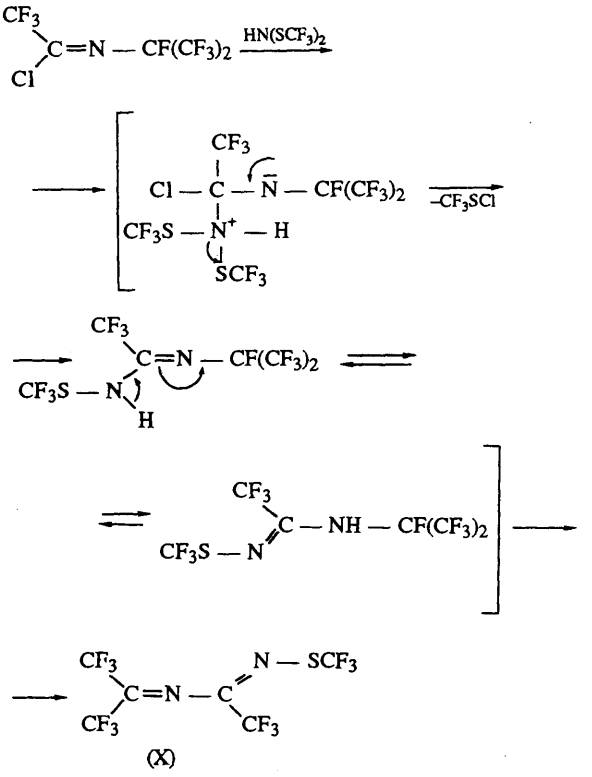
The reaction of imidoyl chlorides with CH-acids is one of the promising routes for synthesising fluorine-containing *N*-alkenylketimines. For example, the ketimines (IX) are obtained in preparative yield by reacting *N*-(1,2-diarylvinyl)trifluoroacetimidoyl chlorides with sodiomalonic ester.[57]



(IX)

Ar = 4-RC_6H_4 (R = H, OMe, Cl)

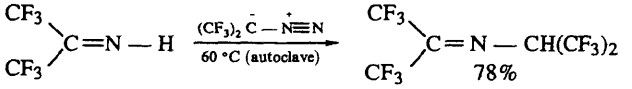
The perfluoroketimine (X) is obtained by the reaction of *N*-perfluoroisopropyltrifluoroacetimidoyl chloride with bis(trifluoromethylthio)amine.[58]



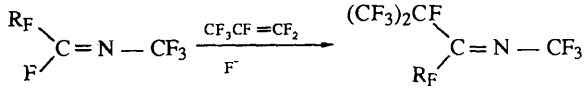
(X)

7. Other reactions

There are few examples of methods of synthesis of ketimines which are specific for fluorine compounds. The preparative value of the reaction of hexafluoroacetone imine with bis(trifluoromethyl)-diazomethane has been shown.[59]

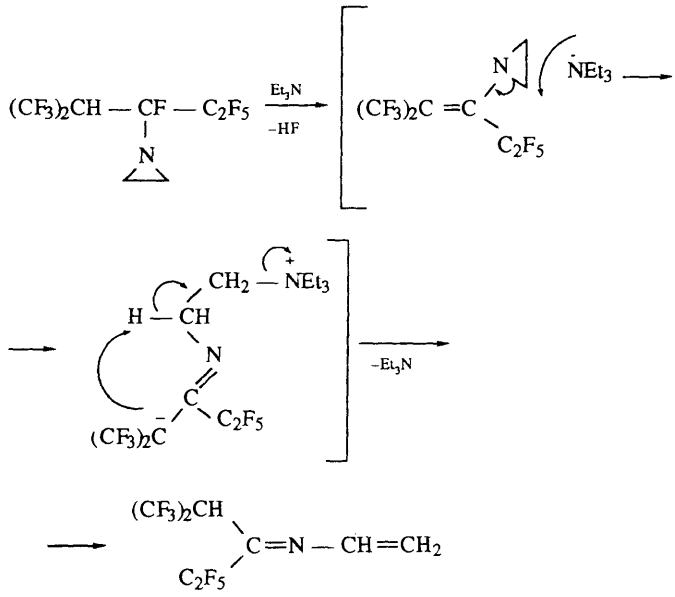


Homologues of perfluoro-2-azapropene form codimerisation products with fluoroolefins in the presence of fluoride ion.[60]

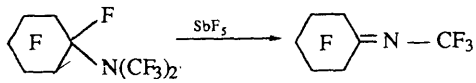


$R_F = CF_3, C_2F_5, C(CF_3)_3$

The addition products of an ethylenimine to an internal fluoroolefin formed under dehydrofluorination conditions undergo an unusual rearrangement with the formation of *N*-vinylpolyfluoroketimines.[61]



Under cationotropic conversion conditions tertiary fluoroamines, such as perfluorodimethylcyclohexylamine, eliminate CF_4 with the formation of a perfluoroketimine.[62]



80%

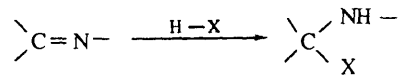
By comparing the data (of the last decade) discussed above on the methods of synthesising fluorine-containing ketimines with the results of previous work,[7] it is easy to see that the investigations in this area have acquired a distinctly applied character. Fundamental attention is now paid to the search for methods of synthesising functionally substituted ketimines. These include the imines of fluorine-containing, α-, β-, and γ-ketocarboxylic acids and their derivatives and various polyunsaturated derivatives, formally belonging to the hetero-1,3-dienes and conjugated heteropolyenes. They are all efficienct precursors of fluorine-containing compounds of various types possessing biological activity.[63,64]

III. Reactivity

At present studies are being vigorously continued on the reactions of fluorine-containing ketimines with nucleophilic reagents and on the cyclocondensation of mono- and bifunctional ketimines with mono- and binucleophiles. A new route has been developed for the polyfluoroalkylamino- and polyfluoroalkylamidoalkylation of aromatic and heteroaromatic π-systems of the donor type by fluorine-containing imines and acylimines. New data have been obtained on various cycloaddition reactions involving ketimines and acylimines.

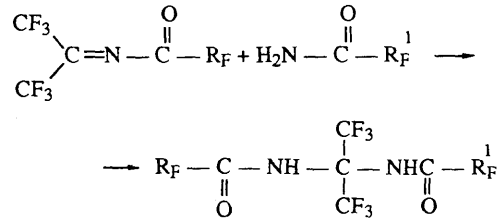
1. Reactions with nucleophilic reagents.

Fluorine-containing ketimines usually react readily with proton-containing nucleophiles giving the corresponding products of addition at the azomethine bond.[7,65–70] Electron-accepting properties and in some cases the structure of the substituent on the nitrogen atom of the C=N bond have a decisive effect on the addition conditions. Sulphonyl- and perfluoroacylimines of polyfluorocarbonyl compounds display the maximum reactivity in these reactions. Reaction of them with O-, N-, S- and P-nucleophiles is effected selectively either on cooling or in dilute solution. It is necessary to carry out the reaction with strong bases under strictly controlled conditions.



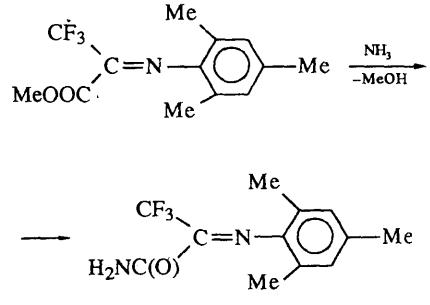
X = OH, OR, OPh, SPh, SR, NH_2, NHR, NR_2, $NHC(O)R$, $NHSO_2R$, PH_2, PHR, $P(O)R^1R$, $P(O)(OR)_2$, P(O)(OR)R.

The nature of the nucleophile used also affects the reaction conditions significantly. Reaction with imines is more difficult with a reduction in nucleophilic basicity. For example, even such highly reactive compounds as the perfluoroacylimines of hexafluoroacetone react with perfluorocarboxylic acid amides only on heating (100–150 °C) in a sealed tube.[71,72]

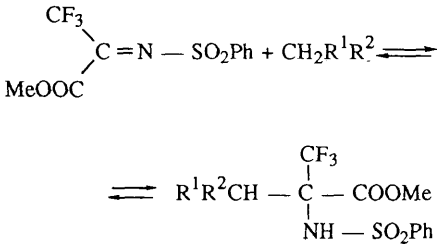


$R_F = CF_3$; $CH(CF_3)_2$; $R_F^1 = CF_3$, $CH(CF_3)_2$, C_4F_9.

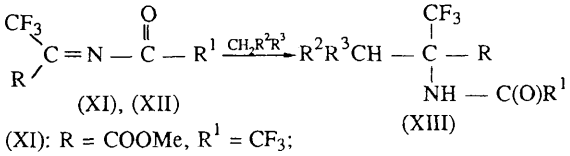
The reaction of nucleophilic reagents with functionally substitued imines occasionally lead to side products. For example, the anils of methyl trifluoropyruvate are converted on treatment with ammonia into anils of trifluoropyruvate amide.[32]



The reactions of sulphonyl- and acylimines of methyl trifluoropyruvate with CH-acids proved to be interesting.[32,70] Products of *C*-alkylation are formed in 25–30% yield on reacting a sulphonylimine with malonic or acetoacetic acid esters or with acetylacetone. The reactions are carried out at room temperature as equilibrium processes.



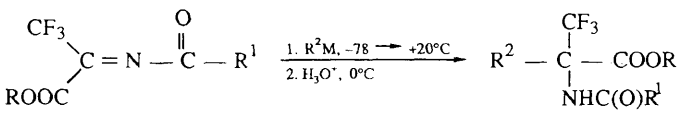
The reaction of the trifluoroacetylimine (XI) with malonic ester is even more difficult and the *C*-amidoalkylation product (XIII) was successfully obtained in 30% yield only on catalysis with toluene-4-sulphonic acid. Furthermore, reaction of the imine (XI) and the benzoylimine of hexafluoroacetone (XII) with CH-acids capable of enolisation, such as acetylacetone, acetoacetic ester and acetophenone, was effected at 20–80 °C leading to the *C*-amidoalkylation product (XIII) in up to 90% yield.[70] It is quite probable that in the latter case the process occurs by a [2 + 4] cycloaddition mechanism with an asymmetrical transition state.



(XI): R = COOMe, $R^1 = CF_3$;

(XII): R = CF_3, R^1 = Ph.

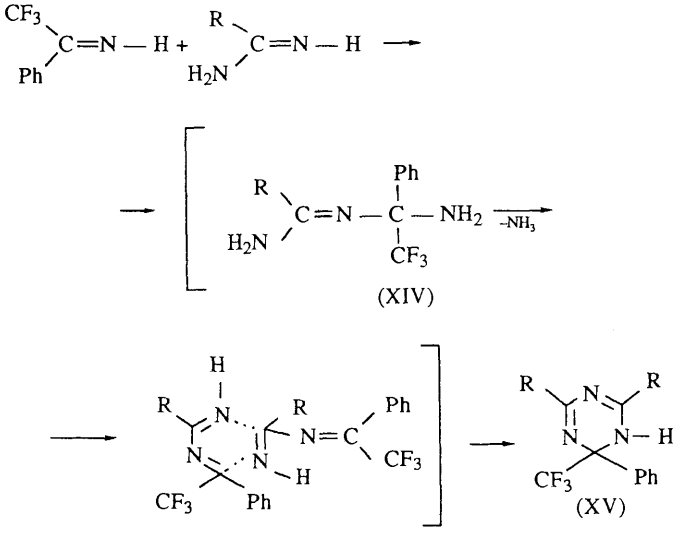
Organometallic compounds of Li, Cd and Mg react extremely vigorously with methyl trifluoropyruvate acylimines. These reactions occur selectively only under strong cooling and lead to derivatives of α-trifluoromethyl-α-amino-acids.[35,73,74]



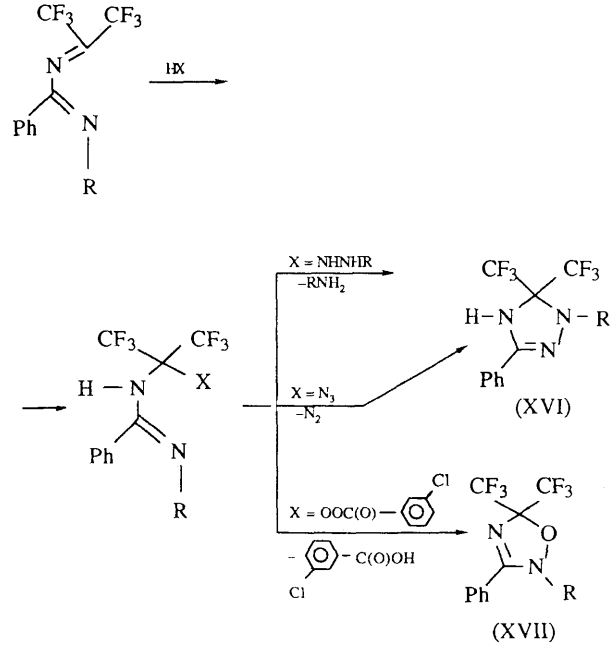
R = Me, Et; R^1 = OAlk, CF_3; R^2 = Me, Pr, Bu, iso-Bu, Ph, $PhCH_2$, $CH_2=CH-(CH_2)_n$ (n = 0 to 4), ; M = Li, CdR^2, MgHal.

The reaction of fluorine-containing ketimines with nucleophilic reagents accompanied by heterocyclisation or cyclocondensation is particularly interesting. Such conversions take place on reaction of functionally unsubstituted ketimines with binucleophiles. For example, reaction of the imine of trifluoroacetophenone with amidines leads to unstable adducts (XIV) which dimerise after elimination of ammonia to the corresponding dihydrotriazines (XV).

An unstable adduct (XIV) is formed with trifluoroacetamidine and is transformed into the triazine only on heating to 200 °C.[75]

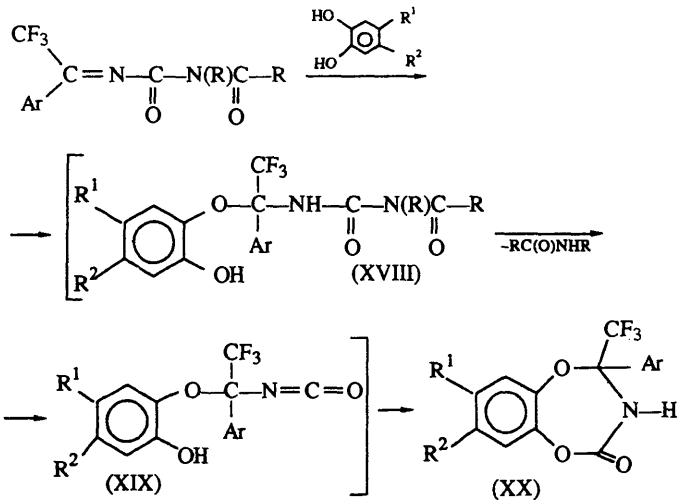


Functionally substituted ketimines also react with mono- and binucleophiles. Burger and collaborators[76–78] showed that the adducts of the iminoacylimines of hexafluoroacetone formed initially with hydrazines,[76] hydrazoic acid[77] and 3-chloroperbenzoic acid[78] cyclise spontaneously into the triazolines (XVI) and the isoxadiazolines (XVII).

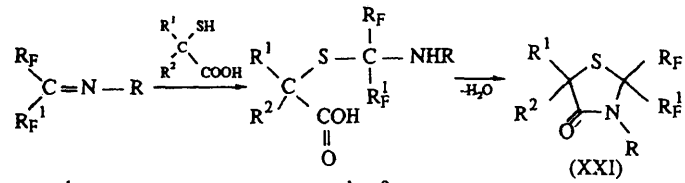


Poorly stable geminal amino-aryloxy compounds (XVIII) are also formed initially on reacting ureidoimines with *o*-dihydroxybenzenes. On boiling in benzene these compounds are converted through the

intermediate isocyanates (XIX) into the 1,3,5-benzodioxazepines (XX).[79]

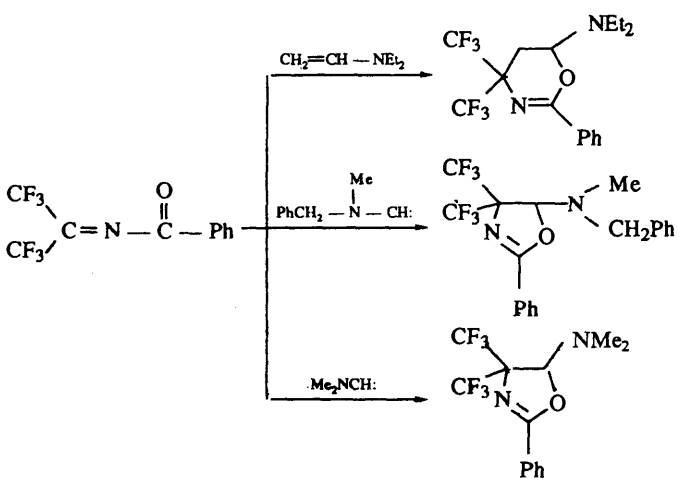


Recently Dupont patented the synthesis of the thiazolidones (XXI) which are plant growth regulators.[80] The method is based on the reaction of various polyfluoroketimines with α-mercaptocarboxylic acids, the first step of which is attack of the S-nucleophile on the C=N bond.

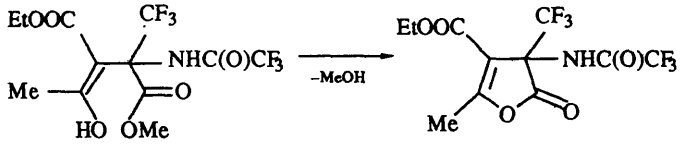


$R_F = R_F^1 = CF_3$, CF_2Cl, C_2F_5, CF_2H; $R^1 = R^2$ = H, Me, CH_2COOH.

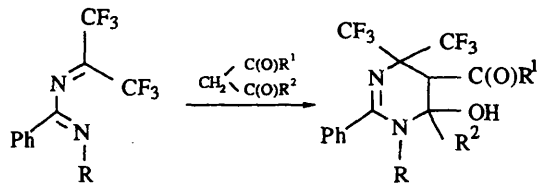
Ring formation also occurs in the reaction of acylimines with tertiary amines. The benzoylimine of hexafluoroacetone, which is an efficient acceptor of hydride ion,[7] converts triethylamine into *N,N*-diethylvinylamine, dimethylbenzylamine into the aminocarbene $PhCH_2(Me)NCH$: and tetramethyldiaminomethane into the aminocarbene Me_2NCH:, which are then stabilised by a second molecule of the benzoylimine as the corresponding [2 + 4] and [1 + 4] cyclic adducts.[81]



Various heterocyclic compounds may be obtained by reacting functionally substituted ketimines with CH-acids. The Michael addition products of acylimines of methyl trifluoropyruvate to enolisable CH-acids cyclise (slowly at 20 °C and rapidly on heating) to butenolides.[70] The mild conditions for the heterocyclisation are due to the stabilisation of the initial compounds in the enolic form.



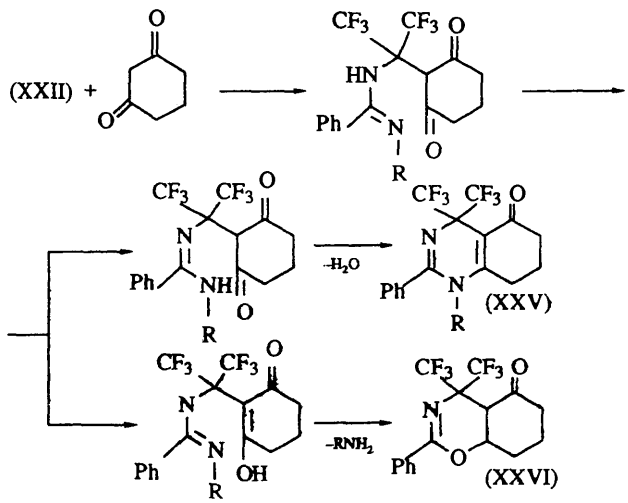
The adducts of CH-acids with acylimines of hexafluoroacetone are not subject to intramolecular heterocyclisation. However, the reaction of the iminoacylimines (XXII) with CH-acids capable of enolisation gives the [2 + 4] cyclic adducts (XXIII) and (XXIV) exclusively.[81]



(XXIII): $R^1 = R^2$ = Me;
(XXIV): R^1 = OEt, $R^2 = CH_2X$.

These differences are explained by the higher nucleophilicity of the terminal nitrogen in the iminoacylimines (XXII) compared to the carbonyl oxygen in the acylimines since the reaction of the acylimines stops at the stage of forming Michael adducts and the initial *C*-amidoalkylation products of (XXII) are transformed further into (XXIII) and (XXIV).

Cyclic 1,3-diketones, the enolic forms of which are not stabilised by an intramolecular hydrogen bond, undergo cyclocondensation with (XXII) giving a mixture of 1,4-dihydropyrimidines (XXX) and 1,3-oxazines (XXVI).[82]

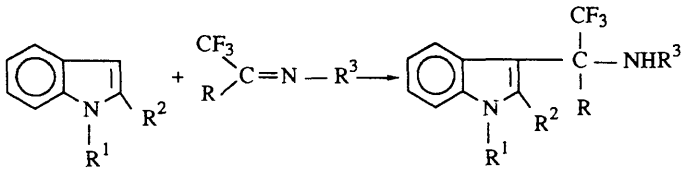


2. Reactions with aromatic and heteroaromatic compounds

A systematic study of the reactions of the imines, sulphonyl- and acylimines of hexafluoroacetone and of methyl trifluoropyruvate with aromatic and heteroaromatic compounds led to the design of a

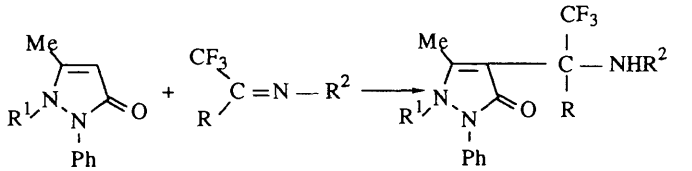
general method for polyfluoroalkyl-α-amino(amido)alkylation of aromatic systems of the donor type. These reactions proved to be closely similar to the known aminomethylation reaction, particularly with several heterocyclic π-donors.

Indole and certain 1- and 2-substituted indoles are almost quantitatively amino(amido)alkylated at position 3. The alkylating properties of $CF_3(R)C=N-R^3$ increase in the following series of R^3: H < $XC_6H_4C(O)$ < RSO_2 < $R_FC(O)$. The optimum reaction temperature in this series is thereby reduced from +120 to −50 °C.[28,83–85]



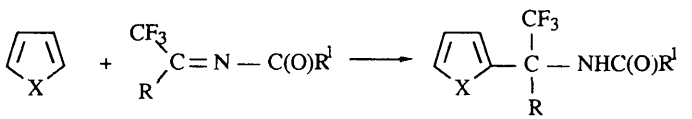
R = CF_3, COOMe; R^1 = H, Me, Ph; R^2 = H, Me, Ph; R^3 = H, 4-$FC_6H_4C(O)$, 2-$FC_6H_4C(O)$, SO_2Me, SO_2Ph, $CF_3C(CO)$, $CF_3(CF_2)_3C(O)$.

Hexafluoroacetone imine, its *N*-acyl derivatives and also the acyl- and sulphonylimines of methyl trifluoropyruvate also display similar properties when reacting with *N*-phenyl-3-methylpyrazol-5-ones.[85,86] Aminoalkylation is effected at the point of maximum π-electron density in the system.



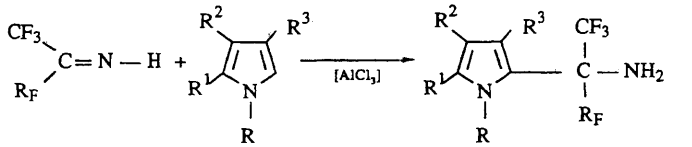
R^1 = H, Me; R = CF_3, COOMe; R^2 = H, SO_2Me, SO_2Ph, $CF_3C(O)$.

Furan, pyrrole and *N*-methylpyrrole are amidoalkylated by *N*-acylimines at −78 °C at position 2.[85,87]

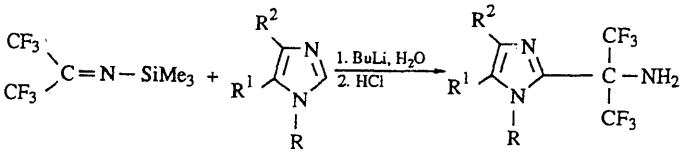


X = O, NH, NMe; R = CF_3 COOMe; R^1 = CF_3, $CH(CF_3)_2$.

According to the patent data the aminoalkylation of substituted pyrroles by imines of polyfluoroketones may be effected in the presence of Lewis acids.[88] The trimethylsilylimines of hexafluoroacetone reacts readily with 2-lithioimidazoles.[89] The *C*(2)-alkylation products formed in both cases possess nonsteroidal antiinflammatory activity.

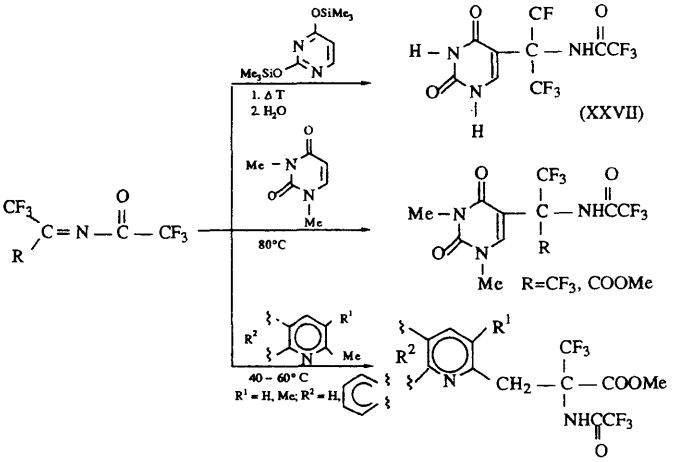


R^1H, Me; $R^2=R^3$=4-FC_6H_4; $R_F=CF_3$, CF_2H CF_2Cl.

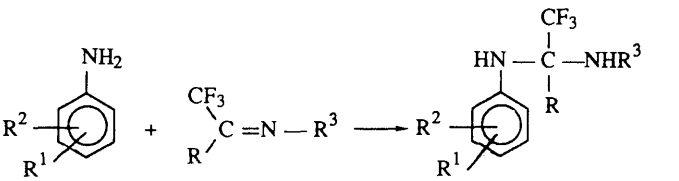


$R^1=R^2$=4-$MeOC_6H_4$; R = CH_2OMe.

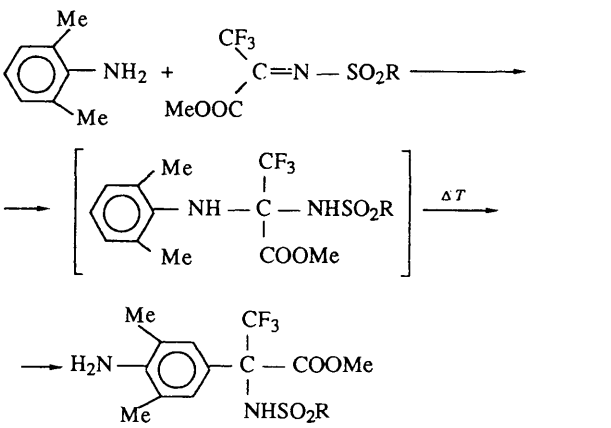
Only the highly electrophilic trifluoroacetylimines of hexafluoroacetone and methyl trifluoropyruvate react successfully with electron-deficient heterocyclic compounds. Thus the trimethylsilyl derivative of uracil forms the *C*(5)-aminoalkylation product (XXVII) on moderate heating.[90] 1,3-Dimethyluracil reacts readily.[91] 2-Methylpyridines and quinolines react at the methyl group with the trifluoroacetylimine of methyl trifluoropyruvate.[32,92]



A systematic study of the reactions of the sulphonyl- and acylimines of hexafluoroacetone and methyltrifluoropyruvate with primary and secondary arylamines[31,32,93–96] led to the conclusion that the *C*-amidoalkylation of these compounds is controlled by the probability of formation and the stability of the *N*-amidoalkylation products. Stable adducts at the nitrogen atom are formed exclusively with primary amines of various structure.

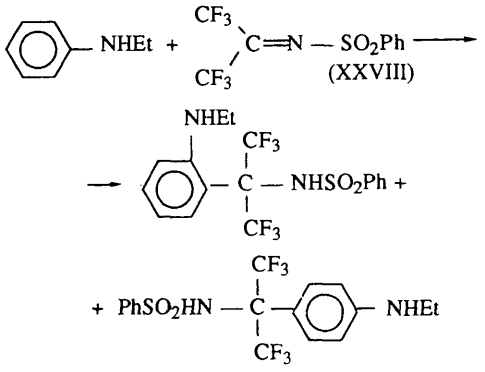


Steric hindrance to the formation of geminal diamino compounds exists in the reaction of the sulphonylimine of methyl trifluoropyruvate with 2,6-dimethylaniline. The initially formed unstable adducts at the nitrogen atom are isomerised quantitatively on boiling for 1–2 h in CCl_4 into products of *C*(4)-amidoalkylation.[32]



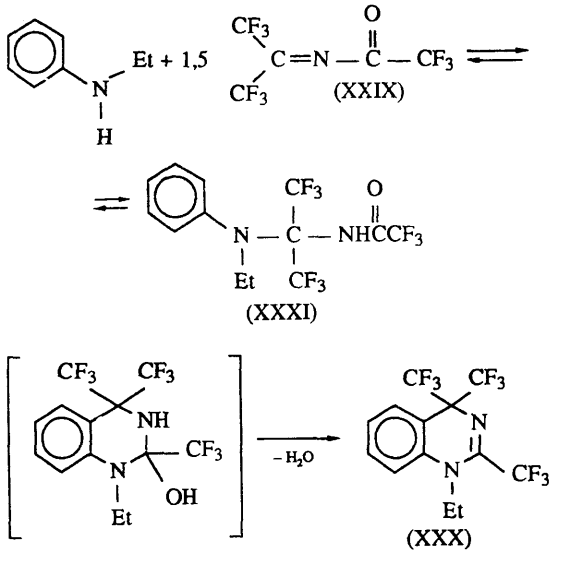
R = Me, Ph.

The probability of *C*-amidoalkylation of secondary arylamines is higher than for primary arylamines. *N*-ethylaniline reacts at 20 °C with the benzenesulphonylimine of hexafluoroacetone (XXVIII) forming products of *C*(2)- and *C*(4)-alkylation in low yield.[95]

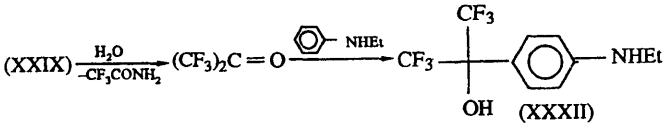


Boiling indoline with the imine (XXVIII) in $CHCl_3$ leads to a complex mixture of products from which the *C*(7)-alkylation product was successfully isolated in low yield (17%). It must be noted that this result is in agreement with the regioselective *C*(7)-alkylation of indoline by hexafluoroacetone described previously.[96]

The reaction of the trifluoroacetylimine of hexafluoroacetone (XXIX) with secondary arylamines is unusual and was studied in detail using *N*-ethylaniline as an example. The reaction unexpectedly leads to the 1,4-dihydroquinazoline (XXX) in 87% yield, i.e. the product of simultaneous *C*(2)-amidoalkylation and cyclocondensation involving the NH and $NHC(O)CF_3$ groups.

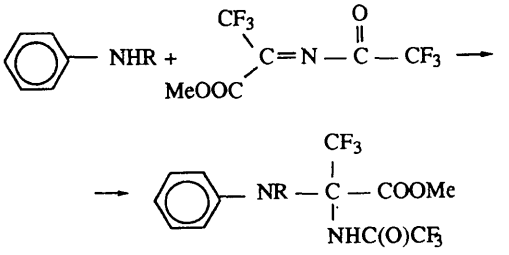


It was shown that the unstable *N*-alkylation product (XXXI) is formed first after mixing the reagents and disappears as compound (XXX) accumulates. The aniline (XXXII) is a side product of the reaction. Its appearance is linked with the decomposition of the acylimine by the water eliminated during cyclocondensation.

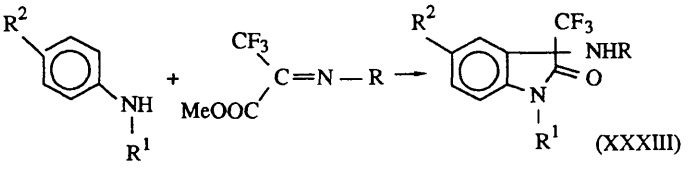


N-Methyl-, *N*-isopropyl- and *N*-phenylanilines and their 4-methoxy and 4-chloro derivatives react like the acetylimine (XXIX).[95] The reaction time was reduced as the volume of the substituent at nitrogen increased in the series of *N*-alkylanilines studied.

The sulphonyl- and acrylimines of methyl trifluoropyruvate give more stable *N*-amidoalkylation products with secondary arylamines. The *C*-amidoalkylation of methyl- and ethylanilines does not take place.

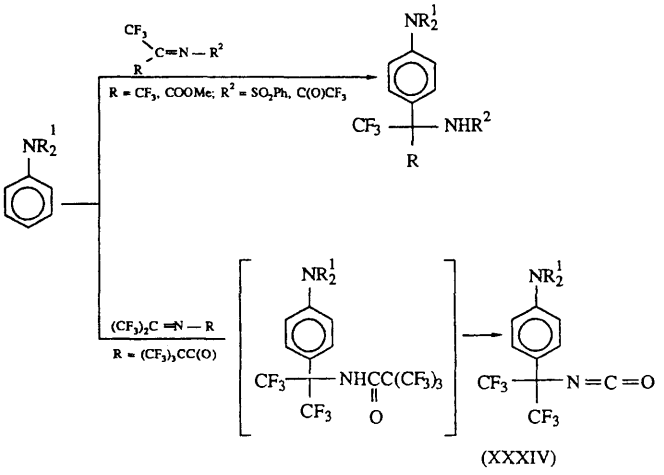


However, the products of simultaneous *C*(2)-amidoalkylation and *N*-acylation, the corresponding indolinones (XXXIII), are obtained in moderate yield with *N*-isopropylaniline, *N*-isopropyl-*p*-toluidine, *N*-isopropyl-*p*-anisidine and diphenylamine.[31]



R_2 = H, Me, OMe; R^1 = iso-Pr, Ph; R = SO_2Me, SO_2Ph, $C(O)CF_3$.

N,*N*-Dimethyl- and *N*,*N*-diethylaniline are *C*(4)-amidoalkylated quantitatively under strong cooling by the sulphonyl- and acylimines of hexafluoroacetone and methyl trifluoropyruvate.[28,31,97] In the case of the *N*-pivaloylimine of hexafluoroacetone the products of *C*(4)-alkylation formed initially eliminates $(CF_3)_3CH$ and is converted into the isocycanate (XXXIV).[97]



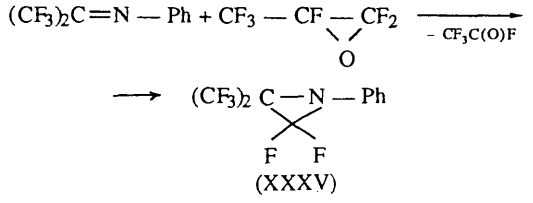
(XXXIV)

3. Cycloaddition reactions

The behaviour of unsaturated compounds in cycloaddition reactions reveals the chemical nature of the fluorine-containing ketimines most completely. It was shown previously[7] that

fluoroketimines with an isolated C=N bond for [1 + 2], [2 + 2], [3 + 2] and [4 + 2] cycloadducts somewhat more readily than their unfluorinated analogues. The sulphonyl-, acryl, thioacyl- and iminoacylimines of hexafluoroacetone are significantly more reactive and react either as activated azomethines or as 1,3-heterodienes in cycloaddition reactions. The new data obtained have extended significantly the concepts of both these reactions and in some cases have enabled electronic models of them to be constructed.

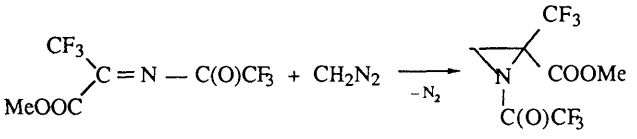
Carbenes, their precursors and the carbenoids usually react unambiguously with fluoroketimines. The reaction of difluorocarbene with fluoroketimines has been demonstrated.[98] The [1 + 2] cyclic adduct, the aziridine (XXXV), was obtained in satisfactory yield by heating a mixture of hexafluoroacetone anil with hexafluoropropylene oxide at 180 °C.



(XXXV)

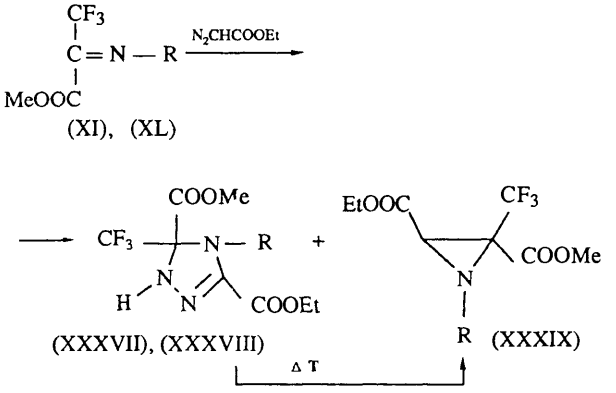
Diazoalkanes are efficient precursors of carbenes in reactions with highly electrophilic fluoroketimines.[7] The behaviour of methyl trifluoropyruvate acylimines in these reactions has been studied.[29,32]

The reaction of trifluoroacetylimine of methyl trifluoropyruvate with diazomethane occurs at −30 °C and is accompanied by elimination of nitrogen and the formation of the aziridine (XXXVI)[29] and not the [1 + 4] cylic adduct as in the analogous reaction with the benzoylimine of hexafluoroacetone.[99]



(XXXVI)

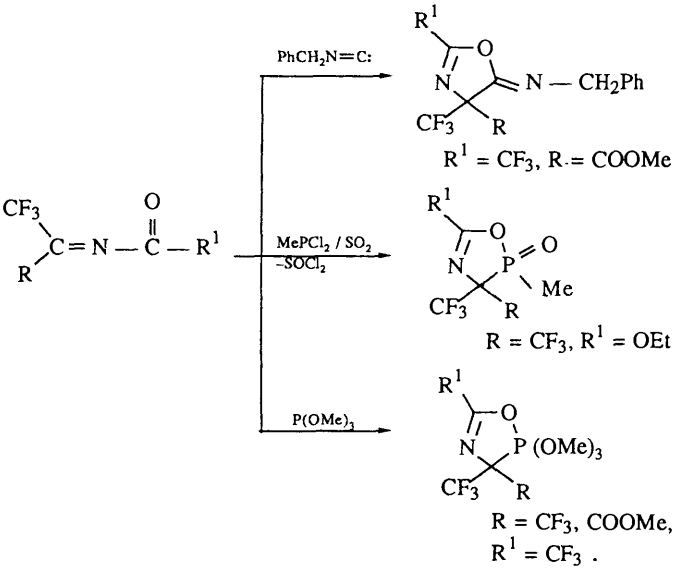
The reaction of the imine (XI) with diazoacetic ester also proceeds in an unusual manner.[29,74] It is effected at 20 °C and leads to a 2:1 mixture of the triazoline (XXXVII) and the aziridine (XXXIX). Thermolysis of (XXXVII) occurs at 180 °C giving the product (XXXIX) in high yield.



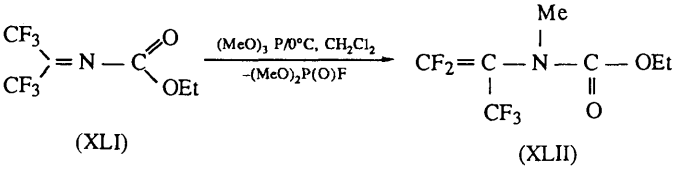
R = C(O)CF$_3$ (XI, XXXVII, XXXIX); SO_2Ph (XL, XXXVIII).

However, diazoacetic ester forms the highly stable [3 + 2] cyclic adduct (XXXVIII) with the sulphonylimine (XL) and no aziridine.[74]

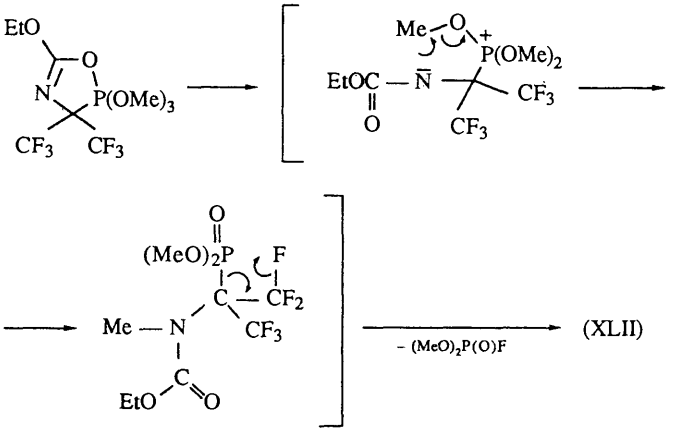
On the other hand, the acylimines of methyl trifluoropyruvate, like the acylimines of hexafluoroacetone,[100] form [1 + 4] cyclic adducts with benzyl isocyanide[32] and with compounds of three-coordinate phosphorus.[74]



An anomalous course for the reaction was established only when reacting the *N*-ethoxycarbonylimine of hexafluoroacetone (XLI) with trimethyl phosphite.[101] The reaction product proved to be the carbamate (XLII) and not the [1 + 4] cyclic adduct.

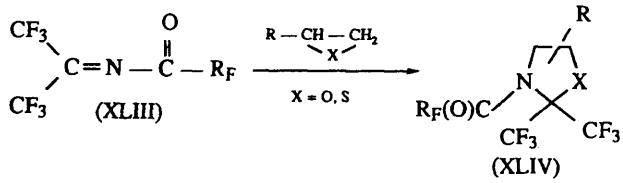


Probably the [1 + 4] cyclic adduct formed initially is readily converted into a zwitterion which is stabilised by intramolecular *N*-methylation with subsequent elimination of dimethyl fluorophosphate.



An important feature of the sulphonylimines of hexafluoroacetone is the extremely mild conditions for their reaction with oxiranes and thiiranes with the formation of [3 + 2] cyclic adducts.[7] The acylimines of hexafluoroacetone react even more vigorously with

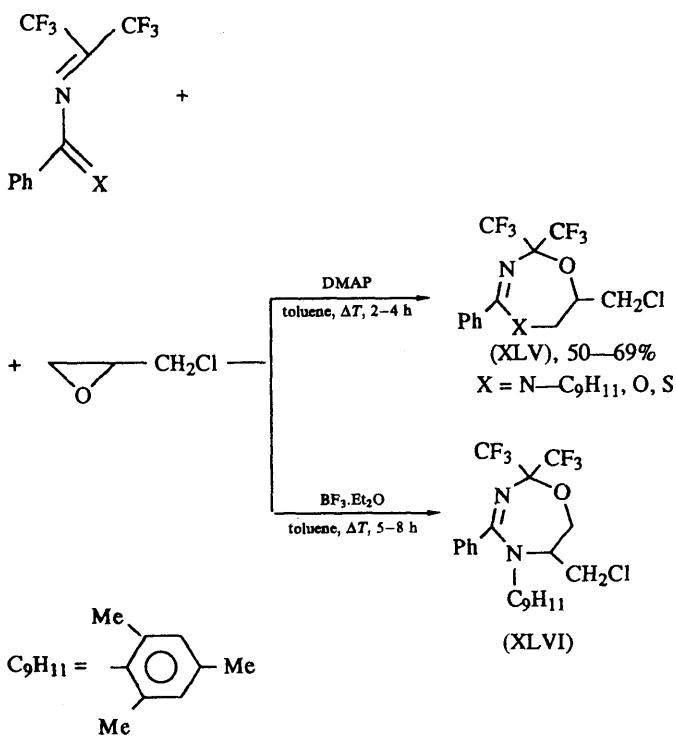
oxiranes and thiiranes.[102] The reaction of the imines (XLIII) with an oxirane occurs even at −70 °C, being accompanied by much oligomerisation, and the corresponding 1,3-oxazolines (XLIV) are successfully isolated in only small yield (15%). Methyloxirane and methylthiirane smoothly add (XLIII) under analogous conditions forming a mixture of regioisomers in 55–75% yield.[102]



(XLIII) (XLIV)

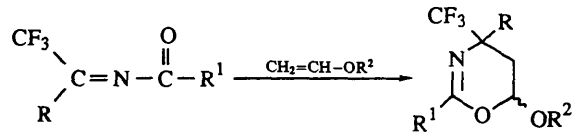
R_F = $CH(CF_3)_2$, CF_3; R = H, Me.

Acyl-, thioacyl- and iminoacylimines of hexafluoroacetone react catalytically with epichlorhydrin[103] giving the [3 + 4] cyclic adducts. On using an equimolar quantity of 4-dimethylaminopyridine (DMAP) as catalyst, the reaction leads to the selective formation of the heterooxazepines (XLV). Conduct of the reaction of the iminoacylimines with a catalytic quantity of boron trifluoride etherate leads to the tetrahydrooxadiazepine (XLVI) in 50% yield. In the absence of catalyst or with an acid catalyst a mixture of compounds is formed.



The properties of acylimines as 1,3-heterodienes have been studied widely.[7] Particular attention has been paid to their reactions with alkenes. Interest in them is due first of all to the fact that the 1,3-oxazine derivatives formed are promising synthetic intermediates.[104–106] Recently acylimines with a prochiral centre in the molecule have been used in these reactions.

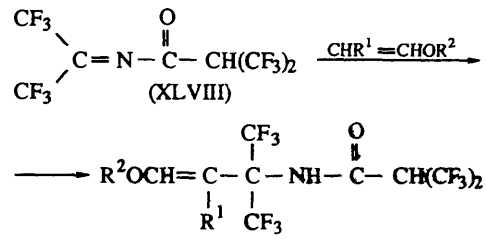
Vinyl acetate and vinyl butyl ether react under mild conditions with the acylimines of methyl trifluoropyruvate and hexafluoroacetone giving the corresponding dihydrooxazines (XLVII). The reaction is effected regioselectively and in certain cases stereoselectively as well.[29,107]



(XLVII)

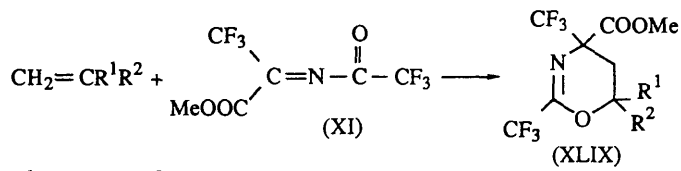
R = COOMe, Ph; R^1 = CF_3; R^2 = Ac, Bu.

The reaction of the *N*-(hexafluoro-α-hydroisobutyroyl)imine of hexafluoroacetone (XLVIII) with alkyl vinyl ethers unexpectedly leads to the product of amidoalkylation of the multiple bond.[108]



This may be explained by the steric effects of the hexafluoroisopropyl group of the imine (XLVIII) which hinders the formation of the symmetrical transition state.

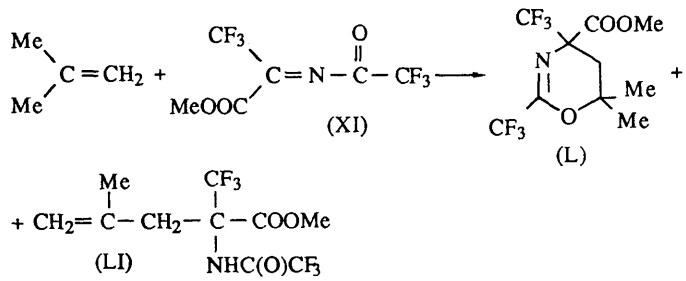
The reaction of the trifluoroacetylimine of methyl trifluoropyruvate (XI) with other terminal olefins such as 2-chloromethylpropene, propylene, methyl allyl ether, allyl iodide, bromide and chloride and methyl methacrylate also occurs regiospecifically giving the corresponding 1,3-dihydrooxazines (XLIX) in preparative yield. The optimum reaction temperature increases from 10 to 70 °C in the series shown.[109]



(XI) (XLIX)

R^1 = H, Me; R^2 = Me, CH_2OMe, CH_2Cl, CH_2Br, CH_2I, COOMe.

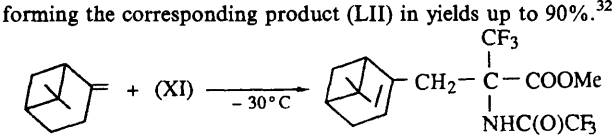
However, the product of the ene reaction (LI) is formed in addition to the 1,3-dihydrooxazine (L) in the reaction of the imine (XI) with 2-methylpropene. The content of (LI) increases from 15 to 25% on increasing the reaction temperature to −78 to 20 °C.[29]



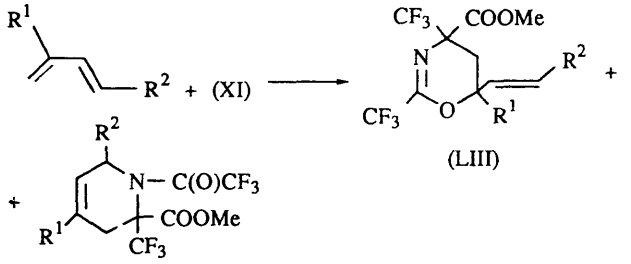
(XI) (L)

(LI)

β-Pinene, being extremely reactive in ene reactions, reacts with (XI) forming the corresponding product (LII) in yields up to 90%.[32]

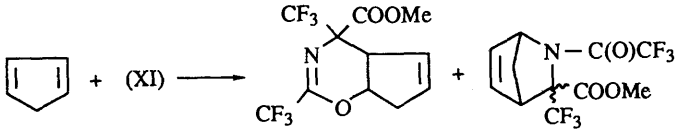


The imine (XI) also displays the properties of a strong 1,3-heterodiene in reactions with 1,3-dienes which is not a characteristic of the perfluoroacylimines of hexafluoroacetone.[110,111] Thus on reacting (XI) with butadiene, isoprene and piperylene the main reaction products proved to be the 1,3-dihydrooxazines (LIII), which are the [2 + 4] cyclic adducts. Products of the Diels–Alder reaction or the [4 + 2] cyclic adducts, which were expected to be the main products, were present only as insignificant contaminants.[109]



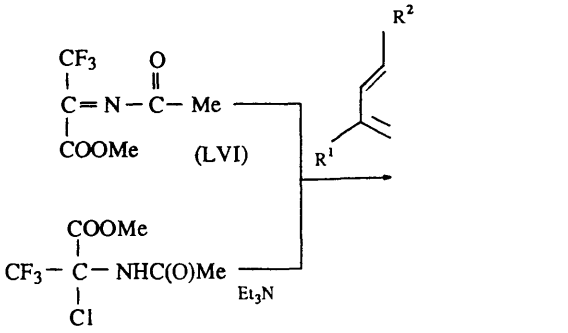
(LIII)

Even such a reactive diene as cyclopentadiene forms with imine (XI) the 1,3-dihydrooxazine (LIV) and the Diels–Alder reaction product (LV) in a ratio of 1 : 3.[109]

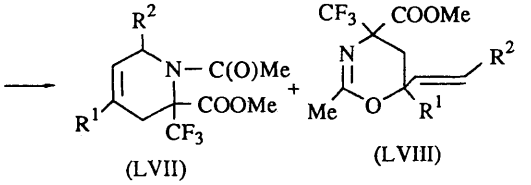


(LIV) (LV)

The character of the reaction of the less electrophilic acetylimine of methyl trifluoropyruvate with 1,3-dienes is reversed. Thus mixtures are formed in the reaction of (LVI) with isoprene and piperylene which contain up to 80% Diels–Alder reaction product (LVII) and no more than 20%, 1,3-dihydrooxazines (LVIII).[32]



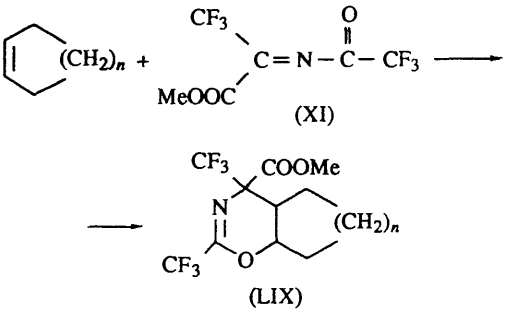
(LVI)



(LVII) (LVIII)

Analogous results were obtained on using the precursor of imine (LVI), the geminal aminochloro compound, and an HCl acceptor (Et_3N) instead of (LVI). The optimum conditions, yield, and product ratio proved to be the same as on using the pure imine.

In contrast to the terminal alkenes, cyclopentene and cyclohexene form [2 + 4] cyclic adducts (LIX) with the imine (XI) only under forcing conditions (150 °C, sealed tube).[29]

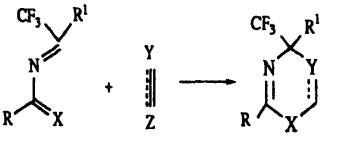


(XI)

(LIX)

$n = 1$ or 2.

Table 2. Reactions of acylimines with aldehydes, ketones and nitriles of carboxylic acids.



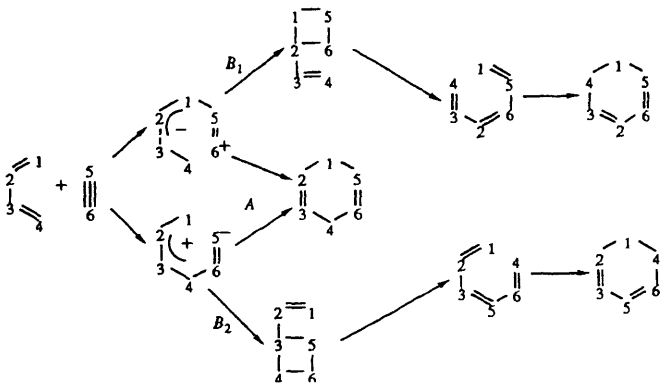
No.	R	R^1	X	Y	Z	Refs.
1	4-ClC_6H_4 Ph	CF_3	O, S, NAr O, S	O N	$C(CF_3)_2$, $CHCCl_3$ $-CCCl_3$, $-CCF_3$	[108]
2	$C(CF_3)=CF_2$	CF_3	O	O	$C(CF_3)_2$ $-CCH_3$	[66]
3	$C(CF_3)_3$	CF_3	O	O	CHPh	[112]
4	4-ClC_6H_4 Ph	CF_3	O, S, NAr	O	$C(R^1)-C(R^2)=CHR^3$, ($R^1=R^2=H$, Me; $R^3=H$, Ph)	[113]
5	Ph	CF_3	NAr	N	$-CCH=CHR$(R = Me, Ph) $-CC(R_1)=CHR^2$(R_1 = H, Me; R_2 = H, Ph). $-CC\equiv CPh$	[114]
6	C_3F_7 $CH(CF_3)_2$	CF_3	O	N	$-CPh$, $-CMe$, $-CCH=CH_2$, $-CCH_2COOEt$	[115]
7	Ph	CF_3	NAr	N	$-CNMe_2$, $-CMe$, $-CPh$	[116]
8	Ph	CF_3	S	N	$-CC(CN)=C(CN)_2$	[117]
9	CF_3	CF_3	O	N	$-C(NH_2)-N=C(Me)-NH-C(O)-P(OEt)_2$ Et	[118]
10	CF_3	CO_2Me	O	N	$-Cr^1$(R^1 = Me, $CH_2=CH-$)	[29, 32]

The acyl-, thioacyl- and iminoacylimines of hexafluoroacetone and the acylimines of methyl trifluoropyruvate are inclined to form rings even with such weak heterodienophiles as aldehydes, ketones and nitriles. Products (heterocycles) typical of [2 + 4] cycloaddition reactions are formed in several cases. Examples of these reactions are shown in Table 2.

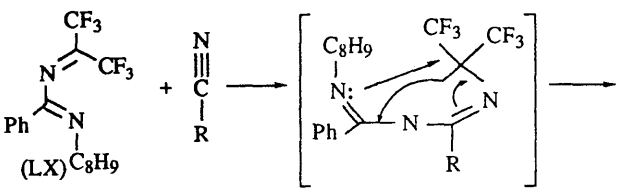
Cases are also known of the formation of compounds of anomalous structure the appearance of which is the result of stepwise conversions. The theoretical aspects of such reactions have

been considered by K Burger and his collaborators.[116] They proceeded from the fact that the reactions of polar 1,3-dienes with polar unsaturated systems usually occur as charge-controlled processes.[119] The stabilisation of the intermediates formed, the 1,X-dipoles (Scheme 1), may be effected by closing either a six- or a four-membered ring. The greater the degree of rotation of the 1,X-dipole the greater its lifetime and the greater the probability of forming a six-membered ring in the reaction. On the other hand, the formation of a four-membered cyclic system is preferred for destabilised 1,X-dipoles and in its turn it may be converted by fission of the 1–2 and 3–4 bonds giving products different from those formed by route *A*.

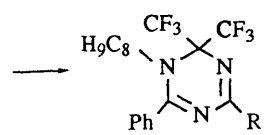
Scheme 1



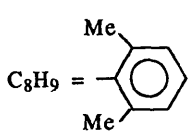
A similar scheme is proposed for the reaction of the 4,4-bis(trifluoromethyl-1,3-diazabuta-1,3-diene (LX) with carboxylic acid nitriles.[116] The reaction of dimethylcyanamide, aceto- and benzonitriles in this system leads to the expected 1,3,5-triazine (Scheme 1, route *A*). However, in the reaction of the diazobutadiene (LX) with electron-deficient nitriles such as 4-chlorophenylazonitrile, trichloro- and trifluoroacetonitrile, the products proved to be the triazines (LXI) with a reorganised diene skeleton which is only possible via route B_1 (Scheme 1).



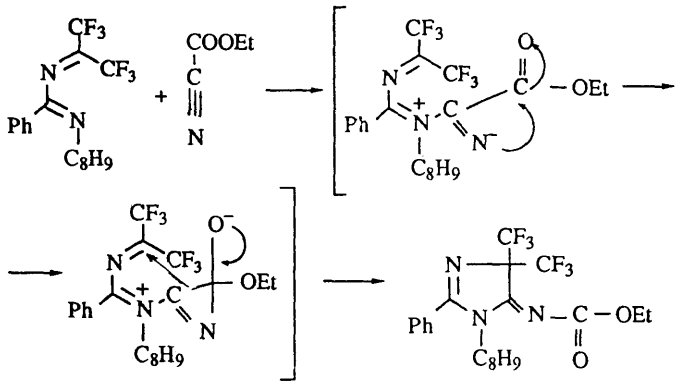
(LX) C_8H_9 =



(LXI)

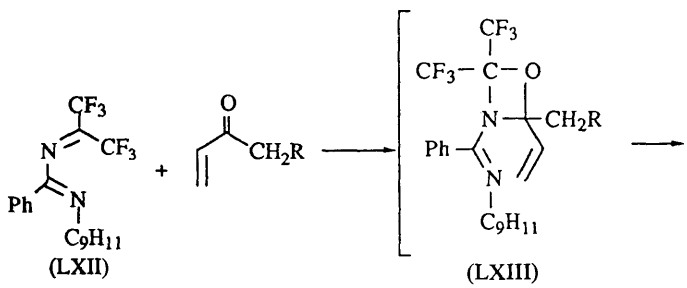


Diazabutadiene (LX) reacts most unusually with ethyl cyanoformate.[120]

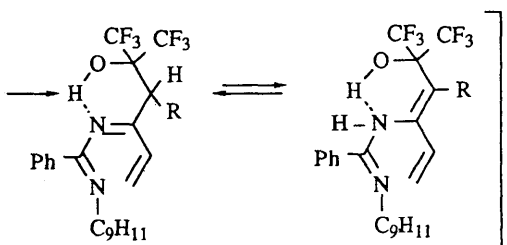


A similar cyclisation was observed previously in the acylation of acetophenone dianion.[121]

The reaction of heterodiene (LXII) with α,β-unsaturated ketones proved to be anomalous in a series of aldehydes and ketones.[122]

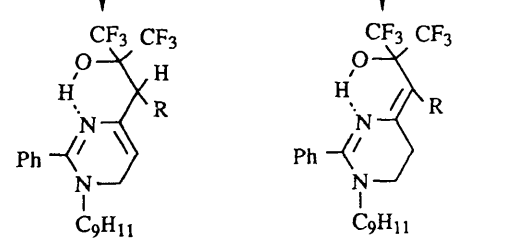


(LXII) (LXIII)



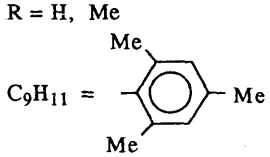
(LXIV) (LXV)

electrocyclisation ene reaction



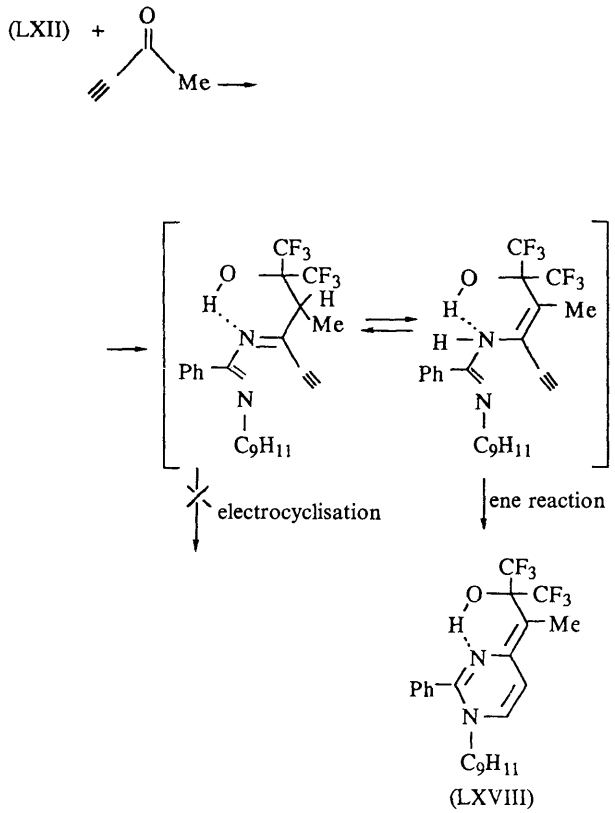
(LXVI) (LXVII)

R = H, Me



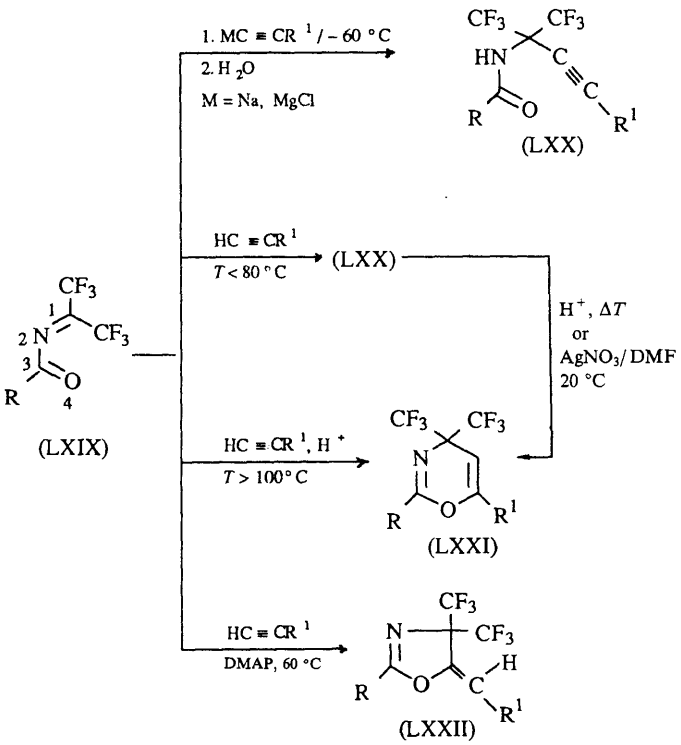
It is considered that the four-membered ring intermediate (LXIII) undergoes decomposition to hexafluoroacetone and a 1,3-diaza-1,3,5-triene which react by an ene mechanism giving the product (LXIV) existing in two tautomeric forms (LXIV) ⇄ (LXV). In their turn compounds (LXIV) and (LXV) cyclise to the final products (LXVI) and (LXVII) electrocyclically and according to an intramolecular ene reaction mechanism respectively.

The heterodiene (LXII) also reacts in a similar manner with acetylacetylene giving only one product (LXVIII) since in this case the electrocyclic reaction is hindered.[122]

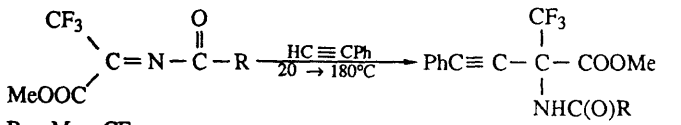


(LXVIII)

Acetylenes react with fluorine-containing 1,3-heterodienes giving the corresponding trifluoromethyl-substituted *N*-propargylamides,[32,123] 4H-1,3-oxazines[118,123] and 2-oxazolines.[123,124] The selectivity of these processes depends on the reaction conditions. Thus the acylimine (LXIX) reacts with electron-rich terminal acetylenes and alkali metal acetylides forming *N*-propargylamides (LXX). Cyclisation of these compounds under the action of acid catalysts or silver nitrate leads quantitatively to the 1,3-oxazines (LXXI). However, the electron-deficient alkynes form five-membered cyclic systems with (LXIX) including in the ring only the terminal carbon atom of the acetylene. The addition of 4-dimethylaminopyridine (DMAP) to the acylimine (LXIX) leads to the reversible blocking of the electrophilic position 1 in (LXIX) which increases the nucleophilicity of position 4. The oxazoline (LXXII) is therefore formed exclusively.

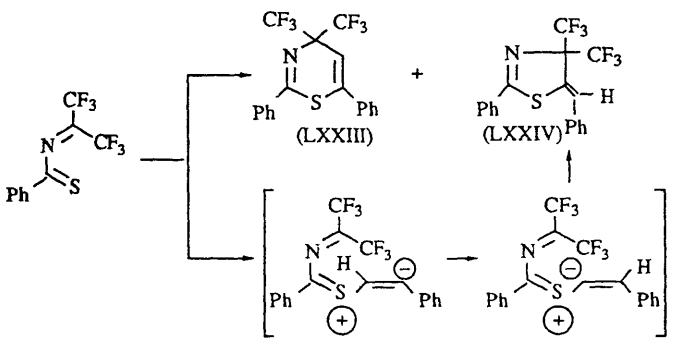


The acylimine (LXIX) forms adduct (LXX) with phenylacetylene by a Michael reaction. On heating the adduct is transformed into the oxazine (LXXI). This was not observed in the case of the acetyl- and trifluoroacetylimines of methyl trifluoropyruvate.[32]



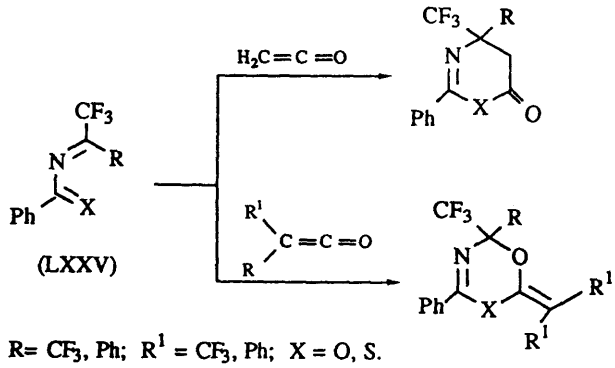
R = Me, CF_3.

On heating in phenylacetylene (80–90 °C) the thio analogue of the acylimine (LXIX) forms a mixture (1 : 1) of the products (LXXIII) and (LXXIV). The product (LXXIII) is formed by a Michael addition but the product (LXXIV) is formed through a cyclisation in which the skeleton of the dienophile is included in the cyclic system only partially. This occurs according to the following postulated mechanism.[124]



An analogous reaction was observed by Giordano[125,126] in the hydrocarbon series when reacting phenylacetylene with the imine generated *in situ* from thiobenzoic acid amide and benzaldehyde by the action of boron trifluoride ethereate.

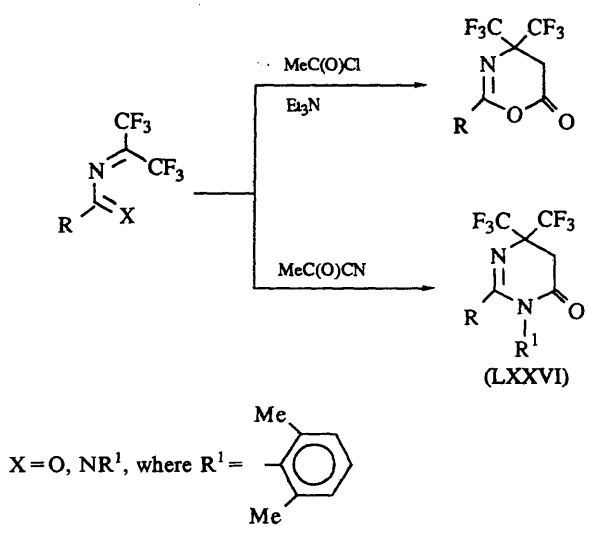
The acylimines of polyfluoroketones react with ketene by a [2 + 4] cycloaddition mechanism forming the corresponding cyclic adducts at the C=C bond.[107,127–129] However, in the reaction of the heterodiene (LXXV) with diphenyl-[127] and bis(trifluoromethyl)-ketenes[129] ring formation occurs at the C=O bond.



R= CF_3, Ph; R^1 = CF_3, Ph; X = O, S.

Desimoni and Tacconi[130] have considered this reaction from the point of view of frontier molecular theory orbitals. They showed by correlation diagrams that the reaction of the benzoylimine of hexafluoroacetone with a ketone occurs as an inverted Diels–Alder reaction, i.e. by a [2 + 4] cycloaddition mechanism. On the other hand the benzoylimine reacts as a π-donor with hexafluorodimethyl-ketene, i.e. a typical [4 + 2] cycloaddition is implemented. This also determines the observed differences in the reaction pathways.

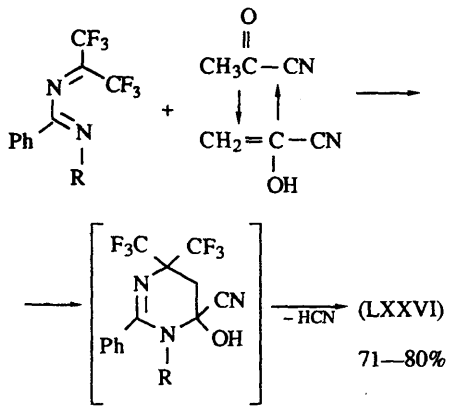
It is also possible to use ketene precursors, such as a mixture of acetyl chloride with triethylamine or nitriles of α-ketocarboxylic acids, in the reaction with acyl- and iminoacylimines.[127]



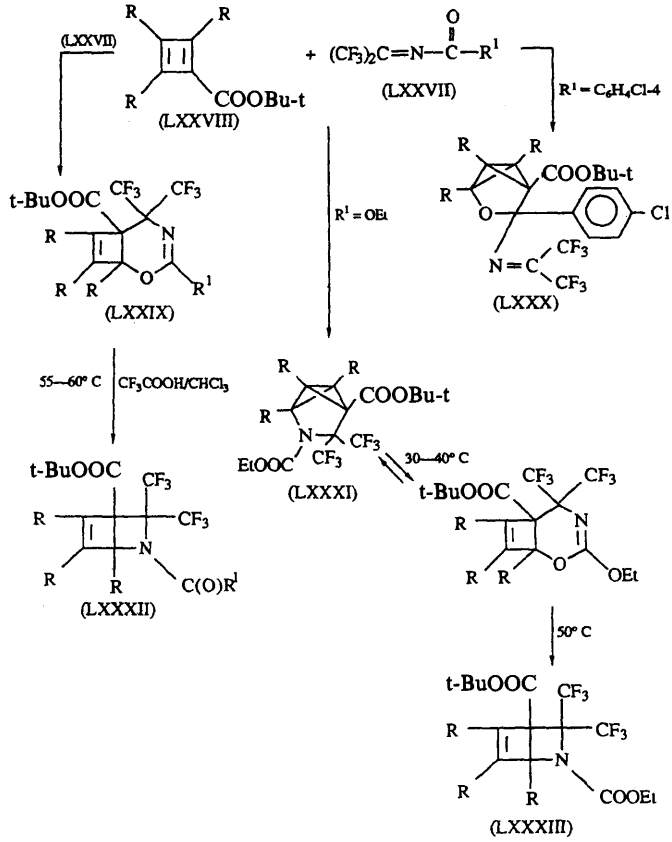
X=O, NR^1, where R^1=

R = Ph, 4-MeC_6H_4, 4-ClC_6H_4 .

Formation of the product (LXXVI) occurs on reaction of the heterodiene with the enolic form of pyruvic acid nitrile. The [2 + 4] cyclic adduct formed initially eliminates HCN spontaneously giving compound (LXXVI) in high yield.



Reaction of the *N*-acylimines (LXXVII) of hexafluoroacetone with cyclobutadiene (LXXVIII) leads to the formation of the oxazabicyclo[4.2.0]octadienes (LXXIX).[131] Exceptions are the reaction of (LXXVIII) with the imine (LXXVII, R^1 = C_6H_4Cl), when the tricyclic isomer (LXXX) is formed, and with the ethoxycarbonylimine of hexafluoroacetone (LXXVII, R^1 = OEt) which leads to the 3-azatricyclo[3.1.0^{2,6}]hexane (LXXXI). Compounds (LXXIX) and (LXXXI) are readily transformed into the bicyclic compounds (LXXXII) and (LXXXIII) respectively.[131]



R = t-Bu; R^1 = iso-Pr, Ph, 4-$MeOC_6H_4$.

(LXXIX) $\xrightarrow[14\ h]{165\ ^\circ C}$ (LXXXII)

The literature data considered in this review suggest that the known methods of synthesising fluorine-containing ketimines may be used for obtaining practically all possible types of these interesting compounds. The broad study of the properties of the various ketimines has increased the preparative accessibility of many biologically active fluorine-containing compounds, particularly fluorine-substituted aminoacids, amines and heterocyclic compounds of various types.

It may be expected that further work on the synthesis and study of the properties of fluorine-containing ketimines will be directed mainly to the development of preparative methods for obtaining various β-fluorine-containing α-aminoacids the biological activity of which is linked with the selective irreversible inhibition of pyridoxal phosphate-dependent enzymes.[132] This will probably trigger research in the least studied areas of the chemistry of these highly reactive synthons, for example, the ene reaction, various heterocyclisation reactions and further conversions of the primary products of cycloaddition reactions.

References

1. A V Fokin, A T Uzun, V P Stolyarov *Usp. Khim.*, 1977, **46**(11) 1995 [English translation in *Russ. Chem. Rev.*, 1977(11)]
2. A V Fokin, Yu N Studnev, L D Kuznetsova *Reaktsii i Metody Issledovaniya Organicheskikh Soedinenii. Kn. 24* (Reactions and Methods of Investigating Organic Compounds. Book 24), Khimiya, Moscow, 1976
3. N P Gambaryan *Usp. Khim.*, 1976, **45**(7) 1251 [English translation in *Russ. Chem. Rev.*, 1976(7)]
4. D P Del'tsova, Dissertation for Candidate of Chemical Sciences, INEOC AN SSSR, Moscow, 1974, p. 38
5. N De Kimpe, N Schamp *Org. Prep. Proced. Int.*, 1979, **11** 115
6. N De Kimpe, H Verhe *Org. Prep. Proced. Int.*, 1980, **12** 53
7. A V Fokin, A F Kolomiets, N V Vasil'ev *Usp. Khim.*, 1984, **43**(2) 398 [English translation in *Russ. Chem. Rev.*, 1984(2)]
8. M C Salon, S Hamman, C G Beguin *J. Fluorine Chem.*, 1985, **27** 361
9. M Remli, A I Ayi, I Condom, et al. *J. Fluorine Chem.*, 1987, **35** 71
10. US P. 3976689; *Chem. Abs.*, 1977, **86** 121774g
11. M Remli, A I Ayi, I Condom, et al. *Bull. Soc. Chim. Fr.*, 1986, **6** 864
12. J Welch, K W Seper *J. Org. Chem.*, 1986, **51** 119
13. J Welch, K W Seper *J. Org. Chem.*, 1988, **53** 2991
14. Japanese P. 59-273294; *Ref. Zh. Khim.*, 1987, 190461P
15. N Naji, P Moreau *J. Fluorine Chem.*, 1987, **37** 289
16. P Moreau, N Naji, A Commeyras *J. Fluorine Chem.*, 1987, **35** 28
17. V A Soloshonok, Yu L Yagupol'skii, V P Kukhar' *Zh. Org. Khim.*, 1988, **24** 1638
18. V P Kukhar', V A Soloshonok, S I Galushko, et al. *Dokl. Akad. Nauk SSSR*, 1990, **31** 986
19. A E Zelenin, N D Chkanikov, A F Kolomiets, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 231
20. US P. 4411912; *Chem. Abs.*, 1983, **99** 122072o
21. A E Zelenin, N D Chkanikov, A F Kolomiets, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2080
22. I L Knunyants, N P Gambaryan, C Y Ch'en, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1962, 684
23. N D Chkanikov, V D Sviridov, A E Zelenin, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 383
24. Shin-Ya Seiji, N Ishikawa *Bull. Chem. Soc. Jpn.*, 1977, **50** 1
25. A V Fokin, V P Stolyarov, I A Timofeenko, et al. *V Vsesoyuz. Konf. po Khimii Ftora: Tez. Dokl.* (Vth All-Union Conference on Fluorine Chemistry: Abstracts), Zvenigorod, 1986, p. 42
26. K Burger, U Wassmuth, S I Penninger *J. Fluorine Chem.*, 1982, **20** 813
27. K Burger, E Höss, K Gaa *Chem. Ztg.*, 1989, **113** 243
28. S N Osipov, N D Chkanikov, A F Kolomiets, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1384
29. S N Osipov, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 132
30. S N Osipov, A F Kolomiets, A V Fokin *V Vsesoyuz. Konf. po Khimii Ftora: Tez. Dokl.* (Vth All-Union Conference on Fluorine Chemistry: Abstracts), Zvenigorod, 1986, p. 125
31. S N Osipov, N D Chkanikov, A F Kolomiets, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1684
32. S N Osipov, Dissertation for Candidate of Chemical Sciences, INEOC AN SSSR, Moscow, 1991, 50 pp
33. S N Osipov, A F Kolomiets, A V Fokin *J. Fluorine Chem.*, 1991, **54** 272
34. V A Soloshonok, I I Gerus, Yu L Yagupol'skii *Zh. Org. Khim.*, 1986, **22** 1335
35. V A Soloshonok, I I Gerus, Yu L Yagupol'skii, et al. *Zh. Org. Khim.*, 1987, **23** 2308
36. V A Soloshonok, I I Gerus, Yu L Yagupol'skii, et al. *Zh. Org. Khim.*, 1988, **24** 993
37. R W Hartman, M D Orde, A Heinde, et al. *Arch. Pharm. (Weinheim, Ger.)*, 1988, **321** 497
38. W Zidy, W Sundermeyer *Chem. Ber.*, 1976, **109** 1491
39. A S Golubev, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2461
40. L A Lazukina, V P Kuchar *Synthesis*, 1979, (9) 383
41. L A Simonyan, Z V Safronova, I L Knunyants, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 358
42. V N Fetyukhin, M V Vovk, L I Samarai *Zh. Org. Khim.*, 1983, **19** 1232
43. V N Fetyukhin, A S Koretskii, V I Gorbatenko, et al. *Zh. Org. Khim.*, 1977, **13** 271
44. O V Korenchenko, V B Sokolov, A Yu Aksinenko, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 373
45. V I Gorbatenko, N V Mel'nichenko, L I Samarai *Zh. Org. Khim.*, 1986, **22** 1184
46. M V Vovk, M N Bretsko, V I Dorokhov *Zh. Org. Khim.*, 1989, **25** 759
47. M V Vovk, V I Dorokhov, V V Pirozhenko, et al. *Zh. Org. Khim.*, 1989, **25** 1634
48. V N Fetyukhin, M V Vovk *Zh. Obshch. Khim.*, 1983, **53** 1763
49. M V Vovk, V I Dorokhov, L I Samarai *Zh. Org. Khim.*, 1989, **25** 754
50. V I Fetyukhin, M V Vovk, V V Pirozhenko, et al. *Zh. Org. Khim.*, 1983, **18** 2071
51. M V Vovk, V I Dorokhov, L I Samarai *Zh. Org. Khim.*, 1988, **24** 727
52. M Iznaden, C Portella *Tetrahedron Lett.*, 1988, **29** 3683
53. T Ishihara, T Mackawa, T Ando *Tetrahedron Lett.*, 1983, **24** 4229
54. Y Yamasaki, T Mackawa, T Ishihara *Chem. Lett.*, 1985, **9** 1387

55. P P Stepanova, M A Orlova, E S Turbanova, et al. *V Vsesoyuzn. Konf. po Khimii Ftora: Tez. Dokl.* (Vth All-Union Conference on Fluorine Chemistry: Abstracts), Zvenigorod, 1986, p. 165
56. I Froissard *J. Fluorine Chem.*, 1981, **17** 249
57. French P. 2612189; *Chem. Abs.*, 1989, **110** 38902y
58. A Haas, K Peterman *J. Fluor. Chem.*, 1986, **30** 438
59. D Sohu, W Sundermayer *Chem. Ber.*, 1982, **115** 3334
60. A F Gontar', E M Glotov, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 691
61. V F Snegirev, E V Zakharova, K N Makarov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1352
62. V A Petrov, V K Kunanets, B A Kvasov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 122
63. N Ishikawa *Preparation and Function of Fluorine Compounds* (Translated into Russian), Mir, Moscow, 1990, 183 pp
64. V P Kukhar', Yu L Yagupol'skii, V A Soloshonok *Usp. Khim.*, 1990, **59**(1) 149 [English translation in *Russ. Chem. Rev.*, 1990(1)]
65. H Seltzman, T M Chapman *J. Org. Chem.*, 1975, **40** 2414
66. L N Kryukov, L Yu Kryukova, A I Poletaev, et al. *V Vsesoyuzn. Konf. po Khimii Ftora: Tez. Dokl.* (Vth All-Union Conference on Fluorine Chemistry: Abstracts), Zvenigorod, 1986, p. 21
67. H Kischkel, G V Roschenthaler *Z. Naturforsch.*, 1984, **39** 356
68. I V Martynov, A Yu Aksinenko, A N Chekhlov, et al. *Zh. Obshch. Khim.*, 1989, **59** 809
69. A F Janren *J. Inorg. Nucl. Chem.*, 1981, **43** 629
70. S N Osipov, V B Sokolov, A F Kolomiets, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1185
71. Yu V Sinyakov, N V Vasil'ev, A F Kolomiets, et al. *Zh. Org. Khim.*, 1986, **22** 232
72. Yu V Sinyakov, N V Vasil'ev, A F Kolomiets, et al. *Zh. Org. Khim.*, 1989, **25** 642
73. K Burger, K Gaa *Chem. Ztg.*, 1990, **114** 101
74. S N Osipov, A F Kolomiets, A V Fokin *6th Regular Meeting of Soviet–Japanese Fluorine Chemists*, Novosibirsk, 1989, F
75. V M Cherkasov, N A Kapran, Yu L Yagupol'skii *Khim. Geterotsikl. Soedin.*, 1982, 842
76. K Burger, T Kahl *Chem. Ztg.*, 1988, **112** 109
77. K Burger, K Seith, T Kahl *J. Fluorine Chem.*, 1987, **35** 25
78. K Burger, T Kahl *J. Fluorine Chem.*, 1987, **37** 53
79. M V Vovk, V I Dorokhov, L I Samarai *Zh. Org. Khim.*, 1989, **25** 2457
80. US P. 3853902; *Chem. Abs.*, 1975, **82** 112959a
81. N P Gabaryan, D P Del'tsova, Z V Safronova *Izv. Akad. Nauk SSSR, Ser Khim.*, 1987, 1814
82. K Burger, H Partseht, E Huber *Chem. Ztg.*, 1985, **109** 185
83. A V Fokin, N D Chkanikov, V L Vershinin, et al. *Izv. Akad. Nauk SSSR, Ser Khim.*, 1985, 1364
84. N D Chkanikov, V L Vershinin, S V Sereda, et al. *Izv. Akad. Nauk SSSR, Ser Khim.*, 1986, 1546
85. S N Osipov, N D Chkanikov, A F Kolomiets, et al. *Izv. Akad. Nauk SSSR, Ser Khim.*, 1989, 2131
86. N D Chkanikov, V L Vershinin, A F Kolomiets, et al. *Izv. Akad. Nauk SSSR, Ser Khim.*, 1987, 684
87. L Yu Kryukova, L N Kryukov, G A Sokol'skii *Zh. Org. Khim.*, 1986, **22** 1334
88. US P. 4335136; *Chem. Abs.*, 1982, **96** 68815g
89. US P. 4348404; *Chem. Abs.*, 1982, **97** 6299d
90. S Ya Mel'nik, A A Bakhmedova, A A Yartseva, et al. *Bioorg. Khim.*, 1987, **13** 934
91. V D Sviridov, N D Chkanikov, I A Korbukh, et al. *Izv. Akad. Nauk SSSR, Ser Khim.*, 1989, 1656
92. S N Osipov, N D Chkanikov, A F Kolomiets, et al. *Izv. Akad. Nauk SSSR, Ser Khim.*, 1989, 213
93. N D Chkanikov, V L Vershinin, A F Kolomiets, et al. *Izv. Akad. Nauk SSSR, Ser Khim.*, 1986, 952
94. N D Chkanikov, V L Vershinin, A F Kolomiets, et al. *V Vsesoyuz. Konf. po Khimii Ftora: Tez. Dokl.* (Vth All-Union Conference on Fluorine Chemistry: Abstracts), Zvenigorod, 1986, p. 98
95. N D Chkanikov, V L Vershinin, M V Galakhov, et al. *Izv. Akad. Nauk SSSR, Ser Khim.*, 1989, 126
96. N D Chkanikov, A E Zelenin, M V Galakhov, et al. *Zh. Org. Khim.*, 1985, **21** 1358
97. N P Gambaryan, D P Del'tsova, Z V Safronova *Izv. Akad. Nauk SSSR, Ser Khim.*, 1987, 2022
98. Yu V Zeifman, L T Lantseva *Izv. Akad. Nauk SSSR, Ser Khim.*, 1986, 248
99. Yu V Zeifman, N P Gamaryan, L A Simonyan, et al. *Zh. Obshch. Khim.*, 1967, **37** 2476
100. V B Sokolov, A Yu Aksinenko, O V Korenchenko, et al. *Izv. Akad. Nauk SSSR, Ser Khim.*, 1989, 1213
101. O V Korenchenko, A Yu Aksinenko, V B Sokolov, et al. *Izv. Akad. Nauk SSSR, Ser Khim.*, 1990, 2879
102. L Yu Kryukova, L N Kryukov, A F Kolomiets *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1986, **31** 112
103. K Burger, G Maier, T Kahl *Chem. Ztg.*, 1988, **112** 111
104. R R Schmidt *Synthesis*, 1972, 333
105. S N Osipov, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser Khim.*, 1989, 746
106. S N Osipov, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser Khim.*, 1990, 2456
107. M T Kolycheva, I I Gerus, Yu L Yagupol'skii, et al. *Zh. Org. Khim.*, 1991, **27** 117
108. L Yu Kryukova, L N Kryukov, G A Sokol'skii *Zh. Org. Khim.*, 1987, **23** 230
109. S N Osipov, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser Khim.*, 1991, 1130
110. L N Kryukov, L Yu Kryukova, A F Kolomiets *Zh. Org. Khim.*, 1981, **17** 2629
111. L N Kryukov, L Yu Kryukova, A F Kolomiets *Zh. Org. Khim.*, 1982, **18** 1873
112. D P Del'tsova, Z B Safronova, N P Gambaryan *IV Vsesoyuz. Konf. po Khimii Ftora: Tez. Dokl.* (IVth All-Union Conference on Fluorine Chemistry: Abstracts), Moscow, 1982, p. 208
113. K Burger, W Schontag, U Wassmuth *Z. Naturforsch., B*, 1982, **37** 1669
114. K Burger, W Schontag, U Wassmuth *J. Fluorine Chem.*, 1983, **22** 99
115. Authors Certificate 743997 USSR, 1981; *Ref. Zh. Khim.*, 2N184P
116. K Burger, U Wassmuth, H Partsch, et al. *Chem. Ztg.*, 1984, **108** 205
117. J R Moran, R Huisgen, J Kalwinsch *Tetrahedron Lett.*, 1985, **26** 1849
118. A N Chekhlov, A Yu Aksinenko, O V Korenchenko, et al. *Dokl. Akad. Nauk SSSR*, 1988, **302** 107
119. R Compper *Angew. Chem., Int. Ed. Engl.*, 1969, **8** 322

120. K Burger, H Partsch, E Huber, et al. *Chem. Ztg.*, 1984, **108** 209
121. J Smith, E Simpson *Tetrahedron Lett.*, 1971, **35** 3295
122. K Burger, U Wassmuth, E Huber, et al. *Chem. Ztg.*, 1984, **108** 213
123. K Burger, N Sewald, H Huber, et al. *Z. Naturforsch.*, 1989, **44** 1298
124. K Burger, E Huber, W Schöntag, et al. *J. Chem. Soc., Chem. Commun.*, 1983, 945
125. C Giordano *Gazz. Chim. Ital.*, 1974, **104** 849
126. C Giordano *Gazz. Chim. Ital.*, 1975, **105** 1265
127. K Burger, E Huber, N Sewald, et al. *Chem. Ztg.*, 1986, **110** 83
128. Yu V Zeifman, N P Gmbaryan, L A Simonyan, et al. *Zh. Obshch. Khim.*, 1967, **37** 2476
129. N P Gambaryan, Yu V Zeifman *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 2059
130. G Desimoni, I Tacconi *Chem. Rev.*, 1975, **75** 651
131. G Michels, M Hermesdorf, J Schneider *Chem. Ber.*, 1988, **121** 1775
132. J Welch *Tetrahedron*, 1987, **43** 123

Received 5th March 1992

Translated from *Uspekhi Khimii* 61 1491 – 1514 (1992) U.D.C. 543.253.577.087

Chemically modified electrodes as amperometric sensors in electroanalysis

G K Budnikov, J Labuda
Kazan State University
Slovak Technical University

ABSTRACT. The state and prospects in the development of new fields of electroanalytical chemistry, namely amperometric sensors based on chemically modified electrodes, are examined. The methods for the construction of these electrodes, the types of modifying agents, and the mechanisms of their response to substrates are discussed. The analytical possibilities of chemically modified electrodes, including amperometric biosensors based on them, in the solution of problems associated with ecology, medicine, and pharmacology are demonstrated.

Contents

I. Introduction 816
II. Amperometric sensors based on chemically modified electrodes 817
III. Applications of chemically modified electrodes in electroanalytical chemistry 825

I. Introduction

The conviction that success in research and analysis is associated with the degree of purity of the surfaces of electrodes has held sway in electroanalytical chemistry for a long time. Specialists in electroanalysis endeavoured to achieve an ideal insert surface reproducible from measurement to measurement. Such a surface was provided by a mercury drop flowing from a capillary (mercury dropping electrode). The creation of the mercury dropping electrode gave rise to a renaissance in voltammetry and related methods. However, there exist a number of factors which hinder the extension of voltammetry in various practical applications:

the laborious nature of the electroanalytical methods associated with the use of the mercury dropping electrode;

the toxicity of the material of this electrode;

the difficulty of interpreting the results of measurements in cases where the adsorption of the depolariser and intermediate species, the effect of impurities, and the effect of the structure of the electrical double layer, etc. complicate the electrochemical process.

Apart from mercury, other materials and compositions have been used for electrodes.[2] Among them, the so called chemically modified electrodes (CME) have gained the greatest recognition. The study of the American investigators Miller and Van de Mark[3] on the application of an electrode coated with an electrically conducting polymer film was published in 1978. During modification, a chemical compound or polymer film is deposited in a special way on the electrode surface. This alters its capacity for the voltammetric response as a result of the appearance of new electrocatalytic properties. Electrocatalytically active compounds, for example metal, complexes with organic ligands or certain organic compounds capable of functioning as ligands, or enzymes are "bound" to the electrode surface either chemically (covalently), or as a result of adsorption, or by incorporation into the polymer film. The "contamination" of the electrode surface, with which electroanalytical chemists struggled in earlier days, came to be used beneficially and purposefully under control. The quality of the modification is monitored as carefully as the purity of the electrode surface has been estimated previously.

In principle, the concept of the "chemically modified electrode" can be treated in a broad sense. For example, any electrode the molecular structure of the surface of which has been acted upon appropriately (chemically or physically), altering thereby the electrochemical and in particular the amperometric response, can be included among chemically modified electrodes. In a recently published monograph,[4] certain problems of the modification of electrodes by polymer films, their electrocatalytic properties, the mechanisms of charge transfer through these films, and also their use in organic electrochemistry were discussed in detail.

Chemically modified electrodes can be used for various purposes. Thus, stereospecificity in electrosynthesis can be achieved with the aid of such electrodes. This was observed, for example, when cyclodextrins were used as modifying agents.[5] Chemically modified electrodes have been used[6–8] for electroanalytical purposes. Since the voltammetric cell with two electrodes can be regarded as the prototype of the amperometric sensor, the interest in chemically modified electrodes can be explained by the endeavour to construct on the basis of such a cell a kind of sensor with a specific amperometric response to a particular substance—the substrate. Thus the search for a new type of chemically modified electrodes led to a new chemical sensor. The growing stream of information about this field has now led to the accumulation of such a large amount of data that the discussion of all the characteristic features of the operation of chemically modified electrodes by modification methods is impossible in a single review. We shall therefore consider only the principal aspects of studies in the field of chemically modified electrodes and their practical applications as specific amperometric sensors.

II. Amperometric sensors based on chemically modified electrodes

1. Methods for the modification of electrode surfaces

As noted above, the modification of an electrode can be achieved by acting in different ways on its current conducting surface. The chemical compound (the modifying agent) is usually deposited in a special way on the electrode surface, imparting to the electrode new electrocatalytic properties. The following procedures are used for the immobilisation of the catalyst:

irreversible adsorption on the electrode surface;

chemical binding with fixation of the catalyst via different groups with formation of covalent bonds;

incorporation in a polymer film;

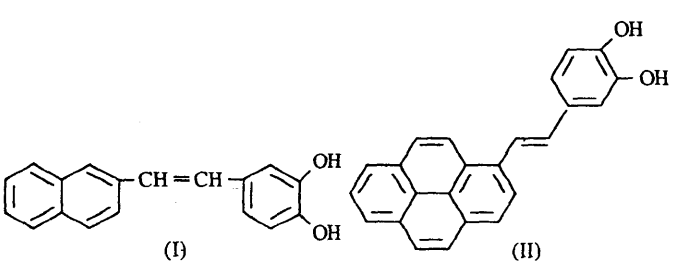
inclusion of various substances, including inorganic materials, in a paste made up of graphite materials.

Modified surfaces containing the so called sensor layer are usually subdivided into three groups depending on the nature of this layer. These can be (1) thin layers of a low-molecular-weight compound, (2) polymer films, and (3) inorganic films. It is not always possible to draw a clear-cut boundary between the groups listed above.[7]

Thus, immobilisation on the electrode surface or in its bulk phase results in the fixation of electrochemically active groups, species, or definite microstructures. The molecules of the modifying agent or its species retain their original nature, i.e. their chemical and physicochemical properties, which they possessed whilst in solution. A number of reviews have been devoted to methods for the immobilisation of modifying agents.[9,11]

The simplest modification procedure is physical or chemical adsorption. Its advantage consists in the fact that it does not require special reagents for the grafting of the catalyst; it is sufficient to activate and purify the electrode surface before depositing the modifying agent. However, its lifetime on the surface is relatively short and it gradually escapes into the solution. Various procedures increasing the retention time of the catalyst on the electrode have been described; they were developed mainly for the immobilisation of various biological materials in the creation of biosensors for a particular substrate.[11] The adsorption of polycyclic aromatic compounds on carbonaceous materials can serve as an example.[10,12] It is based on the principle of the structural similarity of the benzene rings and the hexagons on the carbon surface. Furthermore, adsorption is promoted by the low solubility of these compounds in aqueous solutions.

Adsorption usually results in the immobilisation of several layers of the organic modifying agent, for example, in the case of catalytic oxidation of NADH in the catechol [compounds (I) and (II)]–quinone [the oxidised forms of compounds (I) and (II)] system. The quinones serve as a mediating oxidising agent adsorbed on the graphite electrode. With increase in the number of aromatic rings in the catechols, the degree of their adsorption increases.[10,13]



(I) (II)

The modifying agent was retained on the electrode surface as a result of adsorption forces at a particular potential or its solution was deposited on the electrode surface with the aid of a micropipette with subsequent evaporation of the solvent.[10] This method is satisfactorily reproducible.

In order to increase the surface area of the platinum electrode, the latter is coated with platinum black. This procedure has been extended to retain enzymes as catalysts in biosensors, which will be discussed below.

A more stable immobilisation of the modifying agent can be ensured with the aid of covalent binding.[9,11] Before the chemical binding of the modifying agent, the electrode surface is activated. It is known that the surfaces of carbonaceous materials contain, after a special treatment, quinonoid, carboxy-, and phenolic groups,[2] which are capable of forming covalent bonds, for example, the amide bond, with suitable groups in the modifying agent. Amidation has been used to graft to the surface of a carbon electrode a series of aromatic amines serving as oxidants for ascorbic acid.[14,15] In this case, the carboxy-groups on the electrode surface initially react with thionyl chloride or acetyl chloride with formation of the C–Cl covalent bond which is then converted into an amide bond as a result of treatment with an amine:[6]

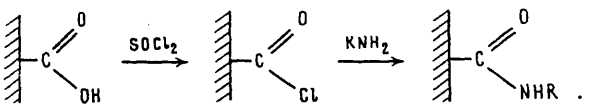


Fig. 1 illustrates schematically the modification of an electrode with the aid of covalent grafting.

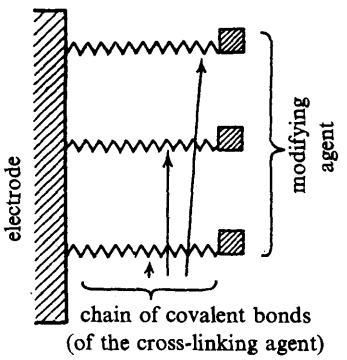
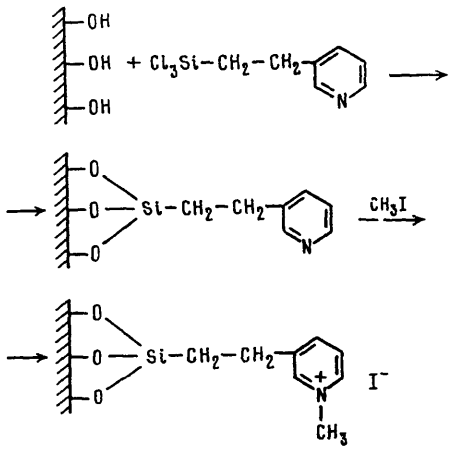


Figure 1. Schematic illustration of an electrode modified by the covalent grafting of a reagent.

Other examples of covalent binding are silanisation and the formation of ether and C–C bonds.[6,16] In this case treatment of a metallic electrode containing oxides with strong acids leads to the

formation of numerous centres with hydroxy-groups, which then interact with chloro- or alkoxy-silanes:



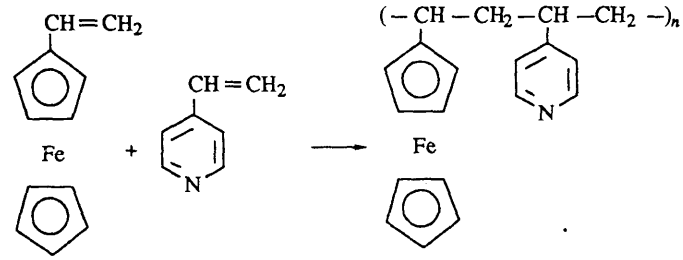
After quaternisation with the aid of methyl iodide, electrode surfaces with new properties are obtained. The coating of the electrode with such a film makes it possible to protect its surface against contamination by, for example, serum proteins, which is particularly important in immunoenzyme analysis.[17] The resulting film acquires ion-exchange properties, by virtue of which it is capable of incorporating in its structure the transferring agent anion $Fe(CN)_6^{4-}$ responsible for the analytical signal. The methods for the activation on the surface of the electrode itself (chemical, thermal, and electrochemical) have been examined in a review.[6]

Procedures for the activation of the surface with subsequent immobilisation of the reagent (catalyst) by covalent binding have been described.[11] Such an activation procedure is used mainly in the construction of biosensors,[11] but it can also be applied to other chemically modified electrodes.

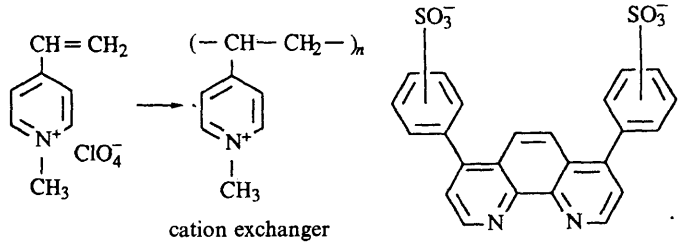
The commonest method for the immobilisation of the reagent is apparently its retention in a polymer film.[3,18–21] For example, an oxidation-reduction modifying agent can be bound to a polymer film on the electrode as a result of the electrostatic interaction of a polyanionic or polycationic electrolyte with a reagent carrying the opposite charge. This procedure is frequently employed to immobilise multicharged ions, for example, $IrCl_6^{2-}$,[22] $Ru(bipy)_3^{2+}$, $Co(bipy)_3^{2+}$, $Ru(NH_3)_6^{3+}$,[23] and $Fe(CN)_6^{4-}$,[24] where bipy represents bipyridyl.

The commonest polyelectrolytes of this kind are perfluorinated Nafion and its analogues.[25,26] In the first studies on chemically modified electrodes, electroactive polymers of the type of polyvinylferrocene were used for the modification. Subsequently, it was noted that polymer films make it possible to achieve reactions and processes such as ion exchange, membrane separation, deposition, coordination, and acid–base and oxidation-reduction equilibria on which analytical chemistry is based. The electroactive fragments of polyvinylferrocene responsible for the reversible electron transfer are the monomer units. In other films, the monomer units perform the function of ligands in reactions with metal ions. For example, the ruthenium(III) complex of EDTA is retained by coordinate bonds in a polyvinylpyridine film.[27]

The polymer film may be polyfunctional, for example, it may contain a complex-forming group in addition to the oxidation-reduction couple. The former binds selectively a particular metal ion, while the redox couple ensures contact with the electrode surface. The copolymer of vinylferrocene (ensures the presence of redox centres) and vinylpyridine (vinylbipyridyl, vinylphenanthroline) can serve as a film of this kind for chemically modified electrodes:[28]



In certain cases, the modifying agent is retained in the polymer film as a result of an ion-exchange interaction: for example, between the anionic form of the modifying agent and the cation-exchange resin:



cation exchanger (film)

anion of the sulpho-derivative of bathophenanthroline

The polymer film may contain several tens of thousands of electroactive centres.[29] The electrical conductivity of the films ensures the transfer of electrons and ions. Polymer films with bound electroactive centres (metal ions or complexes) conduct current as a result of electron exchange between the reduced and oxidised forms of these centres. The thicker the films, the greater their stability and the greater the catalytic effect and the corresponding amperometric signal. However, the coordination of a particular metal ion and the transport of charges may be hindered in films of this kind. The oxidation-reduction centres may be incompletely involved in electrocatalytic steps in thick films even at a low rate of change of the polarising potential.[30]

The electron transfer in chemically modified electrodes is influenced by the structure of the polymer and the disposition of the electroactive fragments in the polymer chain. The formal redox potential of the electroactive fragment depends on its local environment in the polymer structure. The morphology of the polymer film is influenced by the solution and the supporting electrolyte. Films characterised by a high ion-exchange capacity, insoluble in water, and swelling in aqueous solutions have been recognised as promising. Although strongly swelling films are most suitable for chemically modified electrodes because electron transfer in them is fastest, nevertheless they can partly dissolve, particularly if the polymer has a linear structure. In order to prevent this, cross-binding with the aid of bifunctional reagents (for example, glutaraldehyde) is used. The modifying agent molecules are then bound to the polymer, the electrode surface, and to one another (Fig. 2). This method is used in those cases where a long-lived

chemically modified electrode and the stability of its sensor component are required.

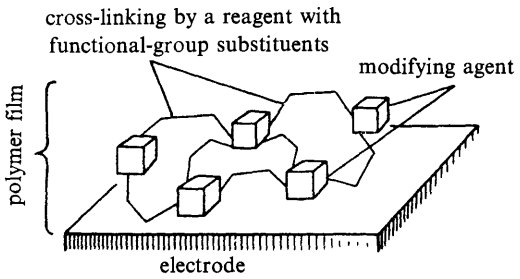


Figure 2. Schematic illustration of an electrode whose surface has been coated by a film with a cross-linked modifying agent.

Polyelectrolyte coatings are formed either by immersing the electrode in a solution (films of the Langmuir–Blodgett type) or by evaporating aliquot parts of the polyelectrolyte solution deposited on the electrode surface. The polyelectrolyte is then retained on the surface by adsorption forces. Electropolymerisation is also used to coat the electrode surfaces with films.

The immobilisation of modifying agents in the paste of a carbon-paste electrode (CPE) merits special attention because of the simplicity and ease of the method of preparation of the electrode and convenience in practical use. The modifying agent together with the carbon powder and the binding hydrophobic filler (oil) are carefully mixed in specified proportions until a homogeneous mixture is obtained and the latter is then placed in the cavity of the carbon paste electrode. The surface of such a modifying electrode is readily renewed mechanically and the amount of the modifying agent can also be readily monitored. The carbon paste electrode can be regarded as an alternative to the mercury dropping electrode (m.c.e.) in view of the ease of the renewal of its surface.

Towards the middle of the 1980s, inorganic materials as modifying agents for chemically modified electrodes attracted the attention of investigators. The layers on the electrode surface, based mainly on zeolites as well as various clays, metal oxides, silicates, etc., exhibit both chemical (in relation to the action of strong acids, oxidants, and other reagents) and thermal stability.[31]

Electrode films made up of zeolites contain three-dimensional rather than two-dimensional structures. The use of the pore dimensions in zeolites for the recognition of particular molecules or ions (the sieve effect), the possibility of discrimination among the latter as regards charge, and also combination of electrocatalysis and heterogeneous catalysis impart extremely attractive properties to such chemically modified electrodes. The cation-exchange capacity of the zeolites, which can be regulated, is also important in such cases. The combination of these factors ensure a fairly high selective response by the chemically modified electrodes. The use of commercial zeolite powders[32–34] has been described: alumino-silicates, aluminophosphates, silicatoaluminophosphates (M = Li, Mg, Be, or a transition metal). The zeolite matrix in the film on the chemically modified electrode plays the role of the "host" for the concentration or retention of a molecule or other species of suitable size ("guest"), which in the case of subsequent reactions and electrodes generate the analytical signal.

A suspension of zeolite powders in solution in a polymer is used to coat the electrode surface. After the deposition of a drop of such a mixture on the electrode, the solvent is evaporated. The retaining film-forming agent is usually polystyrene. The reproducibility of the surface of such a chemically modified electrode does not present special difficulties. Mixtures of zeolites and electrically conducting powders are also promising. The carbon paste composition (the carbon paste electrode) is convenient in this respect. Composite electrodes based on a mixture of a zeolite with a carbon powder and a polymer have also been described. The zeolite and carbon powder particles are then retained with the aid of a copolymer of styrene and a cross-linking reagent (divinylbenzene). The electrode chemically modified with the aid of such a composite mixture has a hard surface which can be readily polished and reproduced. The response time of such a chemically modified electrode is shorter than that of the carbon paste electrode.

It is appropriate to note that the guest–host concept in the mechanism of the response of chemically modified electrodes can be productive not only in the case of zeolites as modifying agents. A wide variety of macrocyclic compounds, forming stable complexes with metal ions, ensure a fairly high selectivity of the determination when present in the sensor component of the chemically modified electrode. This will be discussed below.

2. Electrocatalysis on chemically modified electrodes

It is known that by no means all organic substances are electrochemically active in the accessible range of potentials. Furthermore, the electrode reactions of some of them occur with a high overpotential and the analytical signal under these conditions can acquire a distorted form and can be poorly reproducible. One of the attractive approaches for the elimination of these undesirable phenomena consists in the use of mediators (M) which transport electrons between the electrode and a particular compound (substrate). The mediator species M and M* are components of a reversible oxidation-reduction system capable of subsequently reacting chemically with the substrate S under homogeneous conditions, i.e. in solution:

$$M \pm e \rightleftharpoons M^*, \quad (1)$$

$$M^* + S \rightleftharpoons M + S^* \quad (2)$$

$$S^* \longrightarrow P \text{ (products)}. \quad (3)$$

Thus it is possible to eliminate or greatly diminish the influence of heterogeneous factors (for example, the orientation of the substance at the electrode surface, the effect of the electrode field, the roughness and cleanliness of the surface, etc.) on the rate and degree of completion of the electrochemical reaction of the substrate S. The experimentally observed increase in the mediator current in the presence of the substrate compared with the current in its absence is a source of information about the homogeneous reaction occurring.[10] The substrate can be involved in this way in the electrochemical reaction at the normal potential of the M/M* couple and the overpotential characterising the electrode reaction of the substrate can be reduced. Since M* is regenerated, the homogeneous electron transfer can be included among catalytic processes.

Catalytic processes with subsequent homogeneous oxidation-reduction reaction are described by the familiar mechanism (Fig. 3).[35]

A necessary condition for the occurrence of the homogeneous electron transfer reaction is the stability of M* and the irreversibility of the conversion of the substrate S. Direct electron transfer to S is

characterised by an overpotential determined either by the slowness of the electron transfer stage or by the influence of the subsequent chemical reactions. The mechanism of the homogeneous reaction (2) can be various (Fig. 3). If the reversible M/M* couple functions merely as an electron transferring agent, then one is dealing with oxidation-reduction catalysis[35] or with a homomediator system.[36] On the other hand, if the adduct M*S is forming during the reaction and then decomposes with regeneration of M, then one is dealing with chemical catalysis[35] or a heteromediator system.[36] The pathways in the chemical reactions of the adduct M*S are determined by the experimental conditions (electrode, solvent) and therefore influence the process selectivity.

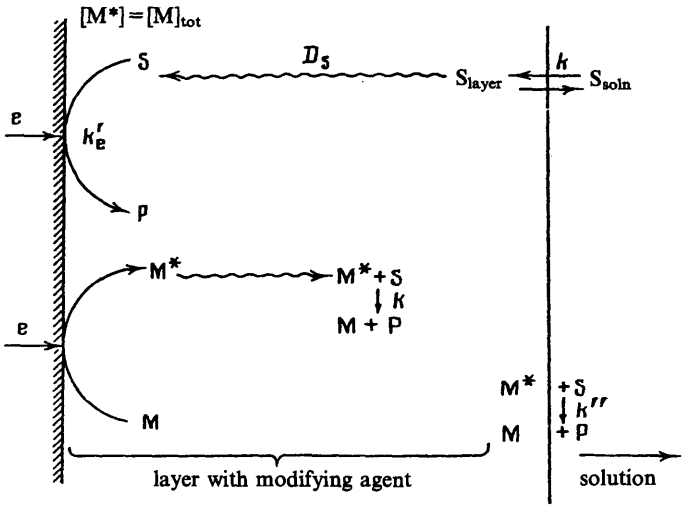


Figure 3. Schematic representation of the electrochemical process on a chemically modified electrode with a polymer coating.

The thermodynamic condition for the occurrence of homogeneous catalysis is that the standard potential of the catalyst couple E^0_{M/M^*} should be more negative (positive) than the potential of the electrode substrate reduction (oxidation) reaction $E^0_{S/P}$, where $E^0_{S/P} - E^{1/2}_S$ is the overpotential. Under these conditions, the regeneration of M depends on the rate of the irreversible reaction (3) (Fig. 3), which shifts the equilibrium in reaction (2) to the right. The irreversible reaction (3) can represent a combination of several stages, which sometimes influence the catalytic current.

Saveant and co-workers[35] considered the difference between the potentials E^0_{M/M^*} and $E^{1/2}_S$ to be the principal factor determining the catalytic effect. This conclusion is based on an experimental fact—the increase in the catalytic current with decrease in ΔE for a number of systems. It is assumed that the rate of the homogeneous transfer is higher the closer the energies of the lowest unoccupied molecular orbitals of the transferring agent and the substrate. The rate of homogeneous electron transfer is appreciable already at $E = 0.2-0.7$ V.

The use of the phenomenon of homogeneous electron transfer in electroanalysis stimulated the search for new ways of immobilising the mediators on a current-conducting surface in order to create amperometric sensors for a specific substrate. The methods for the modification of electrodes examined above ensure a high local concentration of the oxidation-reduction centres for a low overall amount of the catalyst and make it possible to consume the latter economically and to avoid special operations involving the separation of the catalyst from the reaction products.

In the study of the amperometric response of chemically modified electrodes with an immobilised mediator, it is possible to establish the influence of immobilisation on the electrochemical parameters of the mediator, the distribution of redox centres within the coating, and the location where the catalytic reaction occurs, to find the relation between the thickness of the coating, the amount of the reagent, and the catalytic current, and to determine the stability of the chemically modified electrode in time and the reproducibility of the analytical signal, i.e. to estimate a series of metrological and operational characteristics.

The study of a large group of mediators bound covalently to the electrode surface and comparison of their behaviour in solution and under heterogeneous conditions showed that the thermodynamic characteristics of the catalysts are relatively insensitive to immobilisation. Cases where the covalent bond involves an electroactive group in the molecule of the modifying agent may be an exception. In this case the maximum difference between the standard redox potentials ΔE^0 is ~90 mV.[37]

The kinetic requirement for the rapid establishment of the electrochemical equilibrium $M \rightleftarrows M^*$ (stage 1, Fig. 3) is fulfilled best for compounds for which the oxidation-reduction process is associated with the small Gibbs free energy characterising the reorganisation of the structure of the reactant molecule and of its solvation shell as a result of electron transfer.[38] Therefore, one uses such modifying agents as transition metal complexes with organic ligands[39] or organic compounds whose structure contains conjugated π-bonds or metallocenes.

Among the main reasons inducing the difference in ΔE^0 noted above, one may specify the following: (1) the increase in the energy of reorganisation of the solvent and the change in the stereochemistry of the modifying agent, which may accompany the electron transfer involving the immobilised centres (for example, as a consequence of Coulombic repulsion); (2) the influence of immobilisation on the retention of the planar structure of the mediator (for example, in the case of a metal complex); (3) the strong interaction of the mediator with the support (this affects the potential); (4) the interaction between the catalyst molecules in the oxidised and reduced forms.[10] All these factors act more or less appreciably for any immobilisation method.

The mediator performs its function of an electron transferring agent via an outer sphere or an inner sphere mechanism. In the outer sphere interaction between M* and S, an electron simply "jumps" between these species (redox catalysis). In the inner sphere mechanism (chemical catalysis), the mediator plays the role of an electron transferring agent and simultaneously binds the substrate into the intermediate. Thus the reduction of oxygen to hydrogen peroxide on a chemically modified electrode based on the porphyrin-cobalt complex (CoP) incorporated in a Nafion film, proceeds in fact via the chemical catalysis mechanism.[40] The electron exchange takes place within the adduct between the substrate O_2 and the modifying agent, i.e. within the complex $CoPO_2$. In the chemical catalysis, there is a possibility of the transfer of two electrons. For a sufficiently large number of catalytic cycles in the construction of the chemically modified electrode, one may deposit thin films (or even a monolayer). In practice, it is best to use under these conditions an

electrode having a large contact surface area, for example, one made from a porous or fibrous material.[41]

The principal requirements which must be not by mediators are listed below:

the mediator must be stable in relation to atmospheric oxygen (its reduced form should not, for example, be oxidised in air);

the oxidation-reduction potential of the mediator must be low and virtually independent of the pH, i.e. the potential of the M/M* redox couple is not a function of H^+;

the stage in which the mediator interacts with the substrate must be rapid, which is best achieved for an inner sphere mechanism;

the mediator must not be transferred from the surface of the chemically modified electrode to the test solution;

the mediator must be non-toxic.

The disadvantages which are encountered in studies with chemically modified electrodes include a decrease in the activity of the modifying agent on immobilisation or its change as a function of time, possible side reactions which deactivate irreversibly the modifying agent, as well as certain other side processes have been noted. However, these disadvantages of chemically modified electrodes are manifested to a greater extent when they are used for electrosynthesis than in electroanalysis.[41]

The theory of charge transfer in a layer of an immobilised modifying agent as well as the reactions of the substrate occurring on the chemically modified electrode have been described by different workers.[42–53] Depending on the immobilisation procedure, the modifier can be deposited, as noted above, on the surface both in the form of a monolayer and in the form of a film having a definite thickness. Multilayer coatings are as a rule discussed in the literature and the monolayer is regarded as a special case. The processes occurring on the surface of chemically modified electrodes are extremely varied; new transport stages and chemical reactions, any of which may limit the rate of the overall process, are manifested here. Fig. 3 presents a general scheme for the amperometric response on a chemically modified electrode with a polymer catalyst film.[52]

The rate of electron transfer in the direction of the redox centres through the electrode–modifying agent interface is fairly high and is determined by the potential. The M and M* centres participate in the electron transfer within the layer.[54] The charge transfer is partly associated either with the diffusion of counterions having oxidation-reduction properties if polycationic film includes an ion exchanger (see, for example, Anson et al.[55] and Pickup and Murray[56]) or with the movement of electrons along the conducting polymer chain.[57] The overall diffusion coefficient D_c characterises this movement of charges.

It has been suggested that the substrate enters the layer of the modifying agents slowly via diffusion. This process is characterised by a partition coefficient K. In the film itself, the migration of the species S is affected both by the pore size[58] and by the density of the polymer film impregnated with the solvent.[59] The diffusion coefficient of the substrate D_S in the layer of the modifying agent can be lower by 3–4 orders of magnitude than in solution.[60,61] It may happen that not all the immobilised modifying agent species participate in the reaction of the substrate, only some of them being involved, which depends on the kinetic and transport parameters k, k'_e, k'', D_S, and D_e. The reduction of the substrate S directly on the electrode surface (determined by the rate constant k_e) can occur only in the case of thin films[62] and is not typical for the usual layers. The difference in the behaviour of the modifying agent bound directly to the surface and present in the film (i.e. in its reaction layer) is explained by the difference in the solvation of the modifying agent.

The use of polymer coatings differing in the structure and composition of the films opens yet another pathway to the attainment of selectivity in the analytical determinations. For example, ascorbic acid and dopamine, which are oxidised on the carbon glass electrode at virtually identical potentials, can be separated on a chemically modified electrode coated by polyvinylpyridine in which the $IrCl_5^{3-}$ transferring agent has been incorporated.[63] Both the peak potentials on the voltammograms and the rates of the catalytic reaction of these substrates differ appreciably under these conditions.

The establishment of the thickness of the coating on the electrode (for the maximum concentration of the modifying agent in the latter), which affects the catalytic activity, is important. The extent X of the reaction zone, determined by the modifying agent (in the film)/solution boundary, is estimated from the relation

$$X_L = (D_S/k[M]_{tot})^{1/2}. \quad (4)$$

For the electrode surface/modifying agent boundary layer, this distance from the electrode surface is determined from the formula

$$X_0 = (D_e/kK[S]_{soln})^{1/2}. \quad (5)$$

Here $[S]_{soln}$ is the substrate concentration in solution at the boundary near the polymer film and the subscripts L and O indicate the distance from the surface of the electrode proper where the reaction zone begins.

Then types of reaction zones, depending on the site where the modifying agent is located, have been proposed in a detailed study of the mechanisms of the response of chemically modified electrodes[64] (Fig. 4). Eqns. (4) and (5) describe the extreme cases where the reaction zone is located directly in the solution and at the electrode proper. If the rate constant for the reaction

$$M^* + S \xrightarrow{k} M + P$$

in the layer of the modifying agent is zero, the substrate reaches the surface of the electrode proper (Ek'_e type of location). If the electron transfer and the mass transfer of the substrate are reversible, then the reaction proceeds in the layer of the modifying agent and for a low value of k the reaction zone is diffused throughout the thickness of the layer of the modifying agent (Vk type of location). When k is large, the reaction zone narrows down to the size of the layer (RZV type of location).

For reaction zones located on the surface of the modifying agent (types Pk'' and VPk), two cases are distinguished. In the reaction zone with Pk'' type of location, a homogeneous reaction takes place at a high rate (high catalytic effect; $k_2 > 10^4$ litre^2 mol^{-1} s^{-1}). The thickness of the sensor layer is then unimportant. Since the thickness of the film may be decisive for electron transfer, it is best to use thin coatings or even a monolayer of the modifying agent for chemically modified electrodes.

The VPk zone occurs for thick coatings and electrodes. In the ideal case the extent of this zone is described by Eqn. (4). Since the concentration of the electrocatalytic centres in the layer is several times greater than that in the solution, for a sufficient mass transfer of substrate into the layer ($D_S \simeq 10^6$ cm^2 s^{-1}) the quantity k_2 in the layer may be appreciably smaller than in the solution ($k_2 > 10$ litre^2 mol^{-1} s^{-1}). It has been suggested that porous film forming

agents be used fot the immobilisation of the modifying agents on such chemically modified electrodes and that the pore diameter in the layer should be approximately an order of magnitude greater than the diameter of the substrate molecule,[41] the optimum thickness of the layer being ~ 1 μm.[52]

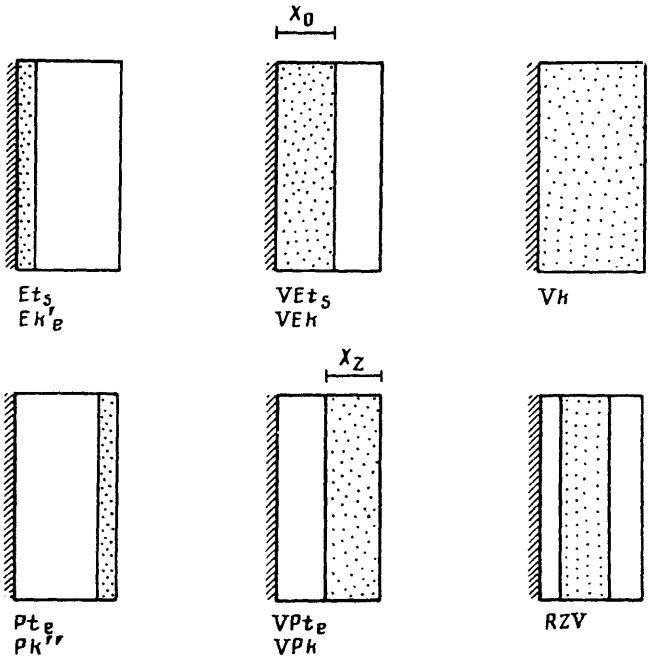


Figure 4. Types of reaction zones in the film of modifying agent on the surface of a chemically modified electrode. Location of the zone: E—electrode; VE—layer at the electrode; V—bulk-phase layer; P—surface of the chemically modified electrode facing the solution; VP—layer at the surface of the chemically modified electrode; RZV—reaction zone in the bulk phase layer. Rate-determining stage: substrate transfer (t_S) and electron transfer (t_e). Rates of reactions: electrochemical reaction (k_e) and catalytic reaction in the layer (k) or on the surface (k'') of the modifying agent (according to Bartlett[64]).

It follows from the data described above that effective catalytic action is observed when the entire bulk of the immobilised catalyst is involved in the process (case Vk), which is difficult to achieve in practice, or when the reaction layer is involved (VPk), its reaction zone being at the maximum distance from the modifying agent/solution interface and extending in the direction towards the surface of the electrode proper. The ratio of the limiting catalytic current at a rotating disc electrode to the limiting current calculated from the Levich equation has been adopted as a measure of the catalytic efficiency of the chemically modified electrodes. For $X < X_{opt}$, the catalytic efficiency of the modifying agent increases with increase in X. For $X > X_{opt}$, a much greater consumption of the modifying agent (which is frequently expensive) is required for a slight increase in efficiency.

Apart from the rotating disc electrode, voltammetry, especially its cyclic version, which makes it possible to determine the rate constant for the reaction of the mediator with the substrate in solution (k_2), is used for the qualitative assessment of the observed kinetic effects. The nature of the catalytic reaction of the substrate can be established in this instance from the cyclic curves.[65] For a low rate of the subsequent chemical reaction (M* + S) and its low constant $k_f = k_2[S]$, the shape of the voltammogram is close to that of the cyclic curve characteristic of a reversible electrode process ($i_p \propto V^{1/2}$; $i_{pa}/i_{pc} = 1$; $\Delta E_p \simeq 0.057/n$ (volts); here V is the rate of change of the polarising potential, i_{pa} and i_{pc} are the currents of the anodic and cathodic peaks, ΔE_p is the difference between the potentials of these peaks, and n is the number of electrons participating in the oxidation-reduction reaction).

For higher values of k_f, the voltammogram contains one step (for example, the cathodic step), the limiting current of which is proportional to $k_f^{1/2}$ and is independent of the rate of change of the polarising potential. In the intermediate situations with average values of k_f, the height of the cathodic peak of the mediator M in the presence of the substrate S is greater, while the height of the anodic peak is lower than in the absence of S. These changes in the peak currents are clearer for low rates of change of the potential ($V = 1-10$ mV s^{-1}).

The diagnostic criteria described in the literature for cyclic voltammetry are used for the qualitative description of the electrochemical behaviour of chemically modified electrodes in the substrate solution.[65] We may recall that useful information can be extracted from the dependence of $i_p/V^{1/2}$ on V. The quantity k_f is found from a series of cyclic voltammograms recorded for different rates of scanning of the potential.[65]

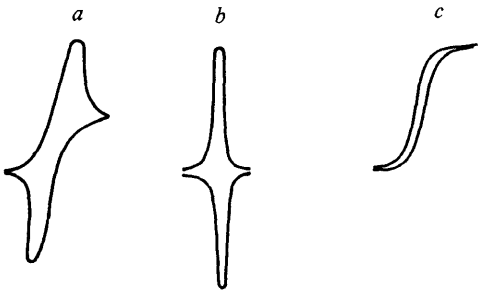


Figure 5. Typical cyclic voltammograms for different types of behaviour of the mediator in the chemically modified electrode: *a*, reversible behaviour of the mediator in solution; *b*, ditto but on the surface of the chemically modified electrode; *c*, catalysis at a high rate (k_f).

As was to be expected, cyclic voltammograms for an immobilised mediator in the absence of the subsequent chemical reactions involving the redox couple contain reversible peaks and we have $i_p \propto V^{1/2}$, $i_{pa}/i_{pc} = 1$, and $\Delta E_p = 0$. Fig. 5 presents for comparison the cyclic voltammograms corresponding to the cases described above.

3. Immobilisation of electron transferring agents in chemically modified electrodes

It follows from subsection 1 that the methods for the retention of modifying agents on the surfaces of electrodes are very varied and one can therefore put forward a large number of procedures for the fixation of the oxidation-reduction centres participating in the catalytic response of the chemically modified electrode. However, in practice, mainly polymer films are used to immobilise electron transferring agents[4,9] because of the simplicity of the operation, its reproducibility, the adequate stability of the chemically modified electrode obtained, and the possibility of varying the film thickness. Here account must be taken only of the fact that the material of the polymer is frequently non-indifferent to the transferring agent, which affects, for example, its formal redox potential.

The electron transferring agent is immobilised in different ways. One of them involves the electrochemical preparation of a conducting polymer with the simultaneous incorporation of the catalyst in the latter. For example, in the electropolymerisation of pyrrole in solution in the presence of hexacyanoferrate(II) ions, quinone, porphyrins, phthalocyanines, and certain other catalysts, films containing these transferring agents are obtained. The polypyrrole films are used more often than other coatings in chemically modified electrodes because polypyrrole is electrically conducting and its thick films do not induce an appreciable passivation of the electrode, are retained both on metal oxide surfaces and on carbonaceous materials, and are chemically stable during the period necessary for analysis.

The use of an *N*-substituted pyrrole as a monomer in electropolymerisation leads to still more stable films. Their polymerisation is accompanied by the immobilisation of bipyridyl and porphyrin metal complexes, ferrocene, anthraquinone, phenothiazine, dyes, and other compounds.[66] However, the polymer films based on *N*-substituted pyrroles exhibit a lower conductivity compared with the unsubstituted analogue, which can be avoided by copolymerising pyrrole and an *N*-substituted pyrrole.[41] Other compositions comprising two polymers are also used.[67,68] The substituted pyrrole as the monomer may contain in its structure groups involved in electron transfer. The substituents in the pyrrole molecule ultimately determine the property of the polymer coating on the chemically modified electrode which influences the mass transfer of the substrate.[69]

The commonest electron transferring agents are the bipyridyl complexes of ruthenium and osmium[57,70] as well as iron and cobalt.[71] They are immobilised in films based on polyvinyls. The porosity of the films, which determines their transport properties, is achieved in different ways, for example, by activating the polymerisation process by means of plasma.[72] The transport of species with electrocatalytic properties from the solution into the polymer film occurs sometimes during a comparatively long period.[73] The cyclic alteration of the potential of the chemically modified electrode over a short time interval in the region of the formal redox potential accelerates this process.[61,74]

As mentioned above, the retention of the species of the modifying and transferring agent can be achieved by means of electrostatic interaction forces. In such cases, an ion exchanger of the type of Nafion is widely used as the retention matrix. Its selectivity in the charge (ion) transfer process is a maximum in relation to hydrophobic species. Another example of the use of electrostatic interactions for the purpose of immobilisation is the fixation of ruthenium hexacyanoferrate(III) complexes on anionic or cationic surfactants immobilised in their turn with polystyrene film.[75] In order to ensure the selectivity of the electrocatalytic response, which is determined by the size and shape of the substrate particles, the modifying and transferring agent is immobilised in various clays or zeolites, which are retained on the electrode surface by polymers, including polymers formed by electropolymerisation.[76] The clay-modified electrode can adsorb certain surfactants, which then extract from the solution transferring agents of the type of hexacyanoferrate(III) ions, ferrocene, etc.[77]

Apart from the immobilisation of transferring agents with the aid of polymer films, their adsorption on the electrode surface is employed. Copper and cobalt complexes with organic ligands and aromatic compounds are immobilised in this way. This method is frequently used to immobilise enzymes or other biological materials in the construction of biosensors.[78] For example, an adsorbed film of microorganisms is capable of retaining combined transferring agents and electrocatalysts comprising hexacyanoferrate(III) ions or ruthenium(III) complexes.[79] The insoluble hexacyanoferrates(II), deposited on the electrode surface, can also function as transferring agents.[80–83] Ruthenium complexes, ferrocene, and benzoquinone are retained on the surface of carbon glass after its electrochemical treatment at an anodic potential.[84]

4. Chemically modified electrodes as biosensors

If a biological material, for example an enzyme or an enzyme-containing preparation, is incorporated in the signal-generating layer of the chemically modified electrode, then such an electrode is called a biosensor or a biochip. Other names are also used.[85] The modifying agent, in the given instance an enzyme, is immobilised by all the procedures which were described above for simpler transferring agents. Much attention has been devoted to the principles of the operation of biosensors and their applications. A series of special reviews have been published, including reviews in Russian journals.[85,86] Here is it appropriate to consider the problems concerning biosensors of the same kind as those arising in the development of chemically modified electrodes. It must be emphasised that studies on chemically modified electrodes, carried out independently and simultaneously with the development of biosensors, made a definite contribution to the expansion of the biosensor field. It was found that many results of studies on chemically modified electrodes have led to advances in the study of biosensors up to the level of their practical application.

In principle, any biosensor can be regarded as one of the versions of the chemically modified electrodes. Since the general principles of the functioning of amperometric sensors based on immobilised enzymes were examined previously,[85] there is no need to return to this problem.

The operation of amperometric biosensors is based either on the direct electron transfer between the active centre of the immobilised enzyme and the surface of the electrode proper or on the involvement of a mediator. In the latter case the biolayer giving rise to a specific response of the substrate is deposited on the modified surface containing an electron transferring agent. In this so called bulk phase technology, the individual components of the biochip constitute, as it were, a physical ensemble. Although such biosensors have now found practical applications, there are difficulties in their preparation on a mass scale. In addition, biochips with comparatively thick membranes have a long response time; complications arise also in their calibration.

The principal requirements which must be met by the mediators in chemically modified electrodes also apply to the biosensors based on them. It must be emphasised that the stage involving the

interaction of the mediator with the active centre of the enzyme must be fairly rapid, i.e. the mediator must behave in essence as if it were a substrate of the enzyme. Ultimately two catalytic cycles occur on such an electrode (Fig. 6).

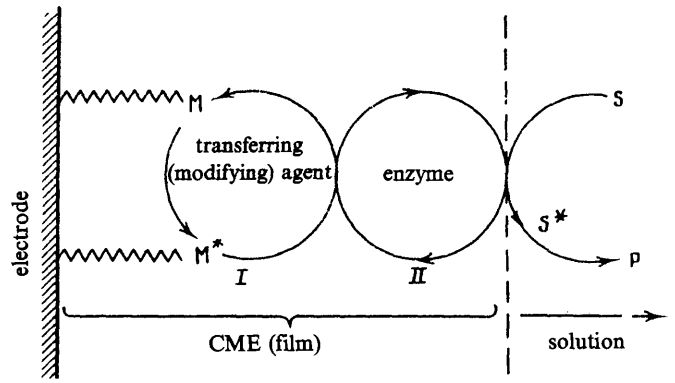


Figure 6. Schematic illustration of the operation of a chemically modified electrode with two catalytic cycles.

Amperometric biosensors are usually based on the so called oxyreductase enaymes in which the electron acceptors are, for example, atmospheric oxygen, nicotinamide-adenine dinucleotide (NAD^+) or nicotinamide-adenine dinucleotide phosphate ($NADP^+$). These components of the chemically modified electrode participate in the recyclisation of the enzyme after its reaction with the substrate. Enzymes employing O_2 as the electron acceptor are usually referred to as oxidases, whereas enzymes operating in combination with NAD^+ or $NADP^+$ are referred to as dehydrogenases or reductases. Among the enzymes in these two groups, oxidases are usually employed for the construction of biosensors.[9,11]

Without going into the details of the practical aspect of the problem of biosensors, the reader being referred to the reviews mentioned above,[9,11] we may note that their selectivity is determined by the specificity of the action of the enzyme and by the nature of the electrochemical reaction proper, in which the components of the enzymic process participate. Oxidases are as a rule highly specific in relation to particular components of the biological specimen. On the other hand, the system transforming the response of the biological reaction involved in the recognition of the substrate molecule into electric current (the system comprising the transferring agent or mediator, also referred to as the transducer) is not always quite as selective as one would wish. Indeed, many metabolites may be oxidised at a platinum microelectrode (transducer) at its operating potential. Thus ascorbic and uric acids, aminoacids, urea, and other components of the biological specimen analysed are oxidised at this electrode at a working potential of +0.6 V.

In order to increase the selectivity of such biosensors, use is made of special films operating on the basis of the principle of filters. For example, in order to suppress the influence of the above components and also of cysteine and proteins, which can be present in biological specimens, for example, in blood serum, use is made of a polymer film based on 1,2-diaminobenzene obtained by electrochemical polymerisation.[87] Such a biosensor with an immobilised glucose oxidase yields satisfactorily reproducible results in the course of 1–1.5 months. Glutaraldehyde may be used to increase the thermal stability of the biolayer.

The advantage of a biosensor with a film permeable only to substrate molecules of a particular size consists also in the fact that such devices have a low noise level in the recording of a useful signal and can be employed in flow injection analysis.

As mentioned above, dehydrogenases can serve as the enzymes in many biosensors.[11] These enzymes operate in combination with NAD^+ or $NADP^+$, the so called coenzymes. During the enzymic process, they are consumed in an amount equivalent to the amount of the substrate. The coenzymes must therefore be regenerated during the operation of dehydrogenase biosensors. This is achieved in a catalytic cycle on an electron transferring agent immobilised on the surface of the transducer proper. Quinone-hydroquinone derivatives are usually employed for this purpose (cycle I, Fig. 6). The coenzyme participates in the second catalytic cycle, which determines jointly with the enzyme the specificity of the response (cycle II, Fig. 6).

A low working potential is applied to such electrodes with an immobilised modifying agent, which imparts to them certain useful properties. Thus an advantage of the biosensors working on the principle of chemically modified electrodes with a double catalytic cycle is the possibility of increasing the selectivity of the response by limiting the number of specimen components, capable of reacting electrochemically when a potential is applied, by increasing the signal/noise ratio. These biosensors have a linear response over a wider range than the biosensors without a modifying agent.

Direct electron transfer between the active centre of the enzyme and the working electrode, i.e. the bioelectrocatalysis proper, is also a method for increasing the metrological and operational characteristics of biosensors. In this case, there is no mediator-transferring agent, in contrast to the previous scheme. A number of reviews and articles have also been devoted to the problem of direct electron transfer.[88–92]

The efficiency of biocatalysis based on an idealised model has been discussed.[88,89] It has been shown that the catalytic activity of enzymes on the surfaces of electrodes can be so great that the amperometric response is determined by the diffusion of the substrate, while the immobilisation of the enzymes ensures a high current density. A limited number of examples of the direct electron transfer from the active centre of the enzyme to the electrode have been described in the literature. Thus the possibility of using cytochrome *c* as the catalyst of the electrochemical reduction of molecular oxygen has been investigated. The rate of formation of hydrogen peroxide increases in the presence of this biocatalyst.[90] Evidence indicating the possibility of the direct electron transfer from the active centre of the enzyme to the electrode has been obtained for the oxygen–laccase–electrode system.[91,92]

Among the amperometric biosensors giving rise to a response in the absence of a mediator, the greatest interest attaches to those where the electrode (the carrier of the immobilised enzymes) is constructed from electrically conducting materials, for example, organic salts of the type tetracyanoquinonedimethane–tetrathiofulvalene (TCQ^-TTF^+).[93] Thus the oxidation of lactate is accelerated catalytically when cytochrome B_2 is immobilised on the complex of TCQ^- with *N*-methylphenazinium. This biocatalytic system has been used as a basis for the functioning of the biosensor for lactate.[94] If instead of cytochrome one uses in this system glucose oxidase immobilised on the same organic salt by means of

irreversible adsorption, then the biosensor makes it possible to determine glucose with an activity which does not change in the course of 100 days.[94] Other enzymes are also adsorbed on this organic conductor. Biosensors for purine, hypoxanthine, and xanthine have been constructed on the basis of such an assembly.[95] Finally one should note that various microorganisms and cells immobilised in a biolayer are used in biosensors, including those with an amperometric response (see, for example, Ivnitskii et al.[86]).

III. Applications of chemically modified electrodes in electroanalytical chemistry

Various practical applications of chemically modified electrodes have been described so far in the literature. Amperometric sensors and the analysers based on them usually give rise to a measured signal which is linear over a wide range as a function of concentration and has a lower detection limit compared with potentiometric sensors. It is noteworthy that each sensor, transducer, or detector, working in accordance with the principles of chemically modified electrodes, is constructed for the solution of a particular specific practical problem and functions under rigorously defined conditions.

After the modification of the electrode surface by one of the methods described above, the resulting chemically modified electrode is introduced into the solution to be analysed. If metal ions are to be determined, then in the course of a certain time (from several minutes to several tens of minutes) the ion is bound (absorbed) on the electrode surface or in its bulk phase as a result of the reaction with the modifying agent. If an immobilised ligand serves as the modifying agent, then the ion is bound as a result of complex formation. The selectivity of the determination is attained not only by selecting the appropriate ligand but also by regulating the pH and the concentration of masking agents.[7] Metal ions may accumulate on the chemically modified electrode due to the electrostatic interaction forces resulting from ion exchange.[7,9,10] Multicharged ions can then be concentrated from highly dilute solutions.

Measurement of the voltammetric response after the electroaccumulation stage gives rise to a peak on the curves whose height (or area bounded by the corresponding contour) is used to determine the concentration of the given ions in the solution. If the electrochemical reaction involving the metal ions to be determined is reversible, then virtually any version of voltammetry or differential-pulse technique can be used to measure the signal. In this case the chemically modified electrode permits single determinations, after which its surface has to be regenerated with repeated modification.[7] On the other hand, if the electrode reaction is irreversible and the metal–ligand bond is ruptured during it but the immobilised ligand is not degraded, then the chemically modified electrode can be used repeatedly.[7]

The lower limit of the determination using chemically modified electrodes depends on the number of binding centres on the electrode surface, the stability of the complexes formed, the parameters of the distribution of ions between the solution and the absorbing phase of the electrode with incorporated modifying agent, and also on the method of recording the voltammetric signal.

Among inorganic ions, those of heavy metals have attracted most attention by investigators, which is associated primarily with the problems of the ecological monitoring of natural and waste waters, air, soils, and agricultural products. The problem of the sensitivity and selectivity of the determination has always been and remains of current interest, particularly now when the importance of analytical monitoring in the community has increased.

Inversion voltammetry combined with chemically modified electrodes has been used recently to increase the sensitivity of the determination. Detection limits for metal ions are then attained at the level of the capacity of physical methods such as atomic absorption voltammetry, which is used most often for such purposes in environmental monitoring. Thus the principles of inversion voltammetry have been used to determine copper(II) on a carbon paste electrode modified with di-8-quinolinyl disulphide.[96] After reduction to quinoline-8-thiol, the latter binds copper(II) ions in a stable complex. The detection limit for copper(II) with the aid of such an electrode reaches 8×10^{-10} M, which is close to the detection limit for copper with the aid of the mercury film electrode.

The carbon paste electrode modified with 2,2′-dithiobipyridyl has been proposed for adsorption accumulation and subsequent voltammetric determination of silver with a detection limit of 8×10^{-9} M. The analysis is hindered by the presence of mercury and copper, but bismuth, antimony, cadmium, cobalt, nickel, and zinc ions present in a 100-fold excess do not interfere.[97]

The carbon glass electrode whose surface has been coated with poly-4-vinylpyridine containing mercury(II) ions makes it possible to determine heavy metal ions (lead, cadmium, and copper).[98] The preliminary accumulation is carried out at a potential of about −1 V for not more than 3 min, after which the differential-pulse voltammogram is recorded.[98]

The graphite electrode modified with diphenylcarbazone has been proposed for the determination of traces of mercury(II) in aqueous solutions.[99] It is made by pressing a mixture of the modifying agent with graphite powder. The mercury(II) ions are concentrated from solutions containing nitric acid. The solution is then changed and the differential-pulse voltammogram is recorded in the new supporting electrolyte. The detection limit is 5×10^{-8} M (for accumulation in the course of 10 min). The determination is interfered with by silver ions, chromate ions, and strong complex-forming ligands.

The principles of inversion voltammetry have also been used to determine small amounts of cobalt with the aid of a carbon paste electrode.[100] The modifying agents were a cation exchanger and phenanthroline. The cobalt(II) detection limit was 8×10^{-10} M. Conditions permitting the analytical determination of this ion in the presence of a number of heavy metal cations have been found.

As an illustration, Table 1 presents data obtained in the determination of certain toxic metal ions, which characterise the analytical possibilities of chemically modified electrodes in voltammetry and its modifications. Although Table 1 does not exhaust all the literature data on the problems involved in the use of chemically modified electrodes in analytical practice, the measured concentrations of metal ions demonstrate convincingly that voltammetry combined with chemically modified electrodes can compete with a method such as atomic-absorption spectrophotometry.

Not only metal ions but also organic compounds are concentrated on the surface of chemically modified electrodes. Ecological as well as medical and pharmacological problems dictate also in this case the choice of the objects for analysis. Substrates with complex structures, proteins, medicinal preparations, vitamins, biologically active compounds, including pesticides, etc. are determined with the aid of voltammetry combined with chemically modified electrodes. Table 2 presents examples illustrating the possibilities of chemically modified electrodes in the electroanalysis of organic substances.

Table 1. Voltammetric determination of inorganic ions in solution with the aid of chemically modified electrodes.

Ion to be determined	Material of electrode	Modifying agent	Method of measurement of signal	Concentration determined, M	Refs.
Cu(II)	Carbon glass	3-Aminopropyltriethoxysilane	Inversion voltammetry, differential-pulse technique	$1\cdot10^{-9}-3\cdot10^{-7}$	[101]
		Poly(pyrrole-*N*-carbodithionate)	Substance concentrated at −0.6 V; cyclic voltammetry	10^{-5}	[102]
As(III)		Ruthenium(II, III) cyanides	Catalysis of oxidation, voltammetry	$5\cdot10^{-6}-2\cdot10^{-3}$	[103]
As(III), Te(II)	Graphite	Mercury complexes	Inversion voltammetry	$3\cdot10^{-9}-5\cdot10^{-10}$	[104]
Sb(III)		Triphenylmethane dyes	–	$3\cdot10^{-8}-4\cdot10^{-9}$	[104]
Ag(I)	Carbon paste	Diethylenetriamine	–	$10^{-11}-10^{-7}$	[106]
Bi(III)		Mercaptans	–	$1\cdot10^{-7}-2\cdot10^{-5}$	[106]
Hg(II)	Graphite	Diphenylsemicarbazone	–	10^{-9}	[99]
UO_2^{2+}	Carbon glass	Tri-n-octylphosphine oxide	Voltammetry	$4\cdot10^{-9}-2\cdot10^{-8}$	[107]
DO_2^{2+}			Inversion voltammetry	10^{-8}	[108]
NO_2^-	Platinum	Poly(4-vinylpyridine) and iodine	Voltammetry	$4\cdot10^{-6}-2\cdot10^{-3}$	[109]
	Carbon glass	$IrCl_6^{3-}$ in a polyvinylpyridine film	Flow-injection analysis	$10^{-4}-10^{-3}$	[110]
		Macrocyclic nickel complex in a Nafion film	Cyclic voltammetry	10^{-4}	[74]
SCN^-	Platinum	Acetylcellulose film with iodide	Flow-injection analysis	$5\cdot10^{-6}-1\cdot10^{-4}$	[111]
	Carbon glass			$2\cdot10^{-7}-4\cdot10^{-6}$	[111]

It does not mention the substrates of enzymes used in biosensors because their determination has already been discussed in detail.[10,11,85]

Table 2 shows that, among the methods for immobilisation of modifying agents on the electrode surface, the incorporation of such agents into a polymer film or into the bulk of the carbon paste electrode is usually employed. Non-traditional solutions are rarely encountered.

Various hydrophobic materials deposited directly on the surface of a solid electrode may be included among unusual modifying agents.[120–122] Thus many medicinal substances reducing blood pressure, of the type of reserpine and rescinnamine, can be determined on lipid-modified electrodes.[121] After the deposition of the lipid film on the carbon glass surface of the electrode, compounds are accumulated in the course of 10 min, whereupon they permeate actively into the hydrophobic layer. The voltammogram is then recorded. The detection limit is 5×10^{-9} M.

Polar electroactive substances (up to a 100-fold excess) do not affect the results of the determination. Electrodes modified by lipid films respond selectively to the presence of hydrophobic organic substances containing the electroactive groups in their structure.[122] Hydrophilic compounds are incapable of permeating into the lipid layer during its accumulation, which prevents their reactions on such a chemically modified electrode. Studies on lipid films prepared on the basis of distearoylphosphatidylcholine and dioleolylphosphatidylcholine showed that the electrode reactions on such chemically modified electrodes are due to the presence of double bonds in the alkenyl chains of the lipids.

Graphite electrodes with stearic acid deposited on their surface have been used to determine dopamine and norepinephrine in rat brain tissues *in vivo*.[120] The carboxy-groups of the modifying agent influence the oxidation potentials of these biogenic amines shifting them towards more positive values. The effectiveness of this chemically modified electrode in the presence of metabolites—electroactive and neurochemical compounds belonging to the group of catecholamines and present in tissue liquids. It has been suggested that there is a relation between the form of the voltammetric signal and the activity of dopamine.

In many instances, chemical modification of the electrodes alters the parameters of the electrochemical reaction and makes the process more reversible, while the form of the analytical signal becomes more convenient. It has been established that the oxidation and reduction of one of the coenzymes in many biological catalysts and in PQQ {sodium salt of 2,7,9-tricarboxy-1*H*-pyrrolo[2,3-*f*]quinoline-4,5-dione—a growth stimulator in a number of microorganisms} on

Table 2. Voltammetric determination of organic compounds in solution using chemically modified electrodes.

Compound determined	Material of electrode	Modifying agent	Method of measurement of signal	Concentration determined, M	Refs.
Ascorbic acid	Carbon glass, carbon paste	Aminophenols	Voltammetry	$10^{-5}-10^{-3}$	[15]
	Graphite	Polypyrrole		10^{-4}	[112]
Catecholamines	Platinum	Iodide ion	Differential-pulse technique	$8\cdot10^{-7}$	[113]
Amines	Carbon paste	Polyvinylpyridine, benzaldehyde-4-carboxylic acid	Square wave voltammetry	$3\cdot10^{-5}-10^{-2}$	[114]
Glutathione		Cobalt-phthalocyanine	HPLC	10^{-10}	[115]
Thiols	Ditto		Ditto	$2.7\cdot10^{-9}$	[115]
Ferredoxin	Gold	Di(4-pyridyl) disulphide	Voltammetry	$4\cdot10^{-4}-9\cdot10^{-5}$	[116]
Oxalic acid	Graphite	Ruthenium and iron complexes in a Nafion film	Voltammetry and chemiluminescence	$5\cdot10^{-2}$	[117]
Hypoxanthine	Carbon paste	Hydroxymethylferrocene + xanthine oxidase in a cellulose triacetate film	Voltammetry	$6\cdot10^{-7}$	[118]
	Graphite	Ferrocene, iron-phthalocyanine	Voltammetry	$1.5\cdot10^{-7}$	[115, 119]
Dopamine, norepinephrine		Stearic acid		$1.5\cdot10^{-7}$	[120]
Reserpine, rescinnamine	Carbon glass	Lipids	Inversion voltammetry	$5\cdot10^{-9}$	[121]
Hydrophobic organic compounds with multiple bonds	Platinum	Phosphatidylcholine	Voltammetry	$5\cdot10^{-9}$	[122]
Alcohols	Graphite	$Fe[(CN)_6]^{3-}$ in a polyvinylpyridine film	Flow-injection analysis	$2\cdot10^{-6}$	[123]
Phenols		Ditto	Cyclic voltammetry, flow system	$0.5\cdot10^{-6}$	[124]
Dopamine, ascorbic acid	Carbon glass	$Fe_4[Fe(CN)_6]_3$	Cyclic voltammetry	10^{-2}	[125]
	Platinum	Ferrocene		$10^{-4}-10^{-3}$	[126]
	Carbon glass	$IrCl_5^{2-}$ in a polyvinylpyridine film		10^{-3}	[127]
Cysteine		$Os(bipy)_3^{3+}$ in a Nafion film	HPLC	$2\cdot10^{-5}-10^{-3}$	[128]

platinum and gold electrodes are irreversible. However, if these electrodes are coated by a polypyrrole film, then cyclic voltammograms show reversible two-electron peaks.[129] If pyrrole is electropolymerised in the presence of PQQ, then the latter is incorporated in the polymer matrix, retaining its oxidation-reduction properties, i.e. it can play the role of a mediator. The latter factor leads to the possibility of preparing biosensors for the determination of sugars.

In the solution of the problems of monitoring (continuous analysis) on the real time scale of the on-line or in-line type, a notable place has been assigned to voltammetry and chemically modified electrodes. In many instances, the aim of the development of chemically modified electrodes was in fact to use them as amperometric transducers in a stream, for example, in flow-injection analysis (FLA) or in high performance liquid chromatography (HPLC). These problems have been partly discussed in other reviews.[11,85] A special review devoted to chemically modified electrodes for the detection of substances in a stream of liquid has been published.[130] In FIA and HPLC, modified electrodes make it possible to ensure high productivity of the determination and ultimately lead to the accumulation of a large amount of information.

Methods for the modification of electrodes designed to impart to them a specific response have begun to be used recently in the miniaturisation of systems for analytical monitoring. This aspect of research and development is regarded as promising because it is possible to obtain ultimately miniature electrodes which permit measurements *in vivo* in tissues or even in individual cells. For example, an ultramicroelectrode based on a carbon fibre modified with tetrakis(4-hydroxy-3-methoxyphenyl)porphyrin in a polymer film has been prepared.[131] It makes it possible to determine nickel in individual biological cells. The film itself, on the surface of the ultramicroelectrode, is formed on electrochemical oxidation of the modifying agent. The number of layers in this film at the tip of the carbon fibre (0.5–1 μm in diameter) reaches 10–90. The calibration plot is linear in the concentration range 5×10^{-5}–5×10^{-3} M. The detection limit is $\sim 10^{-6}$ M nickel(II).

The miniaturisation of chemically modified electrodes makes it possible to construct portable analysers working in an autonomous regime and ensuring the continuous monitoring of biologically active substances in many spheres of human activity.

However, one should note that the chemically modified electrode incorporated in the analyser system is a product of extremely laborious scientific research. Although this problem is in fact of current interest and the need for such sensors is continuously growing, nevertheless more time is required to obtain a device or the corresponding instrument with the required operating properties. Therefore the view that sensors represent the future of analytical chemistry is not without foundation.[85] Advances in related fields of science, particularly in microelectronics, have been attracting increasing attention by researchers in the field of chemically modified electrodes and sensors. The use of the so called planar technology, which is used to create integrated circuits, instead of the traditional three-dimensional technology, in the construction of sensors will probably make it possible to proceed to their mass scale production. The microstructure of the surfaces of electrodes chemically modified with the aid of a multilayer coating has to be monitored already at the molecular level.

References

1. G K Budnikov *Zh. Anal. Khim.*, 1986, **41** 1733
2. M R Tarasevich *Elektrokhimiya Uglerodnykh Materialov* (Electrochemistry of Carbon Materials), Nauka, Moscow, 1984, 253 pp
3. L L Miller, M R Van de Mark *J. Am. Chem. Soc.*, 1978, **100**(1) 639
4. M R Tarasevich, S B Orlov, E K Shkol'nikov, et al. *Elektrokhimiya Polimerov* (The Electrochemistry of Polymers), Nauka, Moscow, 1990, 238 pp
5. T Matsue, M Fujihara, T Osa *J. Electrochem. Soc.*, 1979, **126** 500
6. R W Murray *Acc. Chem. Res.*, 1980, **13** 135
7. J Labuda *Zh. Anal. Khim.*, 1990, **45** 629
8. R W Murray *Electroanalytical Chemistry* (Edited by A Bard), Marcel Dekker, New York, 1984, Vol. 13, p. 192
9. B R Shaw *Electrochemistry, Past and Present* (ACS Symposium Series 390) (Edited by J T Stock and M V Orna), ACS, Washington D.C., 1989, p. 318
10. G K Budnikov, O Yu Kargina, I F Abdullin *Zh. Anal. Khim.*, 1989, **44** 1733
11. P R Stoecker, A M Yacynych *Selective Electrode Rev.*, 1990, **12** 137
12. H Jaegfeldt, A B Torstensson, L G Corton, et al. *Anal. Chem.*, 1981, **53** 1979
13. H Jaegfeldt, T Kuwana, G Johansson *J. Am. Chem. Soc.*, 1983, **53** 1979
14. J F Evans, T Kuwana, M T Henne, G P Royer *J. Electroanal. Chem.*, 1977, **80** 409
15. K J Stutts, R M Wightman *Anal. Chem.*, 1983, **55** 1576
16. K D Snell, A G Keenan *Chem. Soc. Rev.*, 1979, **8** 259
17. R A Durst, A L Plant, L L Brown *1st Bioelectroanalytical Symposium, Matrafured*, 1986, Budapest, 1987, p. 3
18. M R Van de Mark, L L Miller *J. Am. Chem. Soc.*, 1978, **100** 3223
19. A Merz, A Bard *J. Am. Chem. Soc.*, 1978, **100** 3222
20. K Doblhofer, D Neolte, J Ulstrup *Ber. Bunsenges. Phys. Chem.*, 1978, **82** 403
21. R Nowak, F Schultz, M Umana, et al. *J. Electroanal. Chem.*, 1978, **94** 219
22. F Anson, J M Saveant, K Shigehara *J. Electroanal. Chem.*, 1983, **145** 423
23. D A Butrry, F Anson *J. Electroanal. Chem.*, 1981, **130** 333
24. N Oyama, T Ohsaka, T Okajima *Anal. Chem.*, 1986, **58** 979
25. C R Martin, T A Rhoades, J A Ferguson *Anal. Chem.*, 1982, **54** 1639
26. N Oyama, T Ohsaka, T Shimizi *Anal. Chem.*, 1985, **57** 1526
27. E S De Castro, E W Huber, D Villaroll, et al. *Anal. Chem.*, 1987, **59** 134
28. A R Guadalupe, H D Abrima *Anal. Chem.*, 1985, **57** 142
29. J R Schneider, R W Murray *Anal. Chem.*, 1982, **54** 1508
30. N S Scott, N Oyama, F Anson *J. Electroanal. Chem.*, 1980, **110** 303
31. D R Rolison *Chem. Rev.*, 1990, 867
32. B R Shaw, K E Creasy, C J Lanczycki, et al. *J. Electrochem. Soc.*, 1988, **135** 869
33. Z Li, T E Mallouk *J. Phys. Chem.*, 1987, **91** 643
34. K E Creasy, B R Shaw *Electrochim. Acta*, 1988, **33** 551
35. C P Andrieux, J M Dumas-Bouchiant, J M Saveant *J. Electroanal. Chem.*, 1978, **87** 39

36. T Shono *Tetrahedron*, 1984, **40** 811
37. J R Lenhard, R Rocklin, H Abruna, et al. *J. Am. Chem. Soc.*, 1978, **100** 5213
38. O N Efimov, V V Strelets *Coord. Chem. Rev.*, 1990, **99** 15
39. E Steckhan (Editor) *Electrochemistry, Vol. I* (Topics of Current Chemistry), Springer, Berlin–Heidelberg–New York, 1987, Vol. 142, p. 1
40. F C Anson, C L Ni, J M Saveant *J. Am. Chem. Soc.*, 1985, **107** 3442
41. A Merz *Chemically Modified Electrodes* (Topics in Current Chemistry), Springer, Berlin–Heidelberg, 1990, Vol. 152, p. 49
42. C P Andrieux, J M Saveant *J. Electroanal. Chem.*, 1978, **93** 163
43. C P Andrieux, J M Dumas-Bouchiat, J M Saveant *J. Electroanal. Chem.*, 1980, **114** 159
44. C P Andrieux, J M Dumas-Bouchiat, J M Saveant *J. Electroanal. Chem.*, 1982, **131** 1
45. C P Andrieux, J M Saveant *J. Electroanal. Chem.*,1982, **134** 163
46. C P Andrieux, J M Saveant *J. Electroanal. Chem.*, 1982, **142** 1
47. E Laviron *J. Electroanal. Chem.*, 1982, **131** 62
48. T Ikeda, C R Leidner, R W Murray *J. Electroanal. Chem.*, 1982, **138** 343
49. F C Anson, J M Saveant, K Shigehara *J. Phys. Chem.*, 1983, **87** 214
50. C P Andrieux, J M Dumas-Bouchiat, J M Saveant *J. Electroanal. Chem.*, 1984, **169** 9
51. W J Albery, A R Hillman *Roy. Soc. Chem. Ann. Rep.*, 1981, **78** 377
52. W J Albery, A R Hillman *J. Electroanal. Chem.*, 1984, **170** 27
53. J Leddy, A J Bard, J T Maloy, J M Saveant *J. Electroanal. Chem.*, 1985, **187** 205
54. F B Kaufman, A H Schroeder, E M Engler, et al. *J. Am. Chem. Soc.*, 1980, **102** 1483
55. F C Anson, J M Saveant, K Shigehara *J. Am. Chem. Soc.*, 1983, **105** 1096
56. P G Pickup, R W Murray *J. Am. Chem. Soc.*, 1983, **105** 4510
57. P Denisevich, K W Willman, R W Murray *J. Am. Chem. Soc.*, 1981, **103** 4727
58. A Merz, A J Bard *J. Am. Chem. Soc.*, 1978, **100** 3222
59. P J Peerce, A J Bard *J. Electroanal. Chem.*, 1980, **112** 97
60. C P Andrieux, O Haas, J M Saveant *J. Am. Chem. Soc.*, 1986, **108** 8175
61. X Chen, P He, L R Faulkner *J. Electroanal. Chem.*, 1987, **222** 223
62. M Delamer, M C Pham, P-C Lacaze *J. Electroanal. Chem.*, 1980, **108** 1
63. J Facci, R W Murray *Anal. Chem.*, 1982, **54** 772
64. P N Bartlett *Biosensors, Fundamentals and Applications* (Edited by A P F Turner, I Karube, and G S Wilson), Oxford University Press, Oxford, 1987, p. 211
65. R Nicholson, I Shain *Anal. Chem.*, 1964, **35** 706
66. A Deronzier, J-C Moutet *Acc. Chem. Res.*, 1989, **22** 249
67. F R Fan, A J Bard *J. Electrochem. Soc.*, 1986, **133** 301
68. T Shimidzu, A Ohtani, T Iyoda, et al. *J. Chem. Soc., Chem. Commun.*, 1986, 1415
69. A J Downard, N A Surridge, T J Meyer, et al. *J. Electroanal. Chem.*, 1988, **246** 321
70. P G Pickup, W Kutner, C R Leidner, et al. *J. Am. Chem. Soc.*, 1984, **106** 1991
71. K T Potts, D A Usifer, A Guadalupe, et al. *J. Am. Chem. Soc.* 1987, **109** 3961
72. E F Bowden, M F Dautartas, J F Evans *J. Electroanal. Chem.*, 1987, **219** 91
73. D A Buttry, F C Anson *J. Am. Chem. Soc.* 1984, **106** 59
74. H-L Li, J Q Chambers, D T Hobbs *J. Electroanal. Chem.*, 1988, **256** 447
75. S Kuwabata, Y Maida, H Yoneyama *J. Electroanal. Chem.*, 1988, **242** 143
76. N Oyama, F C Anson *J. Electroanal. Chem.*, 1989, **199** 467
77. B Brahimi, P Labbe, G Reverdy *J. Electroanal. Chem.*, 1989, **267** 343
78. T Ikeda, F Fushimi, K Miki, M Senda *Agric. Biol. Chem.*, 1988, **52** 2655
79. J Wang, T Martinez, D Darnall *J. Electroanal. Chem.*, 1988, **259** 295
80. K Itaya, H Akahoshi, S Toshima *J. Electrochem. Soc.*, 1982, **129** 1498
81. P J Kulesza, K Braijter, E Dabek-Zlatorzymska *Anal. Chem.*, 1987, **59** 2776
82. J A Cox, S E Gadd, B K Das *J. Electroanal. Chem.*, 1988, **256** 199
83. Z Gao, G Wang, P Li, Z Zhao *Electrochim. Acta*, 1991, **36** 147
84. M L Bowers, B A Yenser *Anal. Chim. Acta*, 1991, **243** 43
85. G K Budnikov, E P Medyantseva, S S Babkina *Usp. Khim.*, 1991, **60**(4) 881 [English translation in *Russ. Chem. Rev.*, 1991(4)]
86. D M Ivnitskii, I N Kurochkin, S D Varfolomeev *Zh. Anal. Khim.*, 1991, **46** 1462
87. S V Sasso, R J Pierce, R Walla, A Yacyhych *Anal. Chem.*, 1990, **62** 1111
88. S D Varfolomeev *Konversiya Energii Biokataliticheskimi Sistemami* (Energy Conversion by Biocatalytic Systems), Izd. Moskov. Gos. Univ., Moscow, 1981, 256 pp
89. A I Yaropolov, I V Berezin *Usp. Khim.*, 1985, **54**(9) 1448 [English translation in *Russ. Chem. Rev.*, 1985(9)]
90. M R Tarasevich, V A Bogdanovskaya *Bioelectrochem. Bioenerg.*, 1975, **2** 69
91. I V Berezin, V A Bogdanovskaya, S D Varfolomeev, et al. *Dokl. Akad. Nauk SSSR*, 1978, **240** 615
92. M R Tarasevich, A I Yaropolov, V A Bogdanovskaya, S D Varfolomeev *Bioelectrochem. Bioenerg.*, 1979, **6** 393
93. J J Kulys, G-Yu Shvirlitskaya *Dokl. Akad. Nauk SSSR*, 1979, **245** 137
94. J J Kulys *Anal. Lett.*, 1981, **14**(6) 377
95. K McKenna, A Braiter-Toth *Anal. Chem.*, 1987, **59** 954
96. K Sugawara, S Tanaka, M Taga *Analyst*, 1991, **116** 131
97. K Sugawara, S Tanaka, M Taga *J. Electroanal. Chem.*, 1991, **304** 249
98. J Cassidy, C Lowney *Anal. Chim. Acta*, 1990, **234** 479
99. J Labuda, V Plaskon *Anal. Chim. Acta*, 1990, **228**, 259
100. Z Gao, P Li, Z Zhao *Fresenius' Z. Anal. Chem.*, 1991, **339**, 137
101. T Miwa, L-T Jin, A Mizuike *Anal. Chim. Acta*, 1984, **100** 135
102. D M O'Riordan, G G Wallace *Anal. Chem.*, 1986, **58** 128
103. J A Cox, P J Kuesza *Anal. Chem.*, 1984, **56** 1021
104. Kh Z Brainina, A V Tchernysheva, N Yu Stozhko *Anal. Proc.*, 1986, **23** 204
105. G T Cheek, R F Nelson *Anal. Lett.*, 1978, **11** 393
106. K Kalcher *Fresenius' Z. Anal Chem.*, 1986, **325** 186
107. K Izutsu, T Nakamura *Rev. Polarogr.*, 1980, **26** 33
108. K H Lubert, M Schnurrbusch *Anal. Chim. Acta*, 1986, **186** 57
109. J A Cox, P J Kuesza *Anal. Chim. Acta*, 1986, **158** 335

110. J A Cox, K R Kulkarni *Analyst*, 1986, **111** 1219
111. J A Cox, K R Kulkarni *Anal. Chem.*, 1988, **60** 1710
112. R A Soraceno, J G Pack, A G Ewing *J. Electroanal. Chem.*, 1986, **197** 265
113. R T Lane, A T Hubbard *Anal. Chem.*, 1976, **48** 1287
114. A R Guadalupe, J D Abruna *Anal. Chem.*, 1987, **59** 2436
115. M K Halbert, R P Baldwin *Anal. Chem.*, 1985, **57** 591
116. G A Shumakovich, B A Kuznetsov, V K Gins, E N Mukhin *Novye Metody Prakticheskoi Biokhimii* (New Methods in Practical Biochemistry), Nauka, Moscow, 1986, p. 132
117. I Rubinstein, A Bard *J. Am. Chem. Soc.*, 1980, **102** 6641
118. H Okuma, H Takahashi, S Seikmukai *Anal. Chim. Acta*, 1991, **244** 161
119. S A Wring, J P Hart, B J Birch *Analyst*, 1991, **116** 123
120. R Lane, C Blaha *Langmuir*, 1990, **6**, 56
121. J Wang, M Ozsoz *Analyst*, 1990, **115** 831
122. A E Kaifer, M Han, O J Garcie *J. Electrochem. Soc.*, 1990, **137** 154C
123. W W Kubiak, J Wang *Anal. Chim. Acta*, 1989, **221** 43
124. M Bonakdar, J L Vilcher, H A Mottola *J. Electroanal. Chem.*, 1989, **266** 47
125. F Li, S Dong *Electrochim. Acta*, 1987, **32** 1511
126. M Peterson *Anal. Chem. Acta*, 1986, **187** 333
127. J Facce, R W Murray *Anal. Chem.*, 1982, **54** 772
128. X Chen, B Chia, P He *J. Electroanal. Chem.*, 1990, **281** 185
129. H Shinohara, G Khan, Y Ikariyama, et al. *J. Electroanal. Chem.*, 1991, **304** 75
130. J Wang *Anal. Chim. Acta*, 1990, **234** 41
131. F Bailey, T Malinski, F Kiechle *Anal. Chem.*, 1991, **63** 395

Received 21st January 1992

Translated from *Uspekhi Khimii* 61 1515–1549 (1992) U.D.C. 66.061

The dynamic separation of substances by liquid–liquid extraction

N F Kizim
Novo-Moskovsk Branch, Mendeleev Moscow Institute of Chemical Technology

ABSTRACT. Experimental data on the separation of substances by extraction, based on differences in the rates of their extraction, have been given. The physicochemical principles of dynamic separation have been examined. Approaches to the mathematical modelling of the process have been described, and specific models have been analysed.

The bibliography contains 231 references.

Contents

I. Introduction 830
II. Experimental data 830
III. Physicochemical principles of dynamic separation 836
IV. Mathematical models 838
V. Summary 845

I. Introduction

The method for separating substances based on differences in the rates of their liquid–liquid extraction has been known for a long time. As early as 1947, Barnes[1] showed that copper(II) and mercury(II) can be separated by extracting them with a chloroform solution of dithizone at low pH values. Mercury dithizonate was extracted rapidly, and the equilibrium state was reached in less than 1 min under the conditions of the experiments,[1] whereas the extraction of copper dithizonate took place slowly. Few such examples were known, however, and they were regarded as a possible way of improving the separation of substances in analytical determinations.[2]

In the last two decades, there has been a sharp increase in interest in the study of the kinetics of extraction. This has been due to the need to solve a number of theoretical problems, and also to an extension of the range of practical application of extraction methods. A large number of studies have been carried out, important reviews have been published,[3–9] and a new scientific field has developed, namely the kinetics of the extraction of inorganic substances. The kinetic studies have revealed many systems in which equilibrium is established slowly, and these can be used in practice. However, the separation of substances under non-equilibrium conditions, based on the use of kinetic factors (subsequently, the term "dynamic separation" will be used), has not been widely employed, for the following reasons.

Studies of separation by extraction have involved mainly the search for (synthesis of) effective extracting agents giving the required degree of separation as a result of differences in the thermodynamic parameters of the processes. In the list of factors influencing the separation (the nature of the extracting agent and the diluent, the composition of the aqueous solution, pH), the rate of extraction occupied one of the last places. In fact, there were definite grounds for this. The kinetic studies were at the stage of the development of the experimental procedure and the accumulation of data. For the most part, the kinetics of the extraction of individual substances were studied. Because of differences in the experimental conditions and the indeterminate nature of the hydrodynamic conditions close to the inter-phase boundary, the results of studies of the same extraction system were often inconsistent, and even contradictory. The situation was complicated considerably by the wide range of inter-phase phenomena (chemical reaction, adsorption, the formation of inter-phase films, spontaneous surface convection, electrical phenomena) in the extraction of inorganic substances, the non-uniformity of the inter-phase layer, and the consequent complexity of inter-phase mass exchange. Theoretical studies were based on extensive simplifications, and did not have sufficient predictive power.

At the same time, the determination of the factors leading to differences in rates of extraction and the discovery of criteria for identifying those systems for which the application of kinetic factors would lead to a significantly higher selectivity of separation require the systematic study of the kinetics of the simultaneous extraction of several components. However, the still unresolved fundamental problems of the kinetics of the extraction of individual elements, related mainly to the identification of the rate-determining stage and the location of the reaction, make it impossible for research workers to concentrate their attention on more complex systems. The study of the simultaneous extraction of several components is of considerable interest for a deep understanding of the mechanism of multicomponent liquid–liquid extraction and the general mechanism of the transfer of substances through the interface between two immiscible liquids. Moreover, the practical importance and the possibility of further improvement in the separation of substances is increasing interest in the dynamic separation method. The effective application of this method requires fundamentally new apparatus, but definite results can also be achieved using the equipment traditionally employed.[10–17]

The present review gives the results of experimental and theoretical studies of the dynamic separation of substances by liquid–liquid extraction.

II. Experimental data

1. Systems with dynamic separation

The separation of Cu^{II} from Hg^{II} by extraction with a chloroform solution of dithizone at low pH values, based on the difference in their rates of extraction, has been noted not only by the author cited above[1] but also by other workers.[18] The slow extraction of copper(II) dithizonate has been used in the determination of gold.[19]

Gold is extracted rapidly from 0.5 N H_2SO_4 by a chloroform solution of dithizone, whereas copper is extracted slowly and does not interfere in the determination of gold. The difference in the rates of extraction of zinc, cobalt, and nickel by dithizone solution has been made the basis of a method for their separation. In the extraction under the conditions of the experiments,[20] the extraction equilibrium is established in 15 min for zinc, 20 h for cobalt(II), and 10 d for nickel(II). The optimum conditions for separating the pairs Ni–Zn, Zn–Co, and Ni–Co have been determined.[20] It has been suggested that the high rate of extraction of vanadium(V) by β-isopropyltropolone solution could be used to separate vanadium(V) and iron(III).[21] The influence of kinetic factors on the selectivity of separation in the extraction of chelates has been examined by Freiser.[22]

The rate of extraction of Cu^{II} by Kelex 100, the active component of which is a β-alkenyl-8-quinolinol, is much greater than the rate of extraction of Fe^{III}, so that the selective extraction of Cu^{II} in the presence of Fe^{III} is possible.[23,24] For short phase contact times (less than 2 min) and an equilibrium pH of 0, the extraction of copper is not suppressed by iron. On prolonged mixing (up to 48 h), the ratio of the concentrations of copper(II) and $Fe^{(III)}$ in the organic phase at first increases from 20 to 80 (in 0.5–1 h), and then decreases to 18. Without stirring (after preliminary contact between the phases for 1 min), this ratio remains constant;[25] this is important when the extraction assembly is stopped unexpectedly.

In the range far from equilibrium, the rate of extraction of copper by Kelex 100 is 2.81×10^{-7} mol $cm^{-2} s^{-1}$, and that of iron(III) is 2.24×10^{-8} mol $cm^{-2} s^{-1}$. In the extraction from a nitrate solution (pH 2) by a 0.02 mol dm^{-3} solution of Kelex 100 in chloroform, 85% Cu^{II} is extracted after 2 min, whereas only 7% Fe^{III} is extracted.[26] On prolonged contact between the phases (48 h), Fe^{III} displaces Cu^{II} and the extract is saturated with Fe^{III} to the extent of 92%. The selectivity of the extraction of Cu^{II} is explained by kinetic factors.[26] This is indicated by the fact that for the maximum time of mixing, the degree of extraction of Fe^{III} in the absence of Cu^{II} is 98.9% and above, and the extent of the extraction of Cu^{II} in the absence of iron is 72.7%.

The results of an experimental study of the separation of copper from iron have been published.[27] A solution containing 1.3×10^{-2} mol dm^{-3} Cu^{II}, 1.6×10^{-2} mol dm^{-3} Fe^{III}, and 1 mol dm^{-3} Cl^- was shaken for 4 min with an organic phase consisting of a mixture of 2% Kelex 100 and 8% n-dodecanol in kerosene. The acidity was adjusted so that the final pH of the aqueous solution was 0.9; the separation factor was 30. Thus the system formed by Kelex 100 with the metal chlorides is similar to the corresponding sulphate system[23,25] in that the selectivity of the extraction of copper is also due to kinetic factors. Since $pH_{0.5}$ for Fe^{III} is lower than that for Cu^{II}, it might have been expected that Fe^{III} would be extracted more rapidly, but because of the large difference in the rates of extraction, Cu^{II} is extracted preferentially.[27] Determination of the equilibrium constants and rates of extraction showed that the introduction of the modifier nonylphenol into the organic phase leads to an increase in the distribution coefficient of Cu^{II}, but decreases the rate of extraction. The addition of Fe^{III} ions to the solution leads to an almost ten-fold further decrease in the rate of extraction of Cu^{II}, but has practically no influence on the rate of re-extraction of Cu^{II}. In all cases where Kelex 100 and Kelex 120 (20% Kelex 100 and 80% nonylphenol) are used, the rate of extraction of Cu^{II} remains 10^2 times higher,[28] and this ensures the separation of Cu^{II} and Fe^{III}. In the extraction by a solution of Kelex 100 in chloroform with a phase contact time of 0.5 h, the ratio of the concentrations of Cu^{II} and Fe^{III} in the organic phase was 38, whereas the value after stirring for 276 h was 0.5.[29]

The aminophenol extracting agents 7-(t-butylbenzyl)-8-quinolinol and a mixture of isomeric 7-β-decenyl-8-quinolinols are kinetically selective in the extraction of Cu^{II} from iron-containing solutions.[30] With short phase contact times (6–12 min), the selective extraction of Cu^{II} is possible. When equilibrium is reached, however, Fe^{III} is extracted more effectively than Cu^{II}, so that after prolonged contact between the phases, Fe^{III} begins to displace Cu^{II} from the organic phase.

In the extraction of copper, nickel, zinc, and cobalt(II) from ammoniacal solutions containing 300 g $litre^{-1}$ $(NH_4)_2SO_4$ by a 0.5 kmol m^{-3} solution of Kelex 100 and 10% isodecyl alcohol in Solvesso 150, the extraction and separation are influenced significantly by the phase contact time and temperature.[31] The ease of extraction of Cu^{II} at 323 K is higher than that at room temperature for short phase contact times, but with increase in the time of contact the extraction of Cu^{II} becomes less effective, and less Cu^{II} is extracted with increase in temperature. The extraction of Co^{II} increases regularly with increase in the phase contact time and temperature. The extraction of zinc(II) is higher at room temperature for short phase contact times, and with increase in the contact time, zinc(II) is displaced from the organic phase. Almost no nickel(II) is extracted. The optimum conditions for separating copper(II) and cobalt(II) are achieved for a phase contact time of 30 s at 323 K, or 2 min at room temperature. The separation of copper(II) and zinc(II) is improved by increasing the temperature and the phase contact time. Increase in the concentration of the extracting agent increases the efficiency of separation, but the degree of extraction is decreased. The authors cited[31] point out that the extraction of these elements depends on the nature of the anion and its concentration, the pH of the solution, the concentration of the extracting agent, temperature, and the phase contact time, so that the order of extraction may change: zinc(II) and cobalt(II) or zinc(II) and copper(II) may change positions.

In the extraction from the sulphate solution from the leaching of manganese nodules containing copper, nickel, cobalt(II), iron(III) and manganese(II) at pH 0–9 by a 10–15% Kelex 100 solution, the rate of extraction of copper(II) is greater than that of iron(III). The degree of extraction of iron(III) at pH 0.5–1.5 is greater than that of copper.[32] At pH 2, however, the degree of extraction of iron(III) is 80%, and that of copper(II) is 100%. With increase in the phase contact time and decrease in the ratio of the volumes of the organic and aqueous phases, there is a marked increase in the degree of extraction of copper(II) and an increase in the degree of extraction of iron(III). For a phase contact time of 2 min, the degree of extraction of copper is 93.2%, and the ratio of the concentrations of iron(III) and copper(II) in the organic phase is 0.142.[32] A study of the extraction of cobalt(II) and nickel(II) from sulphate solutions containing 0.25 kmol m^{-3} $(NH_4)_2SO_4$ at pH 4.72 by a 0.03–0.62 kmol m^{-3} solution of Kelex 100 in Shellsol containing added isodecyl alcohol established that at 298 K the rate of extraction of nickel(II) is very low, and equilibrium is not established even after mixing the phases for 120 min.[33] Increase in temperature leads to an increase in the rate of extraction. The addition of dinonylnaphthalenesulphonic acid (DNSA) has an even greater effect on the rate of extraction. For Ni^{2+} in the presence of 0.01 kmol m^{-3} DNSA, equilibrium is established in 1.5 h at 298 K, and in 20 min at 323 K. In all cases the rate of extraction of cobalt(II) is higher than that of nickel(II). At 323 K in the presence of 0.005 kmol m^{-3} DNSA, equilibrium in the extraction of cobalt(II) is achieved in

8 min. The data obtained can be used to improve the separation of Co^{II} and Ni^{II}.

Lix extracting agents are also kinetically selective. In the range far from equilibrium, the rate of the extraction of copper(II) from a nitrate solution with pH 2 by a solution of 0.02 kmol m^{-3} Lix 65N in chloroform is 4.42×10^{-9} mol $cm^{-2} s^{-1}$, and that of iron(III) is 3.01×10^{-11} mol $cm^{-2} s^{-1}$. In the extraction of copper(II) and iron(III), equilibrium is not established even after 6 weeks. The displacement of copper(II) from the organic phase by iron(III) is observed only after 140 h from the start of the experiment: this is much longer than in the extraction of these elements by a 0.02 kmol m^{-3} solution of Kelex 100 in chloroform.[26] When the solutions are mixed for a long time, the degree of extraction of iron(III) in the absence of copper reaches 53.7% and above, and the degree of extraction of copper(II) in the absence of iron(III) is 37.5%, indicating that the selectivity is due to kinetic factors.

In the extraction of copper(II) from a sulphate solution containing 5.13 g dm^{-3} copper(II) and 4.9 g dm^{-3} iron(III) (pH 2) by a 10% solution of Lix 63 in kerosene with the addition of 10% α-bromolauric acid and 3% isodecyl alcohol, a slight decrease in the extraction of copper(II) and a gradual increase in the extraction of iron(III) with increase in the phase contact time from 0 to 60 min is observed.[34] The decrease in the extraction of copper(II) is greater for a mixture containing 10% Lix 63 and 10% di-2-ethylhexyl hydrogen phosphate (D2EHHP) in kerosene with the addition of 3% isodecyl alcohol. The extraction of iron(III) increases sharply in the range 0–20 min, and for phase contact times greater than 45 min the degree of extraction of iron(III) becomes greater than that of copper(II).[34]

In the extraction of copper(II) from acid solutions containing iron(III) by a 20% solution of Lix 64N in the diluent Shell 140 with prolonged stirring (0–48 h), the ratio of the concentrations of copper(II) and iron(III) in the organic phase increases from 28 to 107.[25] Without mixing, this ratio remains constant.

For the extraction from the sulphate solution from the leaching of manganese nodules by a 10–15 vol.% solution of Lix 64N[32] it was established that the rate of extraction of copper(II) is greater than that of iron(III) throughout the pH range studied (0–9). At pH 2, the degree of extraction (E) of copper(II) is 75%, and that of iron(III) is 20%. A study of extraction from a solution modelling the leachings and containing 6 g dm^{-3} copper(II), 6 g dm^{-3} nickel(II), 0.15 g dm^{-3} cobalt(II), and 15 g dm^{-3} iron(III) for a phase contact time of 2 min showed that E_{Cu} is 52.1%, and the ratio of the concentrations of iron(III) and copper(II) in the organic phase is 0.007.[32]

It is also known that there is a difference in the rates of the extraction of non-ferrous metals and iron(III) by solutions of chelating extracting agents such as Hostarex DK-16 and SME-529. The extraction of iron(III) by DK-16 solutions takes place very slowly; the other metals are extracted rapidly, except nickel,[35] for which the rate of extraction by SME-529 is determined by the second stage of complex formation or by the diffusion of the complex being extracted.[36] Equilibrium is established in 30–35 min in the extraction of copper(II), and in 60 min in the extraction of iron.[37] Lix 63 is a kinetically synergetic additive to Lix 65N.[38,39]

A separation based on kinetic factors can be acheived in the extraction of zinc(II) and nickel(II) by solutions of dialkyl and diaryl hydrogen dithiophosphates.[40,41] Thus in the extraction by a 0.475 kmol m^{-3} solution of bis(di-isobutylmethyl) hydrogen dithiophosphate in Solvesso-150 containing 160 g dm^{-3} octanol, equilibrium is established in 1 h for zinc(II), and in 6 h for nickel.[40] In the extraction by 0.475 kmol m^{-3} solutions of di-n-butyl, di-isobutyl, di-n-octyl, di-(2-ethylhexyl), di-n-dodecyl, dicyclohexyl, and diphenyl hydrogen dithiophosphates in Solvesso-150 containing 160 g dm^{-3} octanol, equilibrium is established in 15 min for zinc(II), and in 120 min for nickel(II).[40] A study of the combined extraction of zinc(II) and nickel(II) by a 0.475 kmol m^{-3} solution of D2EHHDTP in the same mixed solvent at a ratio of the aqueous and organic phases of 1:1 established that the distribution of coefficient of Zn^{II} increases at first ($t \leqslant 2$ min), and then decreases, whereas the distribution coefficient of nickel(II) increases, indicating in the opinion of the authors cited,[41] the possibility of dynamic separation. For a phase contact time shorter than 2 min, the distribution coefficient (α) is greater than 6 for zinc(II), and less than 0.15 for nickel(II); when equilibrium is established, $\alpha_{Zn} = 0.68$, and $\alpha_{Ni} = 3.4$.

The difference in the rates of extraction of cobalt(II) and nickel(II) by dialkyl hydrogen dithiophosphates[42,43] can be used to increase the efficiency of their separation. Studies of the extraction of cobalt(II) and nickel(II) by solutions of di-(2-ethylhexyl) hydrogen dithiophsphate (D2EHHDTP) in n-decane showed that under equilibrium conditions the separation is not effective; the separation factor $\beta_{Ni/Co} < 2$. Since the extraction equilibrium is established in 10–45 h for cobalt(II) and in 0.5–2 h for nickel(II), it is possible to select conditions under which their effective separation is possible.[44,45] The extraction by a 0.3–0.5 kmol m^{-3} solution of D2EHHDTP in n-decane from a 1–2 kmol m^{-3} solution of $Co(NO_3)_2$ at a phase ratio of 1:1 with stirring for 0.5–2 h gave $\beta_{Ni/Co} = 150-200$. In these systems, the rate of extraction of Ni^{II} is much slower in acidic solutions, whereas the rate of extraction of Co^{II} remains high. By using kinetic factors under conditions close to equilibrium for Co^{II} and far from equilibrium for Ni^{II}, that is by using short phase contact times, it is possible to obtain high separation factors. In the extraction of Co^{II} and Ni^{II} from sulphate solutions by a 0.5 kmol m^{-3} solutions of D2EHHDTP in the presence of 1 kmol m^{-3} tri-n-butyl phosphate (TEP) for a definite phase contact time and a definite intensity of stirring, the separation factor reaches 20–100.[46] A method for separating Co^{II} and NI^{II} by extracting with a monoalkyl alkylphosphonate has been described.[47] The rate of transfer of Co^{II} into the organic phase is restricted by controlling the pH.

It is possible in principle to achieve higher separation factors ($\sim 10^4$) in systems containing D2EHHDTP.[48,49] The addition of oxygen-containing electron-donor additives (TBP, TOPO, etc.) to the system makes it possible to obtain a high efficiency of separation of cobalt and nickel at the re-extraction stage. With phase contact times restricted to several minutes it is possible to achieve effective separation with preferential re-extraction of cobalt.[50] After re-extraction for 2 min, cobalt is extracted to the extent of 99%, and nickel to the extent of less than 0.2%, corresponding to a separation factor of about 10^5. With long phase contact times, the separation factor decreases. Nickel can be re-extracted by an aqueous 9 kmol m^{-3} solution of HCl. With traces of cobalt at a high nickel concentration, partial separation at the extraction stage is appropriate.

A study of the re-extraction of cobalt(II) and nickel(II) from the extracts obtained in the system formed by D2EHHP and aqueous sulphuric acid solution using a single-stage centrifugal extractor[51] established the existence of a kinetic effect. Thus in the re-extraction from an organic phase containing 5.86 g dm^{-3} Co^{II} and 1.71 g dm^{-3} Ni^{II} (concentration of extracting agent in the original solution 0.58 kmol m^{-3}) with a 0.4 kmol m^{-3} aqueous H_2SO_4 solution at a

ratio of the volumes of the aqueous and organic phases of 1:1, the separation factor (β) decreases with increase in the phase contact time (t_c). At 294 K, β = 1.61 for t_c = 0.33s, β = 1.35 for t_c = 0.86 s, and β = 1.27 for t_c = 7.03 s.[51] A kinetic effect at the re-extraction stage is also possible for the pair copper–nickel,[52] cobalt, and nickel.[53]

The increase in selectivity for short phase contact times has been discussed[54] for the extraction of scandium(III), yttrium(III), and the lanthanides from a solution, after the extraction of uranium, containing up to 5 g dm^{-3} Fe_2O_3 as Fe^{2+} ions, using a solution of D2EHHP in kerosene. The extraction of iron(II), thorium(IV), and titanium(II) depends on t_c, but the extraction of scandium(III) and the lanthanides is almost independent of t_c in the range 2–30 s. For t_c = 2 s, non-intensive stirring (185 r.p.m.) in a turbine mixer gives more selective extraction of scandium(III), yttrium(III), and the lanthanides in the presence of iron(II), compared with their extraction in an ordinary mixer–settler for t_c = 30 s.[54]

A difference in the rates of extraction of iron(III) and uranium(VI) by D2EHHP solutions has been noted.[55] The low rate of extraction of Fe^{III} makes it possible to separate it from the lanthanides and yttrium by extraction with D2EHHP solutions in a centrifugal counter-current extractor. For t_c = 10 s and pH 2, yttrium is extracted from the clarified solution to the extent of more than 95% by a 10–12 vol.% solution of D2EHHP in Shell 140 kerosene. For this value of t_c, almost no Fe^{III} is extracted.[56] Increase in t_c leads to a sharp increase in the extraction of Fe^{III}, which suppresses the extraction of the lanthanides.[57] A concentrate of lanthanide oxides containing 30–60% Y can be obtained[58] by extracting with a 0.1 kmol m^{-3} solution of D2EHHP in kerosene at a ratio of the streams of the aqueous and organic phases of 4:1 with stirring for a short time, by varying the pH and the concentration of the extracting agent.

The significant difference in the rates of the extraction of indium and tin(IV) by alkyl hydrogen phosphates [in the extraction of tin(IV), equilibrium is established only after 60–70 min] led to the conclusion[59] that a considerable quantity of tin can be left in the aqueous phase by controlling the phase contact time. 4-t-Butylphenol-2-azo-1′-benzene-carboxylic acid and its mixture with 4-t-butylphenol-2-azo-1′-methoxybenzene are kinetically selective extracting agents for the extraction of copper(II) from iron-containing solutions. In the extraction of Cu^{II}, equilibrium is established in 10 min. The distribution coefficient of iron is higher than that of copper, so that the separation factor decreases with increase in the phase contact time.[60]

In their extraction by solutions of TBP in n-hydrocarbons, the behaviour of zirconium(IV) differs sharply from that of uranium(VI), for which a weak dependence of the rate of extraction on the TBP concentration was established. At low concentrations of TBP and nitrate ions, the separation of these elements under non-equilibrium conditions is much more effective than extraction under equilibrium conditions.[61]

A separation of the lanthanides has been based on the difference in the rates of extraction of these elements from concentrated solutions of salts of nitric and hydrochloric acids in the presence of an excess of acid by TBP containing a small quantity of di-n-butyl hydrogen phosphate.[62] The rate of extraction increases with increase in the atomic mass or atomic number of the element.

A difference in the rates of extraction of uranium(IV), uranium(VI), neptunium(IV), and plutonium(IV) was established[63] in their extraction by a 30% solution of TBP in hydrogenated tetrapropylene using a centrifugal extractor (phase contact time 0.4–2 s). At a high rate of rotation of the cylinder, complete extraction of uranium nitrates is achieved in 2 s. The rate of extraction of uranium(IV) is lower than that of uranium(VI), and only half the rate of extraction of neptunium(IV) and plutonium(IV).

A study[64] of the extraction of thiocyanate complexes of zinc and nickel from aqueous solution using droplet-dispersed n-butanol established that for short extraction times there is appreciable enrichment of the organic phase in zinc. Thus for t_c = 5 min the ratio of the concentrations of zinc(II) and nickel(II) in the organic phase is 6:1, although in the original aqueous solution the ratio of the concentrations was 1:1.

The differences in the rates of the extraction can be increased by adding complex-forming reagents to the system. Sakka and co-workers[65] studied the extraction of cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) from their 2 × 10^{-4} kmol m^{-3} aqueous buffer solutions with an ionic strength of 0.1 kmol m^{-3} (KNO_3) and pH 1–9 by 0.02 kmol m^{-3} solutions of 5-(4-dodecylphenylazo)-8-quinolinol (HL) in chloroform in the presence and absence of complex-forming reagents. In the absence of complex-forming reagents, the extraction of Ni^{II} is slow, and equilibrium is not established even after 10 h. The order of extraction from equilibrium data, Ni→Co→Zn, is reversed when the rates of extraction are compared.

For weak water-soluble complex-forming reagents (polyacrylic acid and citric acid), the extraction curves are displaced slightly to higher pH values. In the stronger reaction when triethylenetetramine (TETA) is added, the value of $pH_{1/2}$ is displaced considerably to higher values, and the slope of the lg α = *f*(pH) relationship, where α is the distribution coefficient, differs considerably from 2, which is observed in the absence of complex formation.[65] In extraction by the "rapid mixing–rapid separation" method or in rate-controlled extraction, as can be seen from the published illustrations,[65] when polyacrylic acid ($\overline{m}$ = 2000) is present, zinc(II) is extracted preferentially, the extraction of cobalt is complex, and the extraction of nickel(II) decreases considerably (pH 4–8). When citric acid is added to the system, similar changes are observed, but the position of cobalt in the order of ease of extraction at pH 7–8.5 is rigorously defined. Its extraction under the conditions indicated (concentration of M^{n+} in the original aqueous solution 2 × 10^{-4} kmol m^{-3}, concentration of HL in the original organic phase 2 × 10^{-3} kmol m^{-3}) does not exceed 25%, whereas the extraction of zinc(II) reaches almost 100%, and that of nickel is close to zero.

The addition of a stronger complex-forming reagent (TETA) leads to a decrease in the rate-controlled extraction of zinc and cobalt, and practically no cobalt is extracted. At pH 8, nickel is extracted preferentially, the extraction of zinc is much lower, and practically no cobalt is extracted. Thus the correct combination of complex-forming reagent, concentration of extracting agent, and pH makes possible the effective separation of zinc, cobalt, and nickel on the basis of kinetic factors.[65]

An analysis of data on the kinetics of the extraction of the trans-plutonium elements (TPE) in systems containing D2EHHP in the presence and absence of complex-forming reagents[66] led to the conclusion that in the absence of a complex-forming reagent the TPE are extracted under diffusion conditions, and the rates of their extraction are approximately equal. The addition of a complex-forming reagent increases the contribution of chemical resistance and produces a difference in the rates of extraction. A Lewis diffusion cell was used to study the kinetics of the extraction of the TPE and various lanthanides by D2EHHP solutions from solutions containing a complex-forming reagent. It was shown for the extraction system

10^{-2} kmol m^{-3} EDTA – 1 kmol m^{-3} ($NaNO_3$, HNO_3) – H_2O – CCl_4 – 1 kmol m^{-3} D2EHHP that extensive purification of the macro-component from micro-impurities is possible. Terbium is extracted more readily than europium, so that the separation of macro-quantities of the former from micro-quantities of the latter is difficult in an equilibrium extraction system. The rate of extraction of europium is much higher than that of terbium, and is independent of the terbium concentration, so that dynamic separation may be effective. Under emulsion conditions, only 15% terbium is transferred to the organic phase in the extraction of 90% europium. The authors cited[66] consider that effective purification of terbium from europium is achieved.

To determine the separation conditions, a study was made of the extraction of a number of TPE (Am, Cm, Cf, Bk), and also La, Ce, Sm, Eu, Gd, Th, Pa, U, Pu, Zr, Nb, Cs, Ru, and Fe using a solution fo 4-(α,α-dioctylethyl)pyrocatechol (Q) in toluene from strongly alkaline solutions in the presence of diethylenetriaminepenta-acetic acid (DETAPA).[67] It was shown that the degree of separation of the elements can be increased by varying the phase mixing time, the alkalinity of the medium, and the concentration of the extracting agent. The degree of extraction of Eu^{III} in the system 10^{-4} kmol m^{-3} Eu^{3+}, 2 kmol m^{-3} NaOH, 5×10^{-3} kmol m^{-3} diethylenetriamine-penta-acetic acid – 0.04 kmol m^{-3} Q in toluene increases from 60% to 100% with increase in t_c from 10 min to 45 – 60 min.[68] The separation of europium from americium can be improved by decreasing t_c. Thus in their extraction from 2 kmol m^{-3} NaOH for a contact time of 10 min, the degree of extraction of europium into the organic phase is 98%, and that of americium only 48%. With increase in the europium concentration, the distribution coefficient decreases, but by varying t_c, the concentration of alkali in the original aqueous solution, and the concentration of the extracting agent it is possibe to find the optimum conditions for their separation.

For 2 kmol m^{-3} NaOH, 10^{-4} kmol m^{-3} DETAPA, 10^{-2} kmol m^{-3} extracting agent, and t_c = 10 min, the degree of extraction of europium into the organic phase is 97%, and that of americium only 10%.[68] Americium(III) is subsequently extracted into the organic phase by a 0.04 kmol m^{-3} solution of Q in toluene with a phase contact time of 45 min.

A decrease was observed[69] in the rate of the extraction of fragment lanthanides from radioactive wastes to which complex-forming reagents (tartrate or citrate ions) had previously been added, in the presence of the ions of various metals (Fe^{3+}, Al^{3+}, Cr^{3+}). The magnitude of the retardation effect is different for different lanthanides. In the presence of Fe^{3+} the extraction of europium(III) and neodymium(III) is suppressed to a greater extent than that of cerium(III), whereas the presence of chromium(III) has a greater influence on the extraction of cerium(III) than on that of europium(III). The undesirable influence of interfering ions is partly eliminated by increasing the concentration of the complex-forming reagent.

The rate of the extraction of the TPE from aqueous solutions containing citric acid by D2EHHP solution is much higher than the rates of extraction of aluminium, iron, and zirconium, and it should be possible to increase the efficiency of separation by carrying out the process under non-equilibrium conditions.[10] The experiments were carried out on a stand of gravitational extractors. The phase contact time was lowered to 1 min, which made it possible to suppress the extraction of impurities. The purification factors achieved were ~10 for the removal of iron and aluminium, and greater than 50 for the removal of zirconium. The losses of the TPE do not exceed 1%. The authors cited[10] pointed out that purification from the elements indicated is not achieved when the process is carried out under equilibrium conditions.

The separation of yttrium and the lanthanides in the D2EHHP – DETAPA system is based on the difference in the rates of extraction; the rate for yttrium is higher than that for the lanthanides.[70]

The degree of extraction of zirconium and niobium from mineral acid solutions containing oxalic acid by solutions of di-n-octyl-methylenediphosphoric acid in petroleum spirit depends on the concentration of the reagents, the acid, and the time of shaking. In their extraction from 0.5 kmol m^{-3} H_2SO_4 solution containing 0.1 kmol m^{-3} $H_2C_2O_4$ and less than 10^{-4} kmol m^{-3} zirconium and niobium, for a concentration of the extracting agent of 2×10^{-3} kmol m^{-3} and a time of shaking of 10 min, the degree of extraction into the organic phase is 95% for zirconium, and 4.9% for niobium.[71]

The separation of zinc and cadmium using dithizone and Complexone III is based on the difference in the rates of their extraction. Thus at pH 8, a ratio of the volumes of the aqueous and chloroform phases of 9:1, and a Complexone concentration of 0.01 kmol m^{-3}, cadmium is practically completely transferred to the aqueous phase in 35 s, whereas significant transfer of zinc is observed only after 90 s.[72] The influence of water-soluble complex-forming reagents on the rate of the extraction of zinc and nickel by a solution of dithizone in chloroform has been studied.[73]

2. Cases where the extraction equilibrium is established slowly

The study of the kinetics of extraction has revealed a whole series of extraction systems, characterised by a sufficiently low rate of attainment of extraction equilibrium, which can be used to develop dynamic separation processes or which must be taken into account in the construction of apparatus for the process.

In the extraction of chromium(III) by a 0.1 kmol m^{-3} solution of 8-quinolinol in isopentyl alcohol at 328 K with a low concentration of sodium acetate (0.3 kmol m^{-3}), equilibrium is not reached even after phase contact for 7 h.[74] The rate is equally slow for the extraction of germanium by 0.01 – 0.1 kmol m^{-3} solutions of 8-quinolinol in chloroform, benzene, nitrobenzene, or isobutyl alcohol from nitrate media with an ionic strength of 0.1 ($LiNO_3$, $NaNO_3$).[75] Nickel is extracted slightly more rapidly.[76] Slow attainment of equilibrium is observed in systems containing dithizone in the extraction of zinc, cobalt, copper,[1,18,19] and bismuth (the equilibrium state at pH 1.0 and a concentration of dithizone in chloroform of 10^{-4} kmol m^{-3} is established in 3 h).[2] The rate of extraction of selenium(IV) by a solution of dithizone in CCl_4 is low. In the extraction from 5 kmol m^{-3} HCl solution by 5×10^{-5} kmol m^{-3} dithizone solution, 98 – 99% selenium is extracted after stirring for 1 – 3 h.[77]

A study of the extraction of indium by 1-(2-pyridylazo)-2-naphthol (PAN) revealed a characteristic feature of the dependence of the degree of extraction on the phase contact time.[78] The form of the kinetic curves depended on the method used to introduce the reagent into the system. When a chloroform solution of PAN was used, the kinetic curves had the usual form, but several hours were required for maximum extraction. When an ethanol solution of the reagent was added to the aqueous phase followed by extraction of the resulting compound with chloroform, indium was extracted almost instantaneously, but with increase in the time of shaking the degree of extraction reached the same values as observed for chloroform solutions of PAN. True equilibrium is established very

slowly. The extraction of indium with the addition of the reagent to the aqueous phase and shaking for 1–3 min[79,80] is carried out under non-equilibrium conditions, although it gives the maximum possible extraction.

Similar relationships were obtained for the extraction of gallium, zinc, iron(III), and manganese(II), but in the extraction of nickel, curves with a maximum were not observed.[78] The extraction of copper by indium and zinc dithizonates, and the extraction of iron(III) by indium, copper, and gallium cupferronates, take place slowly.[76,81] Under conditions in which all the reagent is present in the organic phase as a complex with the macro-element, the rate of extraction of a micro-element is independent of the acidity of the aqueous phase. The rate of exchange extraction decreases with decrease in the concentration of the reagent and with increase in the concentration of the macro-component.[81]

The extraction of iron(III) by a 0.2 kmol m^{-3} solution of thenoyltrifluoroacetone (TTA) in benzene is slow, and equilibrium is established in 12 h.[82] The rate of extraction depends on the composition of the aqueous phase and the acidity.

In the extraction of samarium from nitric acid solutions by a solution of TTA in kerosene with the addition of TBP, carried out in an Erlenmeyer flask with subsequent separation of the phases by centrifuging, the time taken to establish the equilibrium state in all the cases studied[83] is 60 min.

The rate of equilibration in the extraction of gallium, iron(III), zinc, nickel, and manganese depends on the method used to introduce PAN.[78] When a solution of PAN in chloroform is used, equilibrium is established very slowly (in several hours). When PAN is added to the aqueous phase (solution in ethanol) with subsequent extraction of the complexes by the pure solvent, the complexes are transferred instantaneously to the extract, but with increase in the time of shaking the degree of extraction decreases until equilibrium is established. In the extraction of the complexes of zinc, nickel, and manganese(II) by butanol, isopentyl alcohol, and nitromethane, equilibrium is established very rapidly. According to Kuznik's data,[84] in the extraction of dysprosium(III) and ytterbium(III) by PAN, equilibrium is established in 20 min.

A study[85] of the extraction of gallium by bidentate chelating reagents from a solution modelling the liquor of the Bayer process, containing 0.75 g dm^{-3} Ga_2O_3, showed that gallium can be extracted with a distribution coefficient of ~ 1 for a phase contact time of 2 h only by 7-nonyl-8-quinolinol.

There are only a few cases of the slow extraction of metal ions by organic acids. Thus in the extraction of iron(II) from 10^{-3} kmol m^{-3} HCl solution by a 0.5 kmol m^{-3} solution of D2EHHP in kerosene in a nitrogen atmosphere, equilibrium is established in 100 min;[86] in the extraction of titanium from sulphate solutions by D2EHHP the time taken for equilibration is greater than 14 h;[87] equilibrium is also established slowly in the extraction of niobium from fluoride–sulphate media;[88] and in the extraction of tin by a 0.5 kmol m^{-3} solution of D2EHHP in heptane, equilibration requires more than 20 h.[89] Anomalously slow transfer through an impregnated membrane using D2EHHP as the transferring reagent has been detected.[90]

The distribution of europium in the two-phase system Eu^{III}–0.1 kmol m^{-3} $(Na,H)ClO_4$/D2EHHP–toluene is slow, and equilibration takes ~ 4 h.[91] In the extraction of europium from nitric acid solutions by D2EHHP in a diffusion cell with stirring, equilibrium is established in 7 h.[92] In the extraction of yttrium, europium, thulium, lutetium, and americium at an ionic strength of 1 (NaCl, HCl) by a 1 kmol m^{-3} solution of D2EHHP in n-heptane, the time taken for equilibration does not exceed 20 min.[93] The influence of the composition of the aqueous phase on the rate of the extraction of praseodymium(III) by 2-ethylhexyl 2-ethylhexylphosphonate has been noted.[94]

The time taken for equilibration in extraction depends on the method used to bring the phases into contact. Thus in the extraction of uranium from sulphate solutions by D2EHHP the time taken for equilibration is 10 mins in an annular flow reactor, and 1 min in a reactor with mechanical stirring.[95] The kinetic character of the extraction of molybdenum(VI) in the presence of tungstates by D2EHHP solutions has been noted. The extraction of Mo^{VI} from sulphate solutions under emulsion conditions is fairly rapid, and equilibrium is established in 1.5–2 min.[96] The presence of W^{VI} in the acidic solution decreases the rate of extraction of Mo^{VI} by D2EHHP solutions. Equilibration requires phase contact times from 10 min to 6–7 h, depending on the process conditions.[97] The very low rate of equilibration has been attributed[98] to the formation of mixed tungsten–molybdenum polyanions, leading to a sharp decrease in the free concentration of molybdenum(VI).

Cases of slow equilibration in systems with basic extracting agents are known. For example, in the extraction of polymolybdates and the products of their protonation from aqueous solutions with an initial molybdenum concentration of about 0.25 kmol m^{-3} by solutions of trioctylammonium (TOA) chloride in chloroform, the time taken for equilibration increases from 4 h to 24 h with decrease in the pH of the solution from 4 to 1.[99] In the extraction of molybdenum from aqueous solutions containing HNO_3 and $NaNO_3$ by solutions of tri-n-decylamine (TDA) in benzene, the distribution coefficient increases with increase from 5 min to 20 h in the time for which the phases are stirred.[100] The phase contact time influences the distribution coefficient in the extraction of molybdenum(VI) by TBP solutions.[101]

In the extraction of chromium(III) by a 20% solution of Primene JMT in xylene, equilibration requires a phase contact time of 1 h at 80 °C, or 20 d at room temperature.[102] Iron(III) is extracted more rapidly. In the $Fe_2(SO_4)_3$–$(NH_4)_2SO_4$–Primene JMT sulphate–toluene system, equilibrium is established in about 1 h, although some changes take place for 20 h.[103] As a consequence of the higher rate of extraction of iron(III) and the suppression of the extraction of chromium(III), Fe^{III} can be separated from Cr^{III}.[102] A complex dependence of the distribution coefficient (D) on t_c was established for the extraction of Rh^{III} and Pd^{II} by a solution of an alkylthiuronium chloride,[104] of Ir^{IV} by a solution of TBP and diantipyrinylmethane,[105] and of Sb^{III} and Sb^{V} by non-polar solvents.[106] For t_c greater than 1 h, a decrease in D is observed, and the extraction stops after 12 h.[104] Increase in t_c above the value required to establish equilibrium for Sb^{V} leads to an increase in D in the extraction from concentrated H_2SO_4 solution, as a result of the reduction of Sb^{V} to Sb^{III}.[106] The dependence of the extraction of yttrium and strontium by octanoic acid on t_c,[107] and that of the re-extraction of aluminium and iron from aliphatic acids,[108] on the magnitude of t_c have been studied. Hydrolysis and polymerisation of the ions in aqueous solutions have a significant influence on the extraction of Nb, Ta, and Zr. The plot of the degree of extraction against pH shows maxima which disappear with increase in t_c.[109] Systems characterised by a long equilibration time have been noted by a number of authors.[110–118]

III. Physicochemical principles of dynamic separation

In principle, any factor capable of bringing about a difference in the rates of extraction of substances may be responsible for dynamic separation. The factors bringing about dynamic separation can be divided into four groups: differences in mechanisms, differences in conditions, differences in transport and kinetic parameters, and external factors. The following factors lead to dynamic separation.

1. Differences in mechanisms

1.1. Type of reaction
homogeneous/heterogeneous
simple/complex (multistage homogeneous, multistage surface)
1.2. The existence of intermediate steps and stages (in particular surface association, polymerisation, the formation of inter-phase films)
1.3. Colloid-chemical phenomena and processes (micelle formation, solubilisation, etc.)
1.4. The addition of complex-forming reagents, oxidising agents, and surface-active agents to the system

2. Differences in conditions

2.1. Kinetic/diffusion
extraction with a surface reaction
extraction with a bulk reaction
2.2. Intermediate conditions with bulk reaction/diffusion condition
2.3. Intermediate conditions with bulk reaction/kinetic condition

3. Differences in transport and kinetic parameters

3.1. Diffusion mobility
3.2. Rate of chemical reaction
3.3. Adsorption–desorption processes
3.4. The accumulation of intermediate products in the inter-phase region, their aggregation, the formation of a new phase

4. External factors

4.1. The application of external fields
4.2. Change in the process conditions (for example the type of extractor, degree of dispersion, etc.)

The proposed classification of the factors is to some extent arbitrary, but it is sufficiently general. Additional details can be introduced. In particular, in the examination of processes with surface reactions it is possible to note the factors influencing the rate of the surface reaction: adsorption, orientational and steric hindrance, catalysis by the surface, and spatial separation of the charges, leading to the formation of strong electric fields in the region of the phase interface. The ability of charged inter-phase surfaces to accelerate or inhibit extraction has been noted.[5,119] In the examination of differences in mechanisms, when the extraction of one substance can be described by a scheme with a simple reaction, and that of the other by a scheme with a complex reaction, we also have in mind bulk reactions taking place in the aqueous phase and associated with the formation of an extractable form of the substance, for example the displacement of a hydrolytic equilibrium or a monomer–polymer equilibrium, including stable polynuclear compounds. A difference between the relaxation times of these reactions in the extraction of each substance may bring about dynamic separation, but in the proposed classification of factors it will be included in section 3.2. Section 1.4. includes so-called inter-phase transfer catalysts,[120] which are also capable of bringing about differences in the rates of extraction.

Theoretical estimates of the attainable separation effects have been carried out.[121–123] These effects may be considerable when there are differences in the mechanisms and conditions of the processes.

In publications giving the results of experimental studies of the kinetics of the simultaneous extraction of two or more components, insufficient attention is often paid to the description of the method and the apparatus. Unfortunately, this makes it difficult to identify the factors responsible for dynamic separation, and prevents an unambiguous solution of the inverse problem of dynamic separation. At the same time there are publications in which either the authors themselves interpret the factors responsible for dynamic separation or the systems dealt with have been sufficiently well studied from both the thermodynamic and the kinetic viewpoints, and in these cases it is possible to identify the factors responsible for the separation.

The difference between the rates of extraction of U^{VI} and Fe^{III} by D2EHHP[124] is due to a difference in the extraction conditions. At an H_2SO_4 concentration less than 1 M, U^{VI} is extracted under diffusion conditions,[125] and Fe^{III} under kinetic conditions.[126,127] In the opinion of Sato and co-workers,[127] the rate-determining stage includes the reaction of the hydroxo-complex $Fe(H_2O)_3(OH)^{2+}$ with D2EHHP dimers, but in the opinion of Karpacheva and Ilozheva,[126] the rate of extraction of Fe^{III} is limited by the reaction

$$Fe^{3+} + X^-_{(aq)} \rightleftarrows FeX^{2+},$$

which apparently takes place in the aqueous phase. The fairly high activation energy, which according to Sato[128] is 37.8 kJ mol^{-1}, confirms that Fe^{III} is extracted under kinetic conditions.

The separation of Zn^{II} and Co^{II} in their extraction by dithizone, based on kinetic factors,[129] is due to a difference in the mechanisms.[130] It is considered that the limiting stage for the reaction of both Zn^{II} and Co^{II} is the replacement of a water molecule in the inner coordination sphere of the ion by the anion of the extracting agent,[130,131] since its formation is accompanied by the rupture of four coordinate bonds with water molecules. It is suggested that for an aqueous solution with pH 4, the extraction of Zn^{II} is accompanied by a surface reaction,[130,132] and that of Co^{II} by a homogeneous reaction.[130] Other authors,[133,134] however, in a study of the kinetics of the extraction of Zn^{II} and Co^{II} by solutions of dithizone in chloroform with rapid mixing of the aqueous and organic phases, concluded that the rate-determining stage is the formation of the metal chelate in the aqueous phase, and not a surface reaction. The conclusions reached by the authors cited[132] from the results of a study of the kinetics of the extraction of Zn^{II} by the single-drop method do not agree with other conclusions.[134] This difference of opinion makes it impossible to reach an unambiguous conclusion about the mechanism of the dynamic separation of Zn^{II} and Co^{II}. If however it is assumed that in the extraction of both Co^{II} and Zn^{II} the rate-determining reaction takes place in the aqueous phase, it may be assumed that the separation is due to a difference in the rates of the removal of water molecules from the hydration layers of the metal ions. Freiser[135] gives Eigen's

data on the rate constants of the above reaction; the rate constant is 5×10^7 s^{-1} for Zn^{II}, and 5×10^5 s^{-1} for Co^{II}.

Fleming,[26] on the basis of a study of the kinetics of the extraction of iron and copper by Kelex 100 and 8-quinolinol,[24,25,27,136] considers that the selectivity is determined by kinetic factors and is due to the fact that the extraction of copper takes place under diffusion conditions, and that of iron(III) under kinetic conditions. It is known that 8-quinolinol forms much more stable (by factors of $\sim 10^{10}$) complexes with Fe^{3+} than with Cu^{2+}, and that alkyl-substituted 8-quinolinol – Kelex 100 extracts copper(II) more effectively than iron(III).[26] Other authors[23,24,28] reach the same conclusion about the nature of the selectivity. This view is confirmed by the decrease in the rate of the extraction of copper when nonylphenol is added to the organic phase. The decrease in the rate of extraction with increase in the concentration of nonylphenol takes place in parallel with an increase in the inter-phase tension, indicating the formation of hydrogen complexes by Kelex 100 and nonylphenol.[28] The rate of extraction of Cu^{II} remains 10^2 times greater than that of Fe^{III}. At the same time, other authors[137] consider that the rate of the extraction of Cu^{II} from sulphate solutions by Kelex 100 is determined by a surface reaction.

In a study of the difference in the rates of the extraction of Ni^{II}, Co^{II}, and Zn^{II} by HL solutions,[65] it was noted that the rates of extraction change in the same sequence as the rate constants for the replacement of water molecules from the hydration layers of the metal ions, and the difference in the rates of extraction was attributed to a difference in the rates of the chemical reactions, and not to a difference in the rates of "physical" distribution. According to other works,[138] the rate-determining stage is the addition of the second 8-quinolinol molecule. Thus the dynamic separation of Ni, Co, and Zn in their extraction by HL is due to the difference in the reaction rate constants.

The selectivity of the extraction of Cu^{II} compared with Fe^{III} by solutions of hydroxyoximes is attributed to kinetic factors.[26,29,139] If it is assumed, following Danesi and co-workers,[140] that the rate-determining stages in both the extraction of copper(II) and the extraction of Fe^{III} are reactions taking place on the phase interface,

$$Cu(H_2O)_{6-n}Cl_n^{(2-n)+} + Ox^- \rightarrow CuOx^+ + (6-n)H_2O + nCl^-,$$

$$Fe(OH)(H_2O)_{5-n}Cl_n^{(2-n)+} + HOx \rightarrow FeOx^{2+} + (6-n)H_2O + nCl^-,$$

$$Fe(H_2O)_{6-n}Cl_n^{(3-n)+} + HOx \rightarrow FeOx^{2+} + (6-n)H_2O + nCl^- + H^+,$$

it may be assumed that the separation is due to a difference in the rates of these reactions; a possible reason for this difference may be that the copper ions, as a consequence of their small radius, bring about the polarisation of the phenolic oxygen in the hydroxyoxime and facilitate the ionisation of a proton, whereas the Fe^{3+} ions, despite their smaller radius, cannot rapidly form a square-planar complex with hydroxyoximes.[141] A different view of the rate-determining stage in the extraction of copper(II) by Lix 34 has been put forward.[142]

The difference in the rates of extraction of the dithizonates has been used to separate Zn^{II}, Co^{II}, and Ni^{II}.[20] It has been established[130] that the separation of Zn^{II} and Co^{II} is due to a difference in the reaction mechanisms; at pH 4, Zn^{II} is extracted by a heterogeneous mechanism, and cobalt by a homogeneous mechanism. Thus more complete separation, based on the higher rate of extraction of zinc, requires more intensive stirring.[130] The localisation of the reaction is due to the increase in the reactivity of the dithizone ions adsorbed on the phase interface, as a result of the influence of adsorption forces.[130] Other authors[132] also consider that in the extraction of Zn^{II} by dithizone the reaction is localised at the inter-phase surface. In Freiser's opinion,[133,134] the rate-determining stage is the formation of 1:1 chelates in the aqueous phase, but in the case of cobalt(II) at concentrations greater than 8×10^{-5} M the process is limited by the chemical reaction at the phase boundary.[143] The rate constants for the formation of the chelates of zinc, cobalt, and nickel are closely related to the rate constants for the removal of water from the hydration layer of the metal ion.[135] Although the position of the reaction zone has not been finally determined, there is no doubt that the separation is due to kinetic factors, since the thermodynamic approach cannot explain the observed separation effects, even if only because the stability constants of the neutral dithizonate complexes of zinc(II) and cobalt(II) are practically identical.[144] Studies of the kinetics of extraction by halogenated dithizones led to the conclusion[145] that the rate-determining stage is the formation of the metal dithizonate (1:1), which takes place mainly on the surface in the extraction of Ni^{II} and in the bulk of the aqueous phase in the extraction of Zn^{II}.

The rates of the extraction of multivalent ions such as Zr^{IV}, Ru^{IV}, Al^{III}, Ga^{III}, Cr^{III}, and the platinum metals (Pt^{II}, Rh^{III}, Ir^{III}) are often low, so that the separation of these ions from others which are rapidly extracted has been verified under laboratory conditions. The slow extraction of the ions is due to hydrolysis and polymerisation in the aqueous phase and the low rate of formation of the extractable form. The low rate of equilibration in the extraction of molybdates by solutions of tri-n-octylamine in chloroform is due to the existence of polymeric ions, detected by osmometry and chemical analysis.[99] Noting that at low concentrations of TBP and HNO_3 the separation of zirconium and uranium is much more effective under non-equilibrium conditions than under equilibrium conditions, Mailen and co-workers[61] examined the chemistry of the extraction of Zr^{IV}. They assume that of the four complexes present, namely Zr^{4+}, $Zr(OH)^{3+}$, $Zr_3(OH)_4^{8+}$, and hydroxo-polymers, the species extracted are Zr^{4+} and $Zr(OH)^{3+}$, which are present in equilibrium with the other two forms. At $[HNO_3] \geqslant 3$ M, Zr^{4+} ions predominate in the solution, and the rate of extraction is proportional to $[TBP]^2$. At $[HNO_3] \leqslant 1$ M, $Zr(OH)^{3+}$ predominates, and the rate of extraction is proportional to $[NO_3^-]^3$. The behaviour of zirconium differs sharply from that of uranium, which is only weakly dependent on the TBP concentration and which is not influenced by $[NO_3^-]$. The presence in solution of chemical forms of ruthenium with different extraction properties is responsible for the two-stage character of its extraction by TBP — a rapid first stage (~ 0.6 s) and a slow second stage (> 1 h).[146]

The complexity of the ionic equilibria of Sn^{IV} in aqueous solution and the slow transformation of the complexes into the extractable form can be used to separate indium and tin(IV) by extraction using alkyl hydrogen phosphates. By controlling the phase contact time, a large quantity of tin(IV) can be left in the aqueous phase.[59]

The existence of the kinetic factor in the separation of Co^{II} and Ni^{II} in their re-extraction[51] can be attributed to the polymerisation of the Ni^{II} complex in the organic phase.[147] It is known,[148] however, that the view that polymers are formed is not consistent with experimental data on the kinetics of the combined extraction of Co^{II} and Ni^{II} by D2EHHP.

The separation of cobalt(II) and nickel(II) in their extraction by D2EHHDTP is due to a difference in the reaction mechanisms. The extraction of Co^{II} is determined by two factors — the rate of the reaction of Co^{II} with D2EHHDTP and the rate of its oxidation in

the organic phase by atmospheric oxygen. The kinetics of the extraction of Ni^{II} are determined only by the rate of its reaction with the DTP.[48] A study of the extraction of Ni^{II} by solutions of D2EHHDTP in decane showed that nickel is extracted as the diamagnetic complex $Ni[(C_8H_{17}O)_2P(S)S]_2$, which has a low-spin square-planar configuration,[44] whereas in the extraction of cobalt an equilibrium is established in the organic phase between the tetrahedral paramagnetic complex $Co[(C_8H_{17}O)_2P(S)S]_2$ and the diamagnetic low-spin complex $Co[(C_8H_{17}O)_2P(S)S]_3$ with a configuration close to octahedral. The stage of Co^{II} oxidation is relatively slow, and the extraction equilibrium is established in 10–45 h, depending on the conditions, whereas for nickel, equilibrium is established in 0.5–2 h.[44] This provides a basis for separating cobalt and nickel by the preferential extraction of nickel(II).

The addition of donor–acceptor reagents (TBP, TOPO) decreases considerably the rate of oxidation of cobalt. When the phase contact time is restricted, it is possible in principle to separate cobalt and nickel by the preferential extraction of cobalt(II).[46,48] The oxidation of cobalt(II), however, gives kinetically inert complexes,[149] making re-extraction difficult. Various donor–acceptor additives decrease the rate of this process.[50] If the phase contact time is restricted to a few minutes, separation is achieved by the preferential re-extraction of cobalt. The system containing TOPO is preferable to that containing TBP. Re-extraction for 2 min makes it possible to achieve separation factors of $\sim 10^5$.[50]

The separation of zinc and nickel in their extraction by dialkyl hydrogen dithiophosphates (DAHDTP), in particular D2EHHDTP, is due to the difference in the rates of dehydration of zinc and nickel ions.[40,41] Since the rate of extraction is influenced by the nature of the group in the DAHDTP,[150] this may facilitate the choice of separation conditions.

Rates of extraction can be differentiated by adding complex-forming reagents to the system.[65,66,151] The influence of complex-forming reagents is two-fold. On the one hand, complex formation leads to changes in the equilibrium parameters; for example, by adding citrate ion and keeping the solution for 24 h it is possible to suppress the extraction of chromium(III) by D2EHHP almost completely,[152] and in an acetate solution kept for up to 2 d the distribution coefficient of chromium(III) is lowered by a factor of ~ 200.[153] When very weak complex-forming reagents are used, the extraction curves of transition metals are displaced to high pH values, and the $\lg D = f(\mathrm{pH})$ relationship usually studied is linear with a slope differing little from 2, which is characteristic of extraction systems in the absence of complex formation. For a stronger reaction with the complex-forming reagent, the value of $pH_{1/2}$ is displaced considerably to high pH values, and in the case of the strong interaction which takes place, for example, in the Fe^{III}–citrate ion system, the extraction is completely suppressed.[65] Cases are known, however, where the addition of a complex-forming reagent has a levelling action. Increase in the time for which an aqueous solution containing Ni^{II} is kept leads to a three-fold decrease in the distribution coefficient of nickel. The presence of the citrate ion decreases the difference in the distribution coefficients to 1.5. Further increase in the concentration of citrate ions generally counterbalances the effect of keeping the solution beforehand.

On the other hand, the addition of complex-forming reagents influences the rate of extraction.[154] The addition of lactate ion leads to a decrease in the coefficient of mass transfer in the extraction of europium,[155] and produces a marked change in the rate of extraction of copper by SME-529.[156] The extraction of Eu^{III} and Am^{III} by solutions of (α,α-dioctylethyl)-pyrocatechol (Q) in the presence of diethylenetriaminepenta-acetic acid (DETAPA) takes place more slowly, the higher the stability of their complexes in the aqueous phase. Thus in their extraction from 2 kmol m^{-3} NaOH solution by a solution of 0.04 kmol m^{-3} Q in toluene, Eu^{III}, which forms a less stable complex with DETAPA, is extracted into the organic phase to the extent of 98% after 10 min, whereas the degree of extraction of Am^{III} is only 48%.

The transplutonium elements are extracted by D2EHHP under diffusion conditions, and their rates of extraction are identical. In the presence of a complex-forming reagent, the contribution of chemical resistance should be greater, and the rates of extraction will be different.[66] The addition of a complex-forming reagent leads to a change in the extraction conditions for Eu^{III}. With increase in the concentration of the complex-forming reagent, the extraction conditions change from diffusion to kinetic. The authors cited[66] consider that the rate of extraction is determined by the chemical reaction in the aqueous phase or in the inter-phase layer. The results show that to achieve the maximum difference in the rates of extraction of europium(III) and terbium, it is necessary to use the highest possible concentrations of the Complexone. The nature of the functional group of the Complexone has no significant influence, but when the complexes have high stability constants, the concentration of Complexone required to achieve a given effect is lower.[66] In the presence of a Complexone (EDTA), the rate of extraction of europium is much higher than that of terbium, giving effective dynamic separation; under emulsion conditions, only 15% terbium is transferred to the organic phase in the extraction of 90% Eu^{III}.[66]

The dynamic separation of nickel and zinc can be achieved using polyacrylate and citrate as complex-forming reagents.[65] In the extraction of the metal ions from aqueous solutions, the rate of the process is determined by the rate of the removal of water molecules from the hydrated ions. This mechanism does not change significantly in the presence of weak complex-forming reagents, since most of the ions remain hydrated in solution. Greater differences in the rates of the processes may be expected at the re-extraction stage. It appears possible to select catalysts for the decomposition of the complexes.[65] The decrease in the rate of extraction when a complex-forming reagent is added to a system may be due to the appearance of double complexes. For example,[69] in the presence of tartrate ion the addition of chromium(III) for a phase contact time of 3 min lowers the distribution coefficient of Eu^{III} from 1000 to 88 if the concentration of chromium(III) in the solution is 0.001 kmol m^{-3}. A decrease in the rate of the process when a mixture of extracting agents is used has been noted.[157]

IV. Mathematical models

A basis for the mathematical modelling of dynamic separation is provided by the general theory of inter-phase multi-component mass transfer accompanied by inter-phase phenomena. The variety of inter-phase phenomena (adsorption, chemical reaction, inter-phase film formation, spontaneous surface convection, micro-emulsification, association, dissociation, etc.) and the need to take account of the mutual influence of the components being extracted create insuperable mathematical difficulties in this approach, so that a rigorous quantitative calculation of the dynamic separation coefficient is not yet possible.

The simultaneous extraction of several components is complicated by their mutual influence.[158,159] Even in the case of the "physical" distribution of each component, it is necessary in the mathematical modelling of the process to take account of the interaction of the diffusion fluxes in each phase, since it follows from the thermodynamics of irreversible processes that the flux of each component depends on the gradients of the chemical potential of each component of the mixture. The methods described earlier[160–166] can be used. If one of the components is present in the system in microquantities and the other in macro-quantities, the analysis developed earlier[167,168] can be used. The development of this approach is being held up, however, by the absence of published data on diffusion cross coefficients in the organic phase and the extremely limited amount of such data for the aqueous phase. Moreover, allowance for the whole variety of inter-phase phenomena accompanying the extraction of inorganic substances[173–215] practically excludes the possibility of obtaining an analytical solution.

In most cases for specific mechanisms of the process the estimation of the expected value of the dynamic separation factor is carried out using mathematical models based on the assumption that the extraction processes of the separate components are independent, that is that the extraction of one component does not influence the extraction of the other. Naturally, it is assumed that the principle of independence applies at all stages of the extraction process, irrespective of the complexity of the macroscopic process. If it is assumed that the diffusion cross coefficients tend to zero with decrease in the concentrations of the components being extracted, better agreement can be expected between calculation and experiment for dilute solutions containing the extractable components in equal concentrations. With increase in the concentration of the components extracted, the errors in the estimates of the dynamic separation factor will increase not only as a result of the neglect of the mutual influence of the extraction processes but also as a result of the neglect of the non-ideal character of the system and the use of concentrations instead of activities. Nevertheless, this approach is useful for estimating possible values of the dynamic separation factor. When the loading of the organic phase is low, the separation factor can be calculated if the mutual influence of the ions is neglected.[216]

The possibility of a determinate description of the transport stages in non-stirred systems means that an exact analytical solution can be obtained for the flux of the component being extracted by the construction of a mathematical model of the dynamic separation process. For simplicity we shall assume that the phases are semi-infinite, that the diffusion coefficients are independent of the coordinate and of time, that the components being distributed are initially present in only one phase, and that rapid reversible reactions take place at the interface, complicating the processes involved in the distribution of each component. The system of equations with initial and boundary conditions is written in the form[121,122]

$$\frac{\partial C_{ij}}{\partial t} - D_{ij}\frac{\partial^2 C_{ij}}{\partial x^2} = 0, \quad j = \begin{cases} 1, \text{ if } x \in (-\infty, 0) \\ 2, \text{ if } x \in (0, \infty) \end{cases} \qquad (1)$$

for $x = 0$

$$D_{i1}\frac{dC_{i1}}{dx} - D_{i2}\frac{dC_{i2}}{dx} = 0,$$

$$\alpha_i = C_{i1}/C_{i2},$$

$$C_{i1}(x,0) = C_{i1}^0, \qquad C_{i2}(x,0) = 0,$$

where C_{ij}, $C_{ij}(x,0)$ are the current and initial concentrations of the ith component in the jth phase, D the diffusion coefficient, t the time, x the coordinate, and α the local distribution coefficient. The equation† for the flux of the ith component[217]

$$j_i = \frac{C_{i1}^0}{R_i}\left(\frac{D_{i1}}{\pi t}\right)^{1/2},$$

where $R_i = 1 + \alpha_i(D_{i1}/D_{i2})^{1/2}$, determines the quantity of the ith substance (M_i) transferred into phase 2 in a time t through a phase interface F if the integration is carried out in the range from 0 to t,

$$M_{i2} = \frac{2C_{i1}^0 F}{R_i}\left(\frac{D_{i1}t}{\pi}\right)^{1/2}.$$

Adopting for the dynamic separation factor the expression:[121]

$$\beta = \frac{M_{12}}{C_{11}^0} \Big/ \frac{M_{22}}{C_{21}^0},$$

gives

$$\beta = \left(\frac{D_{11}}{D_{21}}\right)^{1/2}\frac{R_2}{R_1}.$$

For a pair of elements with similar properties, the ratio R_2/R_1 can hardly differ greatly from 1, so that high values of β cannot be expected.

The separation of the extractable components may be greater if the extraction of one of the substances is accompanied by a reversible reaction of first order with rate constants k_1 for the forward reaction and k_2 for the back reaction, taking place in the donor phase, while the extraction of the other takes place by a "physical" distribution mechanism. The mathematical formulation of the problem is then altered considerably. The equation for the diffusion of the substance A in the donor phase will be replaced by the equation for diffusion with chemical reaction

$$D_{11}C''_{11xx}(x,t) - \dot{C}_{11t}(x,t) - k_1 C_{11}(x,t) + k_2 C_{21}(x,t) = 0,$$

† It should be noted that the equation for the flux of a substance leads to a situation which cannot be realised physically when $j \to \infty$ as $t \to 0$. This is due on the one hand to the restricted character of the application of the equation of Fick's second law to the description of molecular diffusion when there are large concentration gradients, and on the other hand to the use of the boundary condition $\alpha_i = C_{i1}/C_{i2}$, which reflects an unchanged ratio of the pre-boundary concentrations. As a result, the equation is inapplicable at $t = 0$. If the non-stationary diffusion is described using the hyperbolic equation

$$\frac{\partial C}{\partial t} + \tau\frac{\partial^2 C}{\partial t^2} - D\frac{\partial^2 C}{\partial x^2} = 0,$$

where τ is the relaxation time of the diffusion flux, the divergence of the flux as $t \to 0$ is eliminated. The attainable accuracy of the calculation has been discussed briefly.[5] The unique role of the boundary conditions in the analysis of the kinetics of diffusion-controlled processes has been examined in detail in monographs[169,170] and articles.[171,172]

where C''_{11xx} is the second partial derivative with respect to the coordinate, and C_{11t} the partial derivative with respect to time, and an analogous equation taking account of the diffusion of the reaction product in the donor phase is added. The boundary condition should take account of the fact that there is no accumulation of the reaction product in the inter-phase region.

The time dependence of the dynamic separation factor (β_t) is described by expressions determined by the values of the parameter a_0

$$a_0 = \frac{r_1}{\alpha_1} + \left(1 + \frac{r_1}{\alpha_1}\right) K_c,$$

where D_{11}, D_{21} are the diffusion coefficients of the original substance and the reaction product in the donor phase, α_1 the distribution coefficient of the reaction product at the phase interface, and K_c the equilibrium constant of the chemical reaction:

a, for $a_0 < 1$

$$\beta_t = a_{11} / F_1(t),$$
$$F_1(t) = 1 + a_{12} F_{11}(t) - F_{12}(t),$$
$$F_{11}(t) = \left\{\mathrm{erf}\left[(k_{12} + b_0)t\right]^{1/2} - \mathrm{erf}\left(b_0 t\right)^{1/2}\right\} \exp(b_0 t),$$
$$F_{12}(t) = \left[\sqrt{\pi}\, \mathrm{erfz}(t)\right] / 2a_0 z(t),$$
$$a_{11} = a_2 r_{31} \Big/ \left(1 + \frac{r_2}{\alpha_2}\right), \quad a_{12} = \frac{\sqrt{\pi}}{2} \frac{\left(1 - a_0^2\right)^{1/2}}{a_0},$$
$$a_2 = 1 + \frac{r_1}{\alpha_1} \frac{1 + K_c}{K_c}, \quad b_0 = a_0^2 k_{12} / \left(1 - a_0^2\right),$$
$$k_{12} = k_1 + k_2, \quad K_c = k_1 / k_2, \quad r_1^2 = D_{11} / D_{21},$$
$$r_2^2 = D_{31} / D_{32}, \quad r_{31}^2 = D_{31} / D_{11}, \quad z(t) = \sqrt{k_{12} t},$$

where erf ξ is the probability integral;

b, for $a_0 > 1$

$$\beta_t = a_{11} / F_2(t),$$
$$F_2(t) = 1 + a_{13} F_{21}(t) - F_{12}(t),$$
$$F_{21}(t) = \left[I_1(t) - I_2(t)\right] \exp(-bt) / z(t),$$
$$I_i(t) = \int_0^{\pi_i^2(t)} e^{\lambda^2} d\lambda, \quad \pi_1^2(t) = (b - k_{12})t, \quad \pi_2^2(t) = bt,$$
$$a_{13} = \left(k_{12} / b\right)^{1/2}, \quad b = a_0^2 k_{12} / \left(a_0^2 - 1\right);$$

c, for $a_0 = 1$

$$\beta_t = \frac{K_c r_{31}}{1 + r_2 / \alpha_2} \Big/ \left[1 - F_{12}(t)\right].$$

From the last expression it follows that for short phase contact times, β_t increases with decrease in the time and is given approximately by the expression

$$\beta_t \approx r_{31} F_3(t) \Big/ \left[k_1 \left(1 + \frac{r_2}{\alpha_2}\right) t\right],$$

where

$$F_3(t) = \left[\frac{2}{3} - \frac{1}{5} k_{12} t + \frac{1}{21} (k_{12} t)^2\right]^{-1}.$$

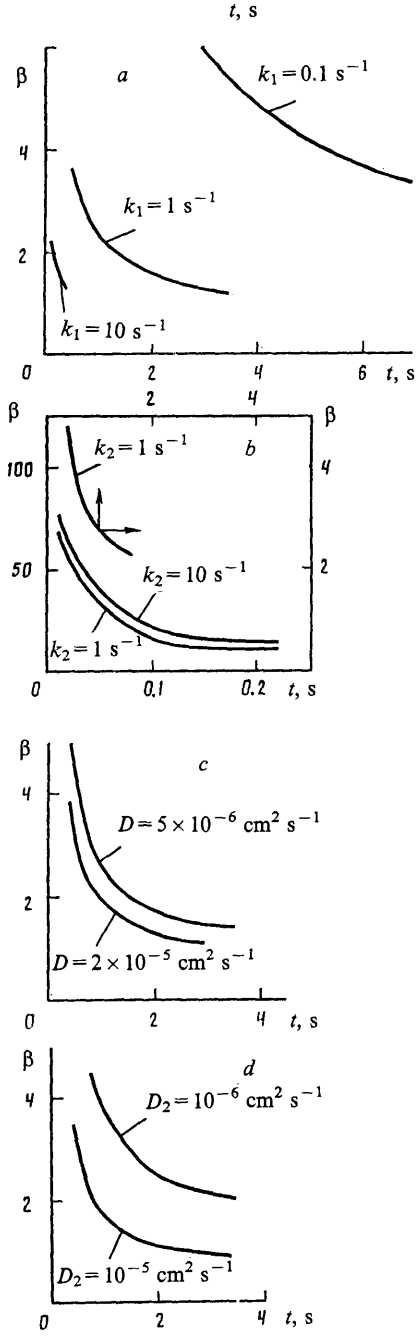


Figure 1. Influence of the rate constants of the forward (*a*) and back (*b*) reactions and the diffusion coefficients of the original substance in the donor phase (*c*) and of the extracted substance in the acceptor phase (*d*) on the time dependence of the dynamic separation factor.

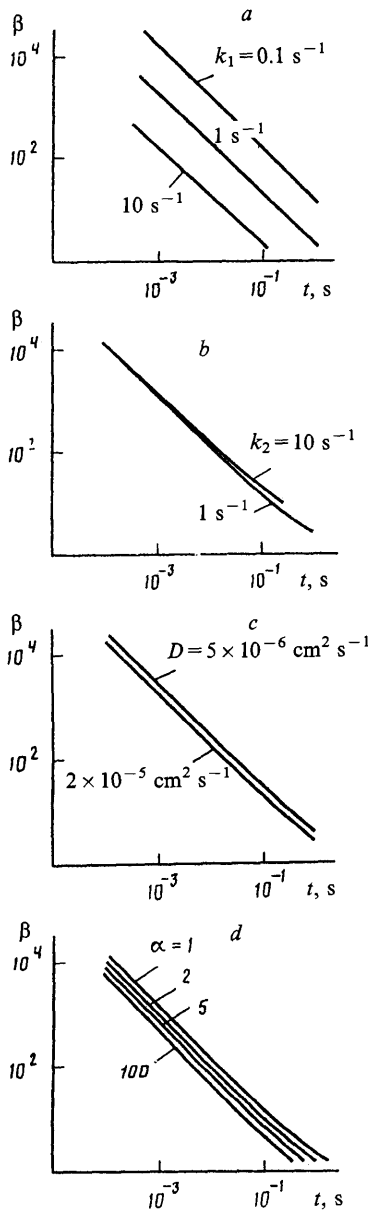


Figure 2. Influence of the rate constants of the forward (*a*) and back (*b*) reactions, the diffusion coefficient of the original substance in the donor phase (*c*), and the distribution coefficient of the reaction product at the phase inter-phase (*d*) on the time dependence of the dynamic separation factor for a short phase contact time; the numbers on the curves give the values of the parameters.

With increase in the time, β_t decreases, and for high values of the time, when $k_{12}t > 25$, the expression for β_t becomes

$$\beta_t = K_c r_{31} \Big/ \left[\left(1 - \frac{\sqrt{\pi}}{2} \frac{1}{z(t)} \right) \left(1 + \frac{r_2}{\alpha_2} \right) \right].$$

It is obvious that as $k_{12}t \to \infty$, β_t tends to a limiting value equal to $K_c r_{31}/(1 + r_2/\alpha_2)$. Restricting the examination to the simplest case ($a_0 = 1$), we note that the range of possible values of β_t is extremely wide. The influence of various parameters on the time dependence of β_t is shown in Figs. 1 and 2. For a slow homogeneous reaction taking place in the donor phase ($k_1 \leqslant 0.1\ s^{-1}$), appreciable dynamic separation factors can be achieved with relatively long phase contact times (~ 10 s).

If the extraction of one of the substances is accompanied in the acceptor phase by a first or pseudo-first order reaction with rate constants of the forward and back reactions k_1 and k_2 respectively, and the extraction of the other takes place under diffusion conditions, the system of equations describing this process has a similar form and an analytical solution is possible.

The expression for β_t depends on the value of the parameter $\bar{a}_0$

$$\bar{a}_0 = K_c/[1 + \alpha_1 r_1 (+ K_c)],$$

where K_c is the chemical equilibrium constant ($K_c = k_1/k_2$):

a, for $\bar{a}_0 < 1$

$$\beta_t = a_1 / F_5(t),$$

$$a_1 = (1 + R_{11}) r_{31} \Big/ \left(1 + \frac{1}{\alpha_2 r_2} \right),$$

$$F_5(t) = 1 + \frac{a_2}{\sqrt{1 - \bar{a}_0^2}} F_{51}(t) - F_{52}(t),$$

$$F_{51}(t) = \exp(-bt) \left[\Phi\sqrt{bt} - \Phi\left(\sqrt{(b - k_{12})t} \right) \right],$$

$$F_{52}(t) = a_3 \operatorname{erf}\left(\sqrt{k_{12}t} \right), \quad a_2 = \bar{a}_0 a_3, \quad a_3 = \frac{\sqrt{\pi}}{2} \frac{\bar{a}_0}{\sqrt{k_{12}t}},$$

$$b = k_{12} / \left(1 - \bar{a}_0^2 \right), \quad k_{12} = k_1 + k_2, \quad r_1^2 = D_{12} / D_{11},$$

$$r_2^2 = D_{32} / D_{31}, \quad r_{31}^2 = D_{31} / D_{11}, \quad R_{11} = \frac{1}{\alpha_1 r_1 (1 + K_c)},$$

$\Phi(\xi)$ is the Kramp function;

b, for $\bar{a}_0 > 1$

$$\beta_t = a_1 / F_6(t),$$

$$F_6(t) = 1 + \frac{a_2}{\sqrt{\bar{a}_0^2 - 1}} F_{61}(t) - F_{52}(t),$$

$$F_{61}(t) = \exp(b_0 t) \left[\operatorname{erf}\left(\sqrt{(k_{12} + b_0)t} \right) - \operatorname{erf}\left(\sqrt{b_0 t} \right) \right];$$

c, for $\bar{a}_0 = 1$

$$\beta_t = a_1 / F_7(t),$$

$$F_7(t) = 1 + \frac{1}{2k_{12}t} \left(1 - e^{-k_{12}t} \right) - F_{52}(t).$$

In particular, it can be seen from the last expression that for low values of t ($k_{12}t \ll 1$)

$$\beta_t \approx a_1 \Big/ \left(\frac{1}{2} + \frac{1}{3} k_{12} t \right).$$

Thus as $t \to 0$, β_t increases and tends to a limiting value $2a_1$. With increase in $k_{12}t$, the value of β_t decreases, and when $k_{12}t \gg 1$ the time dependence of β_t can be approximated by the expression

$$\beta_t \approx a_1 \Big/ \left(1 + \frac{1}{2k_{12}t} - \frac{\sqrt{\pi}}{2}\frac{1}{\sqrt{k_{12}t}}\right).$$

From this it can be seen that with further increase in $k_{12}t$ the second term in brackets can be neglected, so that

$$\beta_t \approx a_1 \Big/ \left(1 - \frac{\sqrt{\pi}}{2}\frac{1}{\sqrt{k_{12}t}}\right).$$

Finally, as $k_{12}t \to \infty$, β_t reaches its lower limiting value a_1.

It can be shown that in cases a and b also, the lower limiting value of β_t, reached as $k_{12}t \to \infty$ and $bt \to \infty$, will also be a_1. Other values of β_t are also possible, however. For example, if $k_c \gg 1$, then $\alpha_1 r_1 < 1$, and the limiting value for β_t is $r_{31}/(1 + 1/\alpha_2 r_2)$, that is $\beta_{t\to\infty}$ is greater, the greater the difference in the diffusion coefficients of the substances in the donor phase and the lower the distribution coefficient of the second substance. By continuing the analysis of the expressions given for β_t, it is possible to establish other particular cases observed for definite ratios of the parameters α_1, r_1, K_c, and t.

The two models of dynamic separation examined above are united by the fact that one of the stages in the extraction of the substance is a homogeneous chemical reaction. This approach, based on the homogenous formation of the complex extracted, is widely used in the description of the kinetics of extraction processes.[5] At the same time, any workers (as indicated, in particular, by discussions of the location of the reaction in the extraction of zinc by dithizone and its derivatives, of various metals by organophosphorus acids, and of copper by extracting agents of the Kelex type) conclude that the chemical reaction involved in the formation of the complex extracted is heterogeneous‡.

In an examination of models of dynamic separation with surface reactions,[122] six models of this type were analysed in considerable detail. A characteristic feature of the mathematical formulation of problems with a surface reaction is that the reaction rate is included in the boundary condition, and not in the equation describing the diffusion from sources and sinks, as has been the case for homogeneous reactions of formation of the complex extracted.

In the mathematical modelling, the accumulation of a substance at the phase interface, leading to the formation of self-generating inter-phase films, can be taken into account formally by the introduction into the boundary condition of an additional term determined by the difference in the fluxes of the substance to the phase interface and from the interface into the depth of the phase. The quantity of substance containing the element being extracted in the acceptor phase can be calculated from the equation

$$m_2(t)/C_2^0 = A_1\sqrt{t} + A_2\left[\exp(\varphi^2 t)\operatorname{erfc}(\varphi\sqrt{t}) - 1\right] - A_3\exp(-k_2 t)\int_0^t \exp(\alpha\tau)\operatorname{erfc}(\varphi\sqrt{\tau})\,d\tau,$$

where A_1, A_2, A_3, α are constants, $\alpha = \varphi^2 + k_2$; $\varphi = k_1\sqrt{D_1}$; k_1 and k_2 are the rate constants for the accumulation of the substance in the inter-phase region and its consumption respectively.

‡ In publications on the kinetics of extraction it is often described as a surface reaction.

Analysis shows that the accumulation of a substance is extremal in character (Fig. 3*a*), in qualitative agreement with experimental data.[212,214] If in the extraction of two elements, one of them can accumulate in the inter-phase region while the extraction of the other takes place by a "physical" distribution mechanism under diffusion conditions, the separation brought about this this difference may be considerable, particularly for short phase contact times (Fig. 3*b*). As expected, the value of β is influenced mainly by the rate constant k_2.

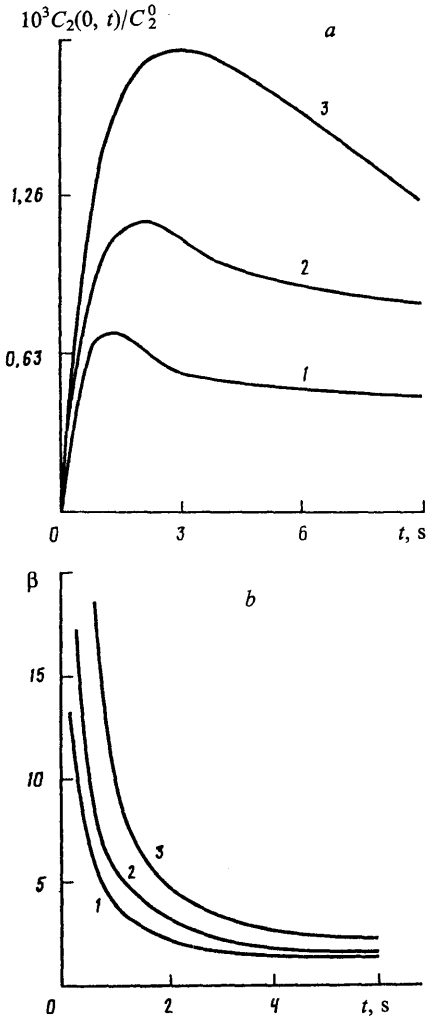


Figure 3. Kinetics of the accumulation of the intermediate product (*a*) and the time dependence of the dynamic separation factor (*b*); calculated for $k_1 = 3.16 \times 10^{-3}$ cm s^{-1}, $D_1 = 10^{-5}$ cm^2 s^{-1}, k_2, s^{-1}: *1*, 2; *2*, 1; *3*, 0.5.

All the above models were based on the distribution of the substance in a system consisting of two semi-finite phases. These models can be used either for comparatively short times, if the phases in contact are finite, or for any values of the time, if the

extent of the phases in the direction of the diffusion flux is considerable.

If the liquid films in contact are sufficiently thin, so that the diffusion front reaches the back boundary in the time of the experiment, it is necessary to include in the mathematical formulation the additional conditions at these boundaries (l_1 and l_2). We can consider, for example, the distribution of two substances (indices 1 and 2) with the assumption that the transfer of the first substance is accompanied by a rapid reversible surface reaction, and that of the second by a fairly slow surface reaction with rate constants k_1 and k_2 for the forward and back reactions respectively. The rate of the surface reaction is taken into account by introducing the additional boundary condition

$$D_{21}C'_{21x}(0,t) - k_1C_{21}(0,t) + k_2C_{22}(0,t) = 0.$$

The conditions for the back boundaries of the phases are written as

$$D_{i1}C'_{i1x}(l_1,t) = 0; \quad -D_{i2}C'_{i2x}(l_2,t) = 0; \quad i = 1;2.$$

It is convenient to express the dynamic separation factor as follows:

$$\bar{\beta}_{12}(t) = \frac{\langle C_{12}(t)\rangle}{\langle C_{11}(t)\rangle} \Big/ \frac{\langle C_{22}(t)\rangle}{\langle C_{21}(t)\rangle},$$

where $< C_{ij}(t) >$ represents the averaged concentrations of the ith component in the jth phase

$$\langle C_{ij}(t)\rangle = \frac{1}{l_j}\int_0^{l_j} C_{ij}(x,t)dx.$$

The expression for the averaged concentrations can be written as the series

$$\langle C_{11}(t)\rangle = \frac{C_{11}^0}{1+K_1l_0} - \sum_{n=1}^{\infty} \frac{C_{11}^0F_4(\mu_n)}{\mu_nF_2(\mu_n)}\exp\left(-\frac{D_{11}}{l_1^2}\mu_n^2t\right),$$

$$\langle C_{12}(t)\rangle = \frac{C_{11}^0}{l_0+K_1^{-1}} + \sum_{n=1}^{\infty}\frac{2C_{11}^0K_1\sin(\mu_n)\sin(\mu_nl_0r)}{\mu_nl_0F_2(\mu_n)}\exp\left[-\frac{D_{12}}{l_2^2}(rl_0\mu_n)^2t\right],$$

$$\langle C_{21}(t)\rangle = \frac{C_{21}^0 + C_{22}^0l_0}{1+K_cl_0} + \sum_{n=1}^{\infty}\frac{a_0\sin(\bar{\mu}_n)\sin(\bar{\mu}_nl_0\bar{r})}{\bar{\mu}_nF_6(\bar{\mu}_n)}\exp\left(-\frac{D_{21}}{l_1^2}\bar{\mu}_n^2t\right),$$

$$\langle C_{22}(t)\rangle = \frac{K_c\left(C_{21}^0 + C_{22}^0l_0\right)}{1+K_cl_0} + \sum_{n=1}^{\infty}\frac{(-a_0)\sin(\bar{\mu}_n)\sin(\bar{\mu}_nl_0\bar{r})}{\bar{\mu}_nl_0F_6(\bar{\mu}_n)}\exp\left[-\frac{D_{22}}{l_2^2}(\bar{\mu}_n\bar{r}l_0)^2t\right],$$

where

$$F_2(\mu_n) = \mu_n\left[(1+K_1l_0)r\cos(\mu_n)\cos(\mu_nl_0r) - \left(K_1 + r^2l_0\right)\sin\mu_n\sin(\mu_nl_0r)\right],$$

$$F_4(\mu_n) = 2K_1\sin\mu_n\cdot\sin(\mu_nl_0r),$$

$$F_6(\bar{\mu}_n) = \frac{1}{2}\bar{\mu}_n\left(\frac{3D_{21}}{l_1} + k_1 + k_2\bar{r}^2l_0\right)\sin\bar{\mu}_n\cdot\sin(\bar{\mu}_n\bar{r}l_0) +$$

$$+\left(\frac{1}{2}\frac{D_{21}}{l_1}\bar{\mu}_n^2 - k_1\right)\cos\bar{\mu}_n\cdot\cos(\bar{\mu}_n\bar{r}l_0) +$$

$$+\bar{r}\left(\frac{1}{2}\frac{D_{21}}{l_1}l_0\bar{\mu}_n^2 - k_2\right)\sin\bar{\mu}_n\cdot\cos(\bar{\mu}_nl_0\bar{r}) -$$

$$-\frac{1}{2}\bar{r}\bar{\mu}_n(k_1l_0 + k_2)\cos\bar{\mu}_n\cdot\cos(\bar{\mu}_nl_0\bar{r}),$$

$$a_0 = k_1C_{21}^0 - k_2C_{22}^0, \quad l_0 = l_2/l_1,$$

$$r^2 = D_{11}/D_{12}, \quad \bar{r}^2 = D_{21}/D_{22}, \quad K_c = k_1/k_2,$$

μ_n are the roots of the equation

$$(K_1/r)\mathrm{tg}\mu rl_0 + \mathrm{tg}\mu = 0,$$

$\bar{\mu}_n$ are the roots of the transcendental equation

$$\sin\bar{\mu}\left(\bar{\mu}\frac{D_{21}}{k_1l_1}\sin\bar{\mu}l_0\bar{r} - \frac{k_2\bar{r}}{k_1}\cos\bar{\mu}l_0\bar{r}\right) - \cos\bar{\mu}\sin(\bar{\mu}\bar{r}l_0) = 0.$$

In some particular cases it is convenient to represent the solution in a different form (for example, using an additional probability integral). Analysis of the given expressions made it possible to distinguish the principal factors influencing $\bar{\beta}_t$. Fig. 4 gives the calculated relationships $\bar{\beta}_t = f(t)$ for the most probable values of the parameters. A noteworthy feature is the complex character of the relationships (curves *6*, *11*) which are realised for definite ratios between the parameters and which are due to the difference in the relaxation times of the diffusion and chemical processes.

A knowledge of the thermodynamic and kinetic parameters of an extraction process (obtained, for example, using the reference literature[218–223] and reviews[3–5]) makes it possible to estimate the possible value of a dynamic separation coefficient without resorting to experiments on the combined extraction of the components.

A formal-kinetic approach was used by Danesi and Chiarizia[224] in an estimation of the dynamic separation factor of Cu^{II} and Fe^{III} in their extraction by a hydroxyoxime. It was based on the kinetic equations describing the extraction of these substances

$$-\frac{d[\mathrm{Cu}]}{dt} = a_ik^*_{1\mathrm{Cu}}\left[\mathrm{Cu}^{2+}\right] - k^*_{-1\mathrm{Cu}}\left[\overline{\mathrm{CuOx}_2}\right],$$

$$-\frac{d[\mathrm{Fe}]}{dt} = a_ik^*_{1\mathrm{Fe}}\left[\mathrm{Fe}^{3+}\right] - k^*_{-1\mathrm{Fe}}\left[\overline{\mathrm{FeOx}_3}\right].$$

The authors cited took as the kinetic parameter of the separation (S_t) the following ratio

$$S_t = \frac{[\overline{\mathrm{Cu}}]_t}{[\overline{\mathrm{Fe}}]_t} \Big/ \frac{[\mathrm{Cu}]_0}{[\mathrm{Fe}]_0},$$

which after integration of the kinetic equations[224] was brought to the form

$$S_t = \left\{1 - \frac{k^*_{-1Cu} + k^*_{1Cu}\exp\left[-\left(k^*_{1Cu} + k^*_{-1Cu}\right)a_i t\right]}{k^*_{1Cu} + k^*_{-1Cu}}\right\} \times$$

$$\times \left\{1 - \frac{k^*_{-1Fe} + k^*_{1Fe}\exp\left[-\left(k^*_{1Fe} + k^*_{-1Fe}\right)a_i t\right]}{k^*_{1Fe} + k^*_{-1Fe}}\right\}^{-1}. \quad (2)$$

For short phase contact times with allowance for the values of the reaction rate constants, the expression for the parameter S_t is simplified considerably:

$$S_0 = \frac{2.83}{0.194 + 9.23\left[H^+\right]},$$

indicating that the separation is influenced by only one factor, namely the acidity of the aqueous phase. For high values of the time, the parameter S_t degenerates into the thermodynamic separation parameter S_∞

$$S_\infty = \frac{\left[\overline{Cu}\right]_\infty}{\left[\overline{Fe}\right]_\infty} \Big/ \frac{[Cu]_0}{[Fe]_0} = \frac{K_{eq(Cu)}K^{-1}_{eq(Fe)}\left[H^+\right]^3 + K_{eq(Cu)}\left[\overline{HOx}\right]_m}{\left[\overline{HOx}\right]_m\left[H^+\right]^2 + K_{eq(Cu)}\left[\overline{HOx}\right]^3_m}.$$

For very low acidities, $S_\infty \simeq 1$, that is separation of Cu^{II} and Fe^{III} does not take place. On the other hand, at a very high acidity, S_∞ becomes large, since the equilibrium for the extraction of Fe^{III} is displaced to the left to a much greater extent than that for Cu^{II}. According to published data,[224] $k_{eq(Cu)} = 0.55$ and $k_{eq(Fe)} = 5.5 \times 10^{-4}$. The authors cited introduce the concept of critical kinetic acidity (CKA), which is defined as the abscissa of the point of intersection of the $S_\infty = f([H^+])$ curve with the $S_0 = f([H^+])$ curve. At acidities lower than the CKA, $S_0 > S_\infty$, and the separation based on kinetic factors is preferable. At acidities greater than CKA, kinetic factors cannot be used, and at an acidity equal to CKA the separation is independent of time. The kinetic separation parameter S_t has been calculated for different values of a_i and t.[224] For acidities lower than CKA, Eqn. (2) can be used to calculate the time necessary to obtain a specified separation; the following quantities must be determined: the chemical composition of the system ($[\overline{HOx}]_m$) and $[H^+]$ and the specific inter-phase surface, which depends on the geometry of the extractor, the intensity of mixing of the phases, the viscosity, density, inter-phase tension, etc. For example, if $[\overline{HOx}]_m = 0.1$ M, $[H^+] = 3 \times 10^{-3}$ M, and $a_i = 5$ cm^{-1}, then after stirring the phases for 2 min, $S_t > 5$ and copper is separated almost completely from iron. After stirring for 5 min, $S_t \simeq 2.5$, and an appreciable quantity of Fe^{III} is transferred into the extract.

If the distribution coefficient of the component extracted and the value of the specific surface (a) of contact between the phases are assumed to be unchanged during the process, the equation for its rate can be written as

$$\frac{dC}{dt} = ka\left(C^* - C\right),$$

where C ad C^* are the current and equilibrium values of the concentration of the component extracted in the acceptor phase, and k the coefficient of mass transfer. Integration of this equation gives

$$\ln(1 - E) = -kat, \quad (3)$$

where $E = C/C^*$ is the degree of completion of the process.

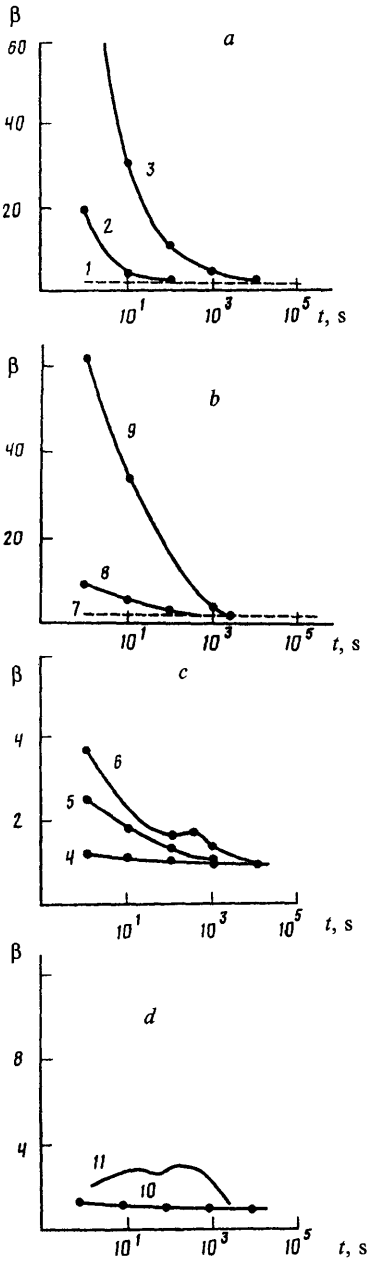


Figure 4. Influence of the equilibrium constant of the surface reaction (a), the rate constants of the forward (b) and back reactions, and the diffusion coefficient (D_{12}) of the substance (d) on the time dependence of the dynamic separation factor; k_1, cm s^{-1}: *1,4–6,7,10,11*, 10^{-3}; *2,8*, 10^{-4}; *3,9*, 10^{-5}; k_2, cm s^{-1}: *7–11*, 10^{-3}; *2,5*, 10^{-4}; *3,6*, 10^{-5}; D_{12}, cm^2 s^{-1}: *1–10*, 10^{-6}; *11*, 10^{-5}.

Relationship (3) is widely used in the treatment of the results of kinetic experiments. If Eqn. (3) is written for each component extracted, it is possible, neglecting the mutual influence of the extraction processes, to obtain expressions for estimating the magnitude of the dynamic separation factor.

If at the initial moment there is a certain amount of substance in the acceptor phase, the equation for the rate of the process becomes[225]

$$1-E=(1-E_0)\exp(-kt),$$

or, expressing E in terms of the extraction coefficient D_e,[226]

$$1-\frac{1+1/D_e^*}{1+1/D_e}=\left(1-\frac{1+1/D_e^*}{1+1/D_0}\right)\exp(-kt).$$

if $E_0 = 0$, the value of D_e attainable at a given stage is determined by the values of D_e^*, t, and k, which the authors cited call the effective rate constant. In general, D_e depends on D_e^0. For a cascade, since the values of D^0 are different for different stages, the values of D will also be variable. From the material balance equation with allowance for the expressions for the extraction coefficients it is possible to obtain relationships between the extraction coefficients in adjacent stages[226]

$$D_{e(i-1)}^{-1}=\frac{1/D_e^*+e^{-kt}}{1+(1/D_e^*)e^{-kt}-(1+1/D_e^*)e^{-kt}A},$$

where

$$A=1-\frac{e^{-kt}(1+1/D_e^*)/(1+1/D_{ei})}{1+(1/D_e^*)e^{-kt}-(1+1/D_e^*)/(1+1/D_{ei})}.$$

The value of D at any of the stages is determined experimentally, after which the values for the other stages of the cascade are calculated.

A mathematical model of the dynamics of counter-current multi-stage extraction in a cascade of mixer–settlers, constructed with allowance for the kinetics of the reactions of the components extracted with the extracting agent, has been published.[227] The introduction of kinetic factors into the model showed that it is possible to increase the selectivity of separation as a result of differences in the kinetics and that there exists an optimum residence time in each stage of the process to give the maximum value of the separation factor. The influence of the constructional parameters of the extraction column on selectivity has been noted.[228]

V. Summary

The present review shows that there exist real possibilities for increasing the efficiency of the extraction separation of substances by making use of kinetic factors. Here it is important to make effective use of differences in the mechanisms of the extraction of the components from a multi-component mixture, or differences in the conditions of the processes, or existing differences in the kinetic or transport parameters of the separate stages of the process. The possibilities for dynamic separation are greatly increased by creating or increasing differences in the parameters of the individual stages under the influence of external factors.

The forms of time dependence of the dynamic separation factor given in the present review show that the efficiency of dynamic separation is greater, the farther the system from the equilibrium state. Thus the realisation of the possibilities of dynamic separation requires a different non-traditional, approach to the construction of equipment for carrying out the process. It is necessary to ensure a short contact time between the phases and effective separation of the phases. The injected flow method which has recently been widely introduced in analytical chemistry would appear to be useful here. It cannot be used to achieve "rapid mixing–separation", however, since only 10–20% of the organic phase is separated from the aqueous phase.[65] The rapid separation of the phases remains a serious problem in the construction of apparatus for carrying out the process. The film systems of Boyadzhiev[229,230] and other methods[231] are of interest in this connection.

The mathematical modelling of the process of dynamic separation is based on a phenomenological and formal-kinetic description, and is greatly simplified. Frequently, no account is taken of the mutual influence of the components in their extraction from a multi-component system; this may be acceptable when modelling the extraction of components from dilute solutions. In the models developed, full account is not taken of the variety of inter-phase phenomena exerting a significant influence on the selectivity of separation. It is important to carry out a detailed analysis of the processes, accompanied by homogeneous and heterogeneous chemical reactions, adsorption–desorption phenomena, the formation of inter-phase films, change in the electrical properties of the phase interface, and spontaneous surface convection. Allowance for inter-phase phenomena or processes complicates the mathematical modelling considerably. The restricted nature of analytical methods can be overcome, however, by using numerical methods, widely employed in the modelling of liquid–liquid extraction processes.

To develop the theoretical ideas it is necessary to establish the relationships between the nature and state of the component extracted and the kinetic parameters of the process, and to select and substantiate criteria for identifying extraction systems for which dynamic separation is preferable to separation based on differences in the thermodynamic parameters of the process.

The solution of these problems associated with dynamic separation will undoubtedly facilitate the practical development of a method which is one of the most promising ways of increasing the selectivity of extraction processes.

References

1. H Barnes *Analyst (London)*, 1947, **72** 469
2. Yu A Zolotov, I P Alimarin, V A Bodnya *Zh. Anal. Khim.*, 1964, **19**(1) 28
3. V V Tarasov, G A Yagodin *Itogi Nauki i Tekhniki. Neorganicheskaya Khimiya. Kinetika Ekstraktsii* (Progress in Science and Technology. Inorganic Chemistry. The Kinetics of Extraction), Vol. 4, Izd. VINITI, Moscow, 1974, 117 pp
4. P R Danesi, R Chiarizia *Crit. Rev. Chem.*, 1980, **10** 1
5. V V Tarasov, G A Yagodin, A A Pichugin *Itogi Nauki i Tekhniki. Neorganicheskaya Khimiya. Kinetika Ekstraktsii Neorganicheskikh Veshchestv* (Progress in Science and Technology. Inorganic Chemistry. The Kinetics of the Extraction of Inorganic Substances), Vol. 11, Izd. VINITI, Moscow, 1984, 171 pp

6. M A Hughes *High Purity Mater. Sci. and Technol.*, 5th Int. Symp. Dresden, 1980, Proc. Dresden, 1979, Vol. 1, p. 187
7. Y Miyake *Bull. Inst. Atom. Energy Kyoto Univ.*, 1987, **71** 14
8. C F Coleman, J W Roddy *Solv. Extr. Rev.*, 1971, **1**(1) 63
9. E Uhlig *Coord. Chem. Rev.*, 1982, **43** 294
10. F D Kasimov, Ya N Gordeev, S N Kovantseva, et al. *Radiokhimiya*, 1986, **28** 552
11. F D Kasimov *Preprint No. 10/575*, NII Atomnykh Reaktorov, Dimitrovgrad, 1983
12. J Shibata, S Nishimura, S Mukai *Nippon Kinzoku Gakkaishi (J. Jpn. Inst. Metals)*, 1976, **40**(2) 147; quoted in *Ref. Zh. Khim.*, 1976, 16V194
13. R J Whewell *Chem. Ind.*, 1977, (18) 755
14. J A Golding, S A Fouda, V N Saleh *Proc. Int. Solv. Extr. Conf. ISEC'77*, Toronto, 1979, Vol. 1, p. 227
15. F D Kasimov, N F Skobelev *Radiokhimiya*, 1984, **26**(5) 714
16. Z Li, R Liu, Z Hou, Z Li *Hydrometallurgy*, 1987, **18**(2) 225
17. S Goto, M Matsubara *J. Chem. Eng. Jpn.*, 1972, **5**(1) 87
18. H M Irving, G Andrew, E J Risdon *J. Chem. Soc.*, 1949, 541
19. A W Titley *Analyst*, 1962, **87**(1034) 349
20. B E McClellan, P Sabel *Anal. Chem.*, 1969, **41**(8) 1077
21. B E McClellan, O Menis *Anal. Chem.*, 1971, **43**(3) 436
22. H Freiser *Abstr. Pap. Pittsburgh Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, New York, March 9–13, 1987*, Pittsburg, 1987, p. 678
23. D R Spink, D N Okuhara *Int. Symp. Hydromet., Chicago, 1973*, New York, 1973, p. 497
24. G J Lawson *Miner. Eng. Soc. Techn. Mag.*, 1976, 56
25. G M Ritcey, B H Lucas *Can. Mining and Met. Bull.*, 1974, **67**(742) 87
26. C A Fleming *Trans. Inst. Mining and Met., C*, 1976, **85**, Dec., 211
27. V I Lakshmanan, G J Lawson, P S Nyholm *Proc. Int. Solv. Extr. Conf. Lyon, 1974, ISEC74*, London, 1974, p. 699
28. D S Flett, D R Spink *Proc. Int. Solv. Extr. Conf. ISEC7'77*, Toronto, 1979, p. 496
29. C A Fleming, B R Green, K G Ashurst *Proc. Int. Solv. Extr. Conf. ISEC'80*, Liege, 1980, p. 224/1
30. S A Osadchii, V A Tatarinov, L Ya Marochkina, et al. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1976, **9**(4) 64
31. G M Ritcey, B M Lucas *Can. Mining and Met. Bull.*, 1975, **68**(754) 105
32. A Okuwaki, H Kawamura, K Tatsuruhama, et al. *Nippon Kagaku Kaishi (J. Chem. Soc. Jpn., Chem. and Ind. Chem.)*, 1977, (8) 1119; quoted in *Ref. Zh. Khim.*, 1978, 2V175
33. L Hummelstedt, H-E Sund, J Karjaluoto, et al. *Proc. Int. Solv. Extr. Conf. Lyon, 1974, ISEC'74*, London, 1974, Vol. 1, p. 829
34. D S Flett, D W West *Trans. Inst. Mining and Met., C*, 1973, **82** 107
35. S Przeszlakowski, H Wydra *Hydrometallurgy*, 1982, **8**(4) 49
36. K Inoe, H Tsunomachi, S Tomita, T Maruuchi *Proc. Int. Solv. Extr. Conf. ISEC'83*, Denver, 1983, p. 303
37. Z Zembura, W Ziolkowska *Pr. Inst. Metali Niezelaz*, 1983, **12**(1/2) 215
38. D R Spink, D N Okuhara *Met. Trans.*, 1974, **5**(8) 1935
39. D S Flett *Chem. Eng. (Gr. Brit.)*, 1972, (268) 465
40. H Nedjate *C. R. Acad. Sci., C*, 1977, **284**(21) 885
41. H Nedjate, J L F Sabot *Bull. Soc. Chim. Fr.*, 1977, Part 1, (11/12) 1089
42. S A Sedova, Yu B Kletenik *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1976, (5) 73
43. S A Sedova, L I Borodikhina, Yu B Kletenik *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1979, (2) 27
44. A I Khol'kin, L M Kuznetsova, L M Gindin, et al. *V Vsesoyuznoi Konferentsii po Khimii Ekstraktsii. Tezisy Dokladov* (Summaries of Papers Presented at the Fifth All Union Conference on the Chemistry of Extraction), Novosibirsk, 1978, p. 196
45. A J Khol'kin, V I Kuz'min, G L Pashkov, et al. *Proc. Intern. Solv. Extr. Conf. ISEC'88, M*, 1988, Vol. 3, p. 215
46. Yu B Kletenik, S A Sedova *Zh. Prikl. Khim.*, 1983, **56**(7) 1510
47. Jpn. P. No. 55-65335, Cl. C22B23/04, Publ. 16th May 1980
48. Yu B Kletenik, S A Sedova, A I Khol'kin *VI Vsesoyuznoi Konferentsii po Khimii Ekstraktsii. Tezisy Dokladov* (Summaries of Papers Presented at the Sixth All Union Conference on the Chemistry of Extraction), Vol. 1, Kemerovo, 1981, p. 103
49. Yu B Kletenik, S A Sedova, A I Khol'kin, et al. *VI Vsesoyuznoi Konferentsii po Khimii Ekstraktsii. Tezisy Dokladov* (Summaries of Papers Presented at the Sixth All Union Conference on the Chemistry of Extraction), Vol. 2, Kemerovo, 1981, p. 223
50. S A Sedova, V A Navrotskaya, Yu B Kletenik *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1984, (17) Part 6, p. 98
51. I V Lanin, A A Baronin, A A Pushkov, V F Travkin *Tsvetnye Metally*, 1985, (11) 21
52. V F Travkin, M V Loseva, V B Bulgakova, et al. *Zh. Neorg. Khim.*, 1987, **32**(3) 732 [English translation in *Russ. J. Phys. Chem.*, 1987(3)]
53. G P Giganov, V F Travkin, A A Pushkov, et al. *Proc. Int. Solv. Extr. Conf. ISEC'88, M*, 1988, Vol. 3, p. 228
54. R G Canning *AMDEL Bull.*, 1970, (10) 35
55. B N Laskorin, V S Ul'yanov, R A Sviridova *Ekstraktsiya. Teoriya, Primenenie, Apparatura* (Extraction. Theory, Applications, and Apparatus), No. 1, Gosatomizdat, Moscow, 1962, p. 171
56. B M Lucas, G M Ritcey *Can. Mining and Met. Bull.*, 1975, **68**(753) 124
57. G M Ritcey, B M Lucas *Techn. Bull. Dep. Energy: Mines. and Resour. Mines Branch Ottawa*, 1969, 30 pp
58. T V Tsygankova *Nauch. Tr. Nauch.-Issled. Proekt. Inst. Redkomet. Prom.*, 1977, **86** 130
59. I S Levin *Zh. Prikl. Khim.*, 1962, **35**(11) 2368
60. I M Ivanov, G I Plotnikova, L M Gindin *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1977, (14) part 6, 65
61. J C Mailen, D E Horner, S E Dorris, et al. *Sep. Sci. Technol.*, 1980, **15**(4) 959
62. US P. 2955913; *Ref. Zh. Khim.*, 1961, (19) 19K66
63. Ph Bergeonneau, C Jaonen, M Germain, A Bathellier *Proc. Int. Solv. Extr. Conf. ISEC'77*, Toronto, 1979, Vol. 2, p. 612
64. G L Starobinets, V L Lomako *Dokl. Akad. Nauk Beloruss. SSR*, 1970, **14**(6) 541
65. H Sakka, H Nakamura, M Takagi, K Ueno *Bunseki Kagaku*, 1983, **32**(10) E335
66. A P Novikov, B F Myasoedov *Solv. Extr. Ion Exch.*, 1985, **3**(3) 267
67. Z K Karalova, B F Myasoedov, L M Rodionova, V S Kuznetsova *Radiokhimiya*, 1981, **23**(1) 52
68. B F Myasoedov, Z K Karalova, L M Rodionova *Proc. Int. Solv. Extr. Conf. ISEC'80, Liege*, 1980, Vol. 3, p. 105/1
69. D J Crouse, D E Horner *Solv. Extr. Chem. Metals*, Macmillan Co., London, 1965, p. 305

70. Y Minigawa, K Kojima, T Kaneko, Y Yamagachi, et al. *Oslo Symp., 1982, Ion. Exch. and Solv. Extr. Pap. Symp., Oslo, 24–25 June*, 1982
71. H Gorican, C Djordjevic *Mikrochim. Acta*, 1966, (4/5) 767
72. A K Babko, G Kh Klibus *Dopov. Akad. Nauk Ukr. RSR*, 1959, (9) 991
73. P R Subbaraman, M Cordes, H Freiser *Anal. Chem.*, 1969, **41**(13) 1878
74. B A Bodnya, I P Alimarin, T F Sedletskaya *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, (6) 1192
75. N P Rudenko, L V Kovtun *Vestn. Mosk. Univ., Khim.*, 1969, (4) 103
76. I P Alimarin, Yu A Zolotov, B A Bodnya *Pure Appl. Chem.*, 1971, **25**(4) 667
77. J Stary, J Marek, K Kratzer, F Sebesta *Anal. Chim. Acta*, 1971, **57**(2) 393
78. I V Seryakova, Yu A Zolotov, G A Vorob'eva *Zh. Anal. Khim.*, 1969, **24**(11) 1613
79. S Shibata *Anal. Chim. Acta*, 1960, **23** 367, 434
80. W Berger, H Elvers *Z. Anal. Chem.*, 1959, **171** 185
81. B Ya Spivakov, Yu A Zolotov *Zh. Anal. Khim.*, 1969, **24**(12) 1773
82. A M Poskanzer, B M Foreman *J. Inorg. Nucl. Chem.*, 1961, **6** 323
83. R A Tournier, M W Davis *Sep. Sci.*, 1972, **7**(2) 159
84. B Kuznik *J. Inorg. Nucl. Chem.*, 1982, **43**(12) 3363
85. E Uhlemann, W Mickler, C Fischer *Anal. Chim. Acta*, 1981, **130**(1) 177
86. C Y Yang, J S Shin, Y C Yoh *J. Chin. Chem. Soc.*, 1982, **29**(1) 15
87. N I Kasikova, A I Nikolaev, L M Zalkina *Issledovaniya po Fizikokhimicheskim Osnovam Tekhnologii Pererabotki Mineral'nogo Syr'ya* (Studies of the Physicochemical Principles of the Technology of Mineral Processing), Nauka, Leningrad, 1983, p. 71
88. A I Nikolaev, N I Kasikova, E G Il'in, M E Ignatov *Zh. Neorg. Khim.*, 1984, **29**(8) 2062 [English translation in *Russ. J. Inorg. Chem.*, 1984(8)]
89. I S Levin, V A Tarasova, V A Varnek, T F Rodina *Zh. Neorg. Khim.*, 1977, **22**(3) 761 [English translation in *Russ. J. Inorg. Chem.*, 1977(3)]
90. S Yu Ivakhno, V Yu Gusev, V A Akutina, D B Kadosov *Ekstraktsiya Kobal'ta(2+) Di-2-etilgeksilfosfornoi Kislotoi Cherez Impregnirovannye i Tolstosloinye Zhidkostnye Membrany* (The Extraction of Cobalt(II) by Di-2-ethylhexyl Hydrogen Phosphate Through Impregnated and Thick-Layer Liquid Membranes), MKhTI im. D I Mendeleeva, Moscow, 1986, 12 pp, Dep. in VINITI, 21st April 1986, No. 2880-V
91. M Aguilar, D H Liem *Acta Chem. Scand., Ser. A*, 1976, **30**(5) 313
92. A V Afanas'ev, O A Sinegribova, G A Yagodin *Zh. Neorg. Khim.*, 1981, **26**(5) 1338 [English translation in *Russ. J. Inorg. Chem.*, 1981(5)]
93. G W Mason, D N Metta, D F Peppard *J. Inorg. Nucl. Chem.*, 1976, **38**(11) 2077
94. D Li, Z Wang, Y Xie, et al. *New Frontiers. Rare Earth. Sci. and Appl. Proc. Int. Conf. Beijing, Sept.10–14, 1985*, Beijing, 1985, Vol. 1, p. 463
95. N L Carr, Y T Shah *Ind. Eng. Chem. Process. Des. Dev.*, 1979, **18**(3) 484
96. A A Palant, L G Panfilova, V A Reznichenko *Zh. Prikl. Khim.*, 1978, **51**(6) 1257
97. A A Palant, L G Panfilova, V A Reznichenko *Kineticheskie Osobennosti Ekstraktsii Molibdena D2EGFK iz Rastvorov Vol'framata Natriya* (Kinetics of the Extraction of Molybdenum by D2EHHP from Sodium Tungstate Solutions), Moscow, 1979, 21 pp, Dep. in VINITI, 3rd April 1979, No. 1153-79
98. G M Vol'dman, A N Zelikman, I Sh Khutoretskaya *Izv. Vyssh. Uchebn. Zaved. SSSR, Tsvet. Metall.*, 1974, (2) 97
99. J I Bullock, R Pathak, A Rusheed, J E Salmon *J. Inorg. Nucl. Chem.*, 1974, **37**(8) 1881
100. V N Shesterikov, V S Shmidt, S S Novikova *Zh. Neorg. Khim.*, 1972, **17**(11) 3044 [English translation in *Russ. J. Inorg. Chem.*, 1972(11)]
101. J J Cruywagen, H A C McKay *J. Inorg. Nucl. Chem.*, 1970, **32**(1) 255
102. D S Flett, D W West *Trans. Soc. Mining Eng. AIME*, 1970, **247**(4) 288
103. F G Seeley, W J McDowell *J. Inorg. Nucl. Chem.*, 1981, **43**(2) 375
104. S N Ivanova, L M Gindin, A S Chernobrov, et al. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1978, (2/1) 92
105. A D Andreyanov, B Z Iofa, A N Nesmeyanov, et al. *Vestn. Mosk. Univ., Khim.*, 1975, **16**(5) 567
106. A Alian, W Sanad *Radiochim. Acta*, 1972, **17**(3) 158
107. Yu G Dubchenko, V V Likhman *Razlichnoe Povedenie Ittriya i Strontsiya pri Ekstraktsii Kaprilovoi Kislotoi* (The Different Behaviour of Yttrium and Strontium in Extraction by Octanoic Acid), Donetsk. Gos. Univ., Donetsk, 1985, 10 pp, Dep. in UkrNIINTI, 18th June 1985, No. 1337Uk-85dep.
108. I B Milovanova, Yu A Pigin *Sintez, Ochistka i Analiz Neorganicheskikh Materialov* (The Synthesis, Purification, and Analysis of Inorgnic Materials), Nauka, Novosibirsk, 1971, p. 27
109. I P Alimarin, O M Petrukhin, Yu A Zolotov *Zh. Anal. Khim.*, 1962, **17** 544
110. N E Kochetkov, M K Chmutova, B F Myasoedov *Radiokhimiya*, 1983, **25**(4) 435
111. S N Kovantseva, V M Nikolaev, V A Kasimova, V T Filimonov *Preprint No. 15/530*, NII Atomnykh Reaktorov, Dimitorvgrad, 1982, 12 pp
112. V M Nikolaev, F D Kasimov, V M Lebedev, V T Filimonov *Khimiya Ekstraktsii* (The Chemistry of Extraction), Novosibirsk, 1984, p. 243
113. V Angelova, R Doicheva *Rudodob. Metallurgiya*, 1969, **24**(7) 40
114. L M Gindin, R S Shul'man, K S Luboshnikova *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1969, (14) part 6, 124
115. D Bauer, G Cote, S Daamach *Mines et Carrieres. Suppl.: Techn.*, 1989, **71**(2) 133
116. G Cote, D Bauer, S Daamach *C. R. Acad. Sci.*, 1988, Ser. 2, **306**(9) 571
117. E E Rakovskii, O M Petrukhin, V I Severin, V M Bolistov *Zh. Neorg. Khim.*, 1970, **15**(7) 1918 [English translation in *Russ. J. Inorg. Chem.*, 1970(7)]
118. S N Ivanova, I A Druzhinina, A P Zubareva, et al. *Proc. Int. Solv. Extr. Conf. ISEC'88, M*, 1988, Vol. 3, p. 198
119. K Osseo-Asare, M E Keeney *Proc. Int. Solv. Extr. Conf. ISEC'80, Leige*, 1980, Vol. 1, p. 121/1
120. Yu B Kletenik, A I Potapova, I N Mar'eva *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1974, No.4(2) 96

121. N F Kizim *Kinetika Reekstraktsii Nekotorykh Mineral'nykh Kislot i Nitratov Metallov iz Rastvorov Neitral'nykh Fosfororganicheskikh Soedinenii* (The Kinetics of the Re-extraction of Mineal Acids and Metal Nitrates from Solutions of Neutral Organophosphorus Compounds), Summary of Candidate's Thesis, Mendeleev Moscow Institute of Chemical Technology, Moscow, 1973, 16 pp
122. N F Kizim, V V Tarasov, G A Yagodin *Izv. Vyssh. Uchebn. Zaved. SSSR, Khim. i Khim. Tekhnol.*, 1980, **23**(4) 458
123. N F Kizim *Povyshenie Effektivnosti, Sovershenstvovanie Protsessov i Apparatov Khimicheskikh Proizvodstv. PAKhT-85. Tezisy Dokladov Vsesoyuznoi Nauchnoi Konferentsii, 11–13 Iyunya 1985* (Summaries of Papers Presented at the All Union Scientific Conference on Increasing the Efficiency and Improving the Processes and Apparatus of Chemical Production, PAKhT-85, 11th–13th June 1985), Khar'kov, 1985, Part 3, p. 82
124. B N Laskorin, V S Ul'yanov, R A Sviridova *Ekstraktsiya. Teoriya, Primenenie, Apparatura* (Extraction. Theory, Applications, and Apparatus), No. 1, Gosatomizdat, Moscow, 1962, p. 185
125. V V Tarasov, A V Fomin, G A Yagodin *Radiokhimiya*, 1977, **19**(6) 753
126. S M Karpacheva, L V Ilozheva *Zhidkostnaya Ekstraktsiya* (Liquid–Liquid Extraction), Khimiya, Leningrad, 1969, p. 202
127. T Sato, T Nakamura, M Ikeno *Denki Kagaku Oyobi Kogyo Butsuri Kagaku*, 1985, **53**(5) 314; quoted in *Ref. Zh. Khim.*, 1986, 5V380
128. T Sato, T Nakamura, M Ikeno *Hydrometallurgy*, 1985, **15**(2) 209
129. B E McClellan, P Sabel *Anal. Chem.*, 1969, **41**(8) 1077
130. O B Vinokurova, Yu B Kletenik *Zh. Anal. Khim.*, 1976, **31**(6) 1067
131. C B Honaker, H Freiser *J. Phys. Chem.*, 1962, **66** 127
132. M A Hughes, S Hou *J. Chem. Soc., Faraday Trans. 1*, 1982, (12) 3447
133. H Watarai, H Freiser *J. Am. Chem. Soc.*, 1983, **105**(2) 189
134. H Freiser *12-i Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii: Referaty Dokladov i Soobshchenii* (Summaries of Papers Presented at the Twelfth Mendeleev Congress of Pure and Applied Chemistry), Vol. 7, Moscow, 1981, p. 105
135. H Freiser *The Chemistry of Extraction* (Translated into Russian), Atomizdat, Moscow, 1971, p. 59
136. C A Fleming, M J Nicol *J. Inorg. Nucl. Chem.*, 1980, **42**(9) 1335
137. R E Molnar, H E Jeffes *Proc. Int. Solv. Extr. Conf. ISEC'80, Liege*, 1980, Vol. 1, pp 80–79/1
138. B A Bodnya, I P Alimarin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, (8) 1726
139. R Chiarizia, P R Danesi *Sep. Sci. Technol.*, 1981, **16**(9) 1181
140. P R Danesi, R Chiarizia, G F Vandegrift *J. Phys. Chem.*, 1980, **84**(25) 3455
141. M J Hudson *Hydrometallurgy*, 1982, **9**(2) 149–168
142. G Sandstroem, L Hummelstedt, M Hagstroem *Oslo Symp., 1982. Ion Exchange and Solv. Extr. Pap. Symp., Oslo, 24–25 June*, Oslo, 1982, pp. 11/1
143. A Freiher von Imhof *Diss. Dokt. Naturwiss. Fak. Chem. Biol. und Geowiss. Techn. Univ. Munchen*, 1987, 143 pp
144. B W Budesinsky, M Sagat *Talanta*, 1973, **20**(2) 228
145. V G Chamupathi, H Freiser *Inorg. Chem.*, 1989, **28**(9) 1658
146. M F Pushlenkov, N N Shchepetil'nikov, G I Kuznetsov, F D Kasimov, et al. *Radiokhimiya*, 1973, **15**(2) 256
147. T Sato, T Nakamura *J. Inorg. Nucl. Chem.*, 1972, **34**(12) 3721
148. J A Golding, V N Saleh *Proc. Int. Solv. Extr. Conf. ISEC'80*, Liege, 1980, Vol. 1, pp. 194/1
149. S A Sedova, Yu B Kletenik *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.Nauk*, 1980, (12/5) 21
150. H Nedjate, J L F Sabot , D Bauer *Hydrometallurgy*, 1978, **3**(3) 283
151. J A Cox, A Bhatnagar *Anal. Chem.*, 1988, **60**(10) 986
152. S N Dobromyslova, V S Smelov, V V Chubukov *Radiokhimiya*, 1977, **19**(2) 224
153. V S Smelov, V V Chubukov *Radiokhimiya*, 1971, **13**(3) 449
154. F D Kasimov, N F Skobelev, V M Nikolaev *Radiokhimiya*, 1984, **26**(3) 404
155. P R Danesi, C Cianetti *Sep. Sci. Sci. Technol.*, 1982, **17**(7) 969
156. P S Ellender, G Harrison, G J Lawson *Proc. Int. Solv. Extr. Conf. ISEC'80, Liege*, 1980, Vol. 3, pp 80–115/1
157. H L Finston, Y Inoue *J. Inorg. Nucl. Chem.*, 1967, **29**(9) 2431
158. A A Vashman, I S Pronin, T V Brylkina *Radiokhimiya*, 1980, **22** 115
159. C Binder, B Rosel, D Leopold, et al. *Int. Conf. Nucl. and Radiochem. Linday. Oct. 8–12, 1984. Abstr. Invit. Pap. Discuss. Pap. Posters, Frankfurt, Moscow*, 1984, p. 74
160. H Fujita, L J Gosting *J. Am. Chem. Soc.*, 1956, **78**(6) 1099
161. E L Cussler, E N Lightfoot *AIChE Journal*, 1963, **9**(5) 702
162. H L Toor *AIChE Journal*, 1964, **10**(4) 448
163. H Kim *J. Phys. Chem.*, 1966, **70**(2) 562
164. M Lao, J P Kingsley, R Krishnamurthy, R Taylor *Chem. Eng. Comm.*, 1989, **86** 73
165. L P Kholpanov, V Ya Shkadov *Gidrodinamika i Teplomassoobmen s Poverkhnost'yu Razdela* (Hydrodynamics and Heat and Mass Exchange from an Interface Surface), Nauka, Moscow, 1990, p. 218
166. R Krishna, C Y Low, et al *Chem. Eng. Sci.*, 1985, **40**(6) 893
167. A M Rozen, V S Krylov *Povyshenie Effektivnosti, Sovershenstvovaniya Protsessov i Apparatov Khimicheskikh Proizvodstv. PAKhT-85: Tezisy Dokladov Vsesoyuznoi Konferentsii, 11–13 Iyunya, 1985* (Summaries of Papers Presented at the All Union Conference on Increasing the Efficiency and Improvement of the Processes and Apparatus of Chemical Production. PAKhT-85, 11th–13th June, 1985), Part 3, Khar'kov, 1985, p. 129
168. A M Rozen, V S Krylov *Teor. Osn. Khim. Tekhnol.*, 1984, 18(2) 155
169. A A Ovchinnikov, S F Timashev, A A Belyi *Kinetika Diffuzionno-Kontroliruemykh Khimicheskikh Protsessov* (The Kinetics of Diffusion-Controlled Chemical Processes), Khimiya, Moscow, 1986, 288 pp
170. S F Timashev *Fizikokhimiya Membrannykh Protsessov* (The Physical Chemistry of Membrane Processes), Khimiya, Moscow, 1988, 240 pp
171. G A Yagodin, V V Tarasov *Solv. Extr. Ion Exch.*, 1984, (2) 1
172. S F Timashev *Zh. Fiz. Khim.*, 1982, **56**(7) 1739 [English translation in *Russ. J. Phys. Chem.*, 1982(7)]
173. J W Roddy, C F Coleman, S Arai *J. Inorg. Nucl. Chem.*, 1971, **33**(4) 1099
174. Z Kolarik, R A Grimm *J. Inorg. Nucl. Chem.*, 1976, **38**(9) 1721
175. T Sato, M Ueda *Proc. Int. Solv. Extr. Conf. ISEC'74, Lyon*, 1974, Vol. 1, p. 871

176. M Cox, M Gray, C G Hirons, N Miralles *Hydromet.: Res., Dev. and Plant. Pract. Proc. 3rd Int. Symp. Hydromet. 112th AIME Annv. Meet., Atlanta, 6–10 March, 1983*, Warrendale, 1982, p. 357
177. P R Danesi, R Chiarizia, A Saltelli *J. Inorg. Nucl. Chem.*, 1976, **38**(9) 1687
178. P R Danesi, R Chiarizia, W A A Sanad *J. Inorg. Nucl. Chem.*, 1977, **39**(3) 519
179. R Chiarizia, P R Danesi *J. Inorg. Nucl. Chem.*, 1977, **39**(3) 525
180. Yu B Kletenik, V A Navrotskaya, N V Pomoshchnikova *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1972, (2) Part 1, 38
181. Yu B Kletenik, V A Navrotskaya, N V Pomoshchnikova *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1972, (2) Part 3, 32
182. P R Danesi, C Cianetti, E P Horwitz, H Diamond *Sep. Sci. Technol.*, 1982, **17**(7) 961
183. I Komasawa, T Otake *Ind. Eng. Chem. Fundam.*, 1983, **22**(1) 122
184. K Haraguchi, H Feiser *Anal. Chem.*, 1983, **55**(4) 656
185. Y Miyake, Y Takenoshita, M Teramoto *J. Chem. Eng. Jpn.*, 1983, **16**(3) 203
186. K Haraguchi, H Freiser *Inorg. Chem.*, 1983, **22**(8) 1187
187. A Grizo, F Poposka, Z Trajcevska *Glas. Hem. Drus., Beograd*, 1983, **48**(1/2) 137
188. M Harada, M Mori, M Adachi, W Eguchi *J. Chem. Eng. Jpn.*, 1983, **16**(3) 193
189. R Paimin, R W Cattrall *Aust. J. Chem.*, 1982, **35**(11) 2345
190. W Sanad, H Flex, A Haggag *J. Radional. Chem.*, 1982, **75**(1/2) 121
191. J C Mailen *Sep. Sci. Technol.*, 1981, **16**(10) 1373
192. G A Yagodin, V V Tarasov, A V Fomin, S Yu Ivakhno *Proc. Int. Solv. Extr. Conf. ISEC'77*, Montreal, 1979, Vol. 1, p. 260
193. P R Danesi, R Chiarizia *Proc. Int. Solv. Extr. Conf. ISEC'77*, Montreal, 1979, Vol. 1, p. 219
194. K Akiba, H Freiser *Anal. Chim. Acta*, 1982, **136** 329
195. K Inoue, H Amano, Y Tomimoto, M Yamamoto *J. Chem. Eng. Jpn.*, 1981, **14**(2) 116
196. G A Yagodin, S Yu Ivakhno, K B Kim *Tr. Mosk. Khim.-Tekhnol. Inst. im. D I Mendeeleva*, 1980, (114) 15, 34
197. W Nitsch, L Navazio *Proc. Int. Solv. Extr. Conf. ISEC'80, Liege*, 1980, Vol. 1, 220/1
198. D E Horner, J C Mailen, J R Coggins, S W Thiel, et al. *Ind. Eng. Chem. Fundam.*, 1980, **19**(3) 287
199. J Szymanowski *Zesz. Nauk. Pozn.*, 1980, (15) 139
200. M Cox, C G Hirons, D S Flett *Proc. Int. Solv. Extr. Conf. ISEC'80, Liege*, 1980, Vol. 1, p. 118/1
201. L A Ajawin, E S Perez de Ortiz, H Sawistowski *Proc. Int. Solv. Extr. Conf. ISEC'80, Liege*, 1980, Vol. 3, p. 112/1
202. V A Kozlov, L Kh Batrakova, B A Yusupov *Khimiya i Tekhnologiya Redkikh Tsvetnykh Metallov i Solei: Tezisy Dokladov Vsesoyuznoi Konferentsii* (Summaries of Papers Presented at the All Union Conference on the Chemistry and Technology of Rare Non-ferrous Metals and Salts), Frunze, 1986, p. 29
203. M F Islam, R K Biswas *Can. J. Chem.*, 1979, **57**(23) 3011
204. G F Vandegrift, E P Horwitz *J. Inorg. Nucl. Chem.*, 1977, **39**(8) 1425
205. G A Yagodin, A A Pichugin, V A Arutyunyan, V V Tarasov *3 Vsesoyuznaya Konferentsiya po Khimii Urana: Tezisy Dokladov* (Summaries of Papers Presented at the Third All Union Conference on the Chemistry of Uranium), Moscow, 1985, p. 50
206. V V Tarasov, A A Pichugin, G A Yagodin *Dokl. Akad. Nauk SSSR*, 1983, **269**(6) 1398
207. T W Chapman, R Caban, M E Tunison *AIChE Symp. Ser.*, 1975, **71**(152) 128
208. F D Kasimov, V M Nikolaev, V A Kasimova, N F Skobelev *Preprint P-14* (280), NII Atomnykh Reaktorov, Dimitrovgrad, 1976, 20 pp
209. S A Sedova, Yu B Kletenev *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1976, (12) Part 5, 73
210. A I Potapova, S A Sedova, N N Mar'eva, Yu B Kletenik *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1976, (12) Part 5, 82
211. R J Whewell, M A Hughes, C Hanson *Adv. Extr. Met. 1977. Int. Symp. London*, 1977, p. 21
212. N F Kizim, Yu P Davydov, A P Lar'kov *Tezisy Dokladov Vsesoyuznogo Soveshchaniya po Primeneniyu Ekstraktsii v Tekhnologii Neorganicheskikh Veshchestv* (Summaries of Papers Presented at the All Union Conference on the Use of Extraction in the Technology of Inorganic Substances), Apatity, 1986, p. 129
213. Y Miyake, Y Takenoshita, M Teramoto *Proc. Int. Solv. Extr. Conf. ISEC'83, Denver*, 1983, p. 301
214. N F Kizim, Yu P Davydov, A P Lar'kov *Proc. Int. Solv. Extr. Conf. ISEC'88, Moscow: Nauka*, 1988, p. 47
215. V S Shmidt, N A Shorokhov, S D Nikitin *Radiokhimiya*, 1985, **27**(4) 504
216. I Komasawa, T Otake, I Hattori *J. Chem. Eng. Jpn.*, 1983, **16**(5) 384
217. E V Yurtov, V V Tarasov *Zh. Fiz. Khim.*, 1972, **46**(9) 2262 [English translation in *Russ. J. Phys. Chem.*, 1972(9)]
218. Z I Nikolotova, N A Kartashova in A M Rozen (Editor) *Spravochnik po Ekstraktsii. T. 1. Ekstraktsiya Neitral'nymi Organicheskimi Soedineniyami* (Reference Book of Extraction. Vol. 1. Extraction by Neutral Organic Compounds), Atomizdat, Moscow, 1976, 600 pp
219. E A Mezhov in A M Rozen (Editor) *Spravochnik po Ekstraktsii. T. 2. Ekstraktsiya Aminami, Solyami Aminov i Chetvertichnykh Ammonievykh Osnovanii* (Reference Book of Extraction. Vol. 2. Extraction by Amines and Salts of Amines and Quaternary Ammonium Bases), Atomizdat, Moscow, 1977, 304 pp
220. B V Martynov in A M Rozen (Editor) *Spravochnik po Ekstraktsii. T. 3. Ekstraktsiya Organicheskimi Kislotami i ikh Solyami* (Reference Book of Extraction. Vol. 3. Extraction by Organic Acids and Their Salts), Atomizdat, Moscow, 1978, 368 pp
221. Z I Nikolotova *Ekstraktsiya Neitral'nymi Organicheskimi Soedineniyami. Aktinoidy. Spravochnik* (Extraction by Neutral Organic Compounds. The Actinides. A Reference Book), Energoatomizdat, Moscow, 1987, 280 pp
222. E A Mezhov *Ekstraktsiya Aminami i Chetvertichnymi Ammonievymi Osnovaniyami. Aktinoidy. Spravochnik* (Extraction by Amines and Quaternary Ammonium Bases. The Actinides. A Reference Book), Energoatomizdat, Moscow, 1987, 200 pp

223. B V Martynov *Ekstraktsiya Organicheskimi Kislotami i ikh Solyami. Spravochnik* (Extraction by Organic Acids and Their Salts. A Reference Book), Energoatomizdat, Moscow, 1989, 272 pp
224. R Chiarizia, P R Danesi *Sep. Sci. Technol.*, 1981, **16**(9) 1181
225. F D Kasimov, N F Skobelev *Radiokhimiya*, 1984, **26**(5) 714
226. F D Kasimov *Preprint No. 21* (355), NII Atomnykh Reaktorov, Dimitrovgrad, 1978, 10 pp
227. J E Sepulveda, J D Miller *Proc. Int. Solv. Extr. Conf. ISEC'80, Liege*, 1980, Vol. 1, pp. 233/1–233/10
228. A S Zheleznyak, K S Levina, I Z Gal'perina *Vliyanie Skorosti Massoperedachi na Selektivnost' Protsessa Zhidkostnoi Ekstraktsii* (The Influence of the Rate of Mass Transfer on the Selectivity of Liquid–Liquid Extraction), Dep. in VINITI, 29th April 1976, No. 1461-76 dep.
229. L Boyadzhiev, Z Lazarova, E Bezenshek *Proc. Int. Solv. Extr. Conf. ISEC'83, Denver*, 1983, p. 391–392
230. L Boyadzhiev *Proc. Int. Solv. Extr. Conf. ISEC'88, Moscow: Nauka*, 1988, Vol. 1, p. 56
231. M H I Baird, A Rohatgi, W He *Chem. Eng. Res. Dev.*, 1988, **66**(2) 121

Received 19th April 1991

Translated from *Uspekhi Khimii* **61** 1550–1563 (1992) U.D.C. 541.128.13

Methods for increasing the efficiency of catalysts for the oxidative condensation of methane

O V Krylov
Institute of Chemical Physics, Russian Academy of Sciences

ABSTRACT. Possible ways of increasing the efficiency of catalysts for the oxidative condensation of methane by increasing the pressure, adding other gases to the reaction mixture (methane + oxygen), and carrying out the process under cyclic redox conditions have been examined. In some cases the yield of C_2-hydrocarbons can be increased to 32%.

The bibliography contains 102 references.

Contents

I.	Introduction	851
II.	Increase in pressure	852
III.	Influence of water vapour	852
IV.	Influence of chlorine	853
V.	Influence of carbon dioxide	854
VI.	Cyclic oxidation and reduction	855

I. Introduction

The oxidative condensation of methane to give C_2-hydrocarbons, which was discovered in 1981–1984, is one of the most rapidly developing and promising fields of catalysis. About 100 papers on the catalysts, mechanism, and characteristics of this reaction are published every year. A number of reviews have been published.[1–7]

There are now a number of catalytic systems showing activity and selectivity in the oxidative condensation of methane. The chemical relationships governing the selection of catalysts for oxidative condensation have not been fully determined. The most active and selective catalysts are the oxides of the non-transition metals of groups I–IV, that is the oxides of metals with outer *sp*-electrons. High and stable yields of C_2-products have been obtained on PbO deposited on Al_2O_3 or MgO; on a number of lanthanide oxides, in particular Sm_2O_3; on BaO_2; and on Li/MgO. Most transition metal oxides catalyse the extensive oxidation of methane. Among transition metal oxides, for some unknown reason, activity and selectivity are shown by manganese oxides, but only in compounds, and not in pure form.

A number of authors report the existence of various limiting yields of C_2-hydrocarbons.[8,9] According to McCarty,[9] the limiting yield of C_2-hydrocarbons is ~26%. With increase in the conversion of methane, the selectivity decreases. On most catalysts studied, the yield is lower than this value. Other authors[8] give slightly higher limiting yields of about 30%. Even higher yields have been reported: 30.8% on an Li–Mn–Ti–O catalyst,[10] 31.6% on $Ce_{1-x}Sr_xYb_xO_3$,[11] and even 32.3% on Li–Nd–O/MgO,[12] although in each case a careful analysis of the conditions giving these yields is required; they may be artefacts. High yields have also been observed on various chlorine-containing systems (see below).

The highest reaction rate has been obtained on Sm_2O_3 [4]— 828 μmol s^{-1} g^{-1} at 1023 K. The best temperature range for carrying out the reaction is 950–1100 K. Extensive oxidation of methane takes place at lower temperatures. At higher temperatures, in addition to extensive oxidation, extensive catalytic cracking takes place. Many catalysts are unstable under the reaction conditions, both as a result of the loss of the active component and as a result of overheating during this exothermic process.

The heterogeneous–homogeneous mechanism of the oxidative condensation of methane, according to which reaction with the surface gives methyl radicals

$$O_S + CH_4 \xrightarrow{k_1} OH_S + CH_3, \quad (1)$$

and their recombination in the gas phase gives ethane

$$CH_3 + CH_3 + M \xrightarrow{k_2} C_2H_6 + M, \quad (2)$$

is now generally accepted.[1–7]

The selectivity of the gas-phase stages of the reaction is determined by the equilibrium

$$CH_3 + O_2 \underset{}{\overset{K_3}{\rightleftharpoons}} CH_3O_2. \quad (3)$$

At high temperatures, equilibrium (3) is displaced to the left, and the selectivity towards C_2H_6 increases. Below 873–973 K, equilibrium (3) is displaced to the right, and the radical CH_3O_2 leads to extensive oxidation.

An examination of a stepwise mechanism for the oxidative condensation of methane for low degrees of transformation made it possible[13] to put forward the following equation for the limiting selectivity with respect to ethane

$$S_{lim} = \frac{1}{1 + K_3 p_{O_2}(K_3 p_{O_2} k_4/k_2 + k_5/k_2)}, \quad (4)$$

where k_2 is the rate constant of reaction (2), K_3 the equilibrium constant of reaction (3), and k_5 and k_4 the rate constants of the homogeneous gas-phase reactions of the further oxidation of CH_3 and CH_3O_2 radicals. Eqn. (4) does not take account of possible reactions on the catalyst surface, for example extensive catalytic oxidation. For high degrees of transformation, reactions of free radicals in the gas phase, not taken into account, may take place. The oxidative dehydrogenation of ethane gives ethylene, apparently with the intermediate formation of C_2H_5 radicals.

Under stationary conditions, the kinetics of the oxidative condensation of methane are described by an equation of the Mars–Van Krevelen type, characteristic of processes taking place by a redox mecanism

$$r = \frac{k_r p_{CH_4} k_{ox} p_{O_2}}{k_r p_{CH_4} + k_{ox} p_{O_2}}, \quad (5)$$

where k_r and k_{ox} are the rate constants for the reduction of the active centres by methane and their re-oxidation by oxygen respectively.[3]

Possible ways of increasing the efficiency of the oxidative condensation of methane are examined below.

II. Increase in pressure

According to the reaction kinetics described by Eqn. (5), increase in the pressure of oxygen and methane should increase the reaction rate. According to Eqn. (4), increase in the O_2 pressure should decrease the selectivity, but increase in the methane pressure should have no significant influence on it. These equations, however, are applicable only for small degrees of conversion. At high degrees of conversion and high pressures, the ratio between the heterogeneous and homogeneous processes may change sharply in favour of the latter. There may be an increase in the part played by processes giving undesirable products of extensive oxidation.

A decrease in selectivity with increase in the oxygen pressure has in fact been observed by a number of authors.[14–16]

Increase in pressure from 0.1 MPa and 0.8 MPa in the empty reactor increased the degree of conversion of CH_4 from a very low value (< 1%) to 32.7% at 1073 K and a volume rate of 24 min^{-1}.[17] In a study of the influence of pressure on the oxidative condensation of methane on an Li/MgO catalyst, Tyulenin and co-workers[18] filled the empty volume beyond the catalyst with the weakly active MgO, to decrease the reaction in the gas phase. Under these conditions, the degree of conversion of CH_4 increased with increase in pressure, from 28.1% to 34.3%, and the selectivity with respect to C_2-hydrocarbons decreased from 41.1% to 36.0%; the selectivity with respect to C_2H_6 decreased from 20.1% to 10.1%, and the selectivity towards C_2H_4 increased from 20.5% to 26.3%, the ratio $[C_2H_4]/[C_2H_6]$ in the reaction products increased from 1.0 to 2.62, the yield of CO increased slightly, and the yield of CO_2 remained unchanged.

An increase in the selectivity towards C_2H_4 with increase in pressure was noted in other papers.[19,20] The yield of C_2H_4 increases and even exceeds the yield corresponding to the equilibrium $C_2H_6 \rightleftarrows C_2H_4 + H_2$, that is the principal role is played by kinetic factors.

Thus increase in pressure has a positive influence mainly on the second stage of the process—the oxidative dehydrogenation of ethane to ethylene.

Increase in pressure may also have a positive influence on the first stage of the process—the formation of C_2H_6 molecules by the recombination of methyl radicals with the participation of a third molecule M. In highly porous catalysts such as MgO or Li/MgO, reaction (2) hardly takes place within the catalyst granules.[21] This is due to the diffusion of the CH_3 species formed under Knudsen conditions, when these species undergo practically no collisions with one another or with the molecule M, but react with the surface, on which extensive oxidation apparently takes place. As a result, only the outer layers of catalyst take part in the formation of C_2H_6. With increase in pressure, the probability of triple collisions according to reaction (2) increases, and the yield of C_2-hydrocarbons shows a corresponding increase. This also explains the observed[22,23] decrease in activity and selectivity in the oxidative condensation of methane with increase in the specific surface, that is decrease in the specific surface and increase in the pressure in this reaction operate in the same direction.

III. Influence of water vapour

Water vapour is formed both in the oxidative condensation and in the extensive oxidation of methane. In the stages of catalyst reduction and oxidation, water may have a negative influence on the catalysis by blocking the active centres.

Nevertheless, the opposite is also observed—an increase in the degree of conversion of methane with increase in the water vapour pressure with no change in selectivity.[24,25] A redistribution of the products of oxidative condensation towards C_2H_4 has also been observed on Sm_2O_3 + CeO_x, PbO–MgO, and ZrO_2–MgO.[26] Thus water vapour apparently influences the heterogeneous but not the homogeneous stages of the process.

At a high temperature (> 1000 K) in the presence of water vapour, steam conversion of methane takes place on oxide catalysts. The formation of H_2, C_2H_4, and C_2H_6 (the last two in smaller quantities than H_2) has been observed in the reaction of methane and water vapour on a CaO catalyst.[27]

Most interesting results were obtained by Pereira and co-workers.[28] At low temperatures (873 K and below) on a Ca–Ni–K-oxide catalyst for a mixture with $[CH_4]:[O_2]:[H_2O]$ = 3 : 1 : 6.5 at atmospheric pressure, 100% selectivity in hydrocarbon formation was observed, with a degree of conversion of ~10% in one operation. Heating in oxygen increased the activity and selectivity. Activation for 1 h gave a mixture of 38% C_2H_4, 48% C_2H_6, 5.3% C_3H_8, 5.6% C_3H_6, and 2.8% hydrocarbons. If water vapour is replaced by helium, the activity decreases rapidly, that is the catalyst is stable towards water vapour. X-Ray photoelectron spectroscopy showed that $Ni(OH)_2$ is formed on the catalyst surface, and calcium nickelate (charge on nickel > 2+) is formed in the bulk. The formation of carbonates leads to a decrease in the activity of the catalyst.

Another paper by the same authors[29] gives the results of prolonged tests confirming the earlier data. An unusually low activation energy E for the oxidative condensation of methane is reported: 84 kJ mol^{-1}, which is much lower than the activation energy of extensive oxidation (~250 kJ mol^{-1}). On most catalysts studied for the higher-temperature oxidative condensation of methane (without water vapour), the opposite was observed: E for the oxidative condensation was greater than E for extensive oxidation.[3] The most active and selective catalyst for the reaction in the presence of water vapour had the composition $Ca_3NiK_{0.1}O_x$. A much lower activity and selectivity were shown by the catalyst $CaK_{0.1}O_x$, indicating that the presence of the transition metal (nickel) in the catalyst is necessary. The transition metal acts as a promoter.

The mechanism of this low-temperature condensation of methane is not yet clear. The possible steam conversion of methane to give synthesis gas CO + H_2 followed by a Fischer–Tropsch synthesis, that is purely heterogeneous reactions, have been suggested.[29] The distribution of the reaction products—$C_1:C_2:C_3:C_4$-hydrocarbons—to some extent resembles the Schulz–Flory distribution.

The authors cited point out that the synthesis of the hydrocarbons may be influenced by carbon particles. This is confirmed by experiments with $^{13}CH_4$. Water vapour does not play a direct role in the synthesis, but has an indirect influence, probably as a result of the formation of OH groups on the surface. The authors cited also point out that $CaK_{0.1}O_x$ is a very good catalyst for the steam gasification of graphite at relatively low temperatures to give H_2 and CO.[30]

Until the radical products above the catalyst have been determined, possible explanations of the influence of water vapour on the homogeneous stages of the process should not be rejected. High concentrations of hydroxyl radicals were observed in the oxidation of methane on platinum.[31] The action of oxygen led to the hydroxylation of molecularly adsorbed water on Ag(110) and Cu(100) with the intermediate formation of O_2^-.[32] The reaction

$$4(OH)_S + O_2 \longrightarrow 4O_S + 2H_2O, \quad (6)$$

observed[33] in the re-oxidation of reduced methane by an Li/MgO catalyst possibly also involves the intermediate formation of OH or HO_2 radicals.

The characteristics of the low-temperature oxidation of methane noted by other workers are probably also related to the influence of water vapour and OH groups. Water has a strong influence on the acidic properties of a surface. Matsuhashi and co-workers,[34] using a 4.3% Na^+/ZrO_2 catalyst at 873 K, were able to carry out the oxidative condensation of methane with 26.5% conversion and 52.8% selectivity towards C_2-hydrocarbons. On the super-acid SO_4^-/ZrO_2 at 873 K, water vapour led to a marked increase in the transformation of a $CH_4 + O_2$ mixture into oxygen-containing products (to 16.2% for a degree of conversion of 10.8%). It has been shown[35] that an iron phosphate catalyst (Fe/P = 0.6), with or without a carrier, functions even at 850 K (yield of C_2-hydrocarbons up to 8%). The activity of this catalyst was very unstable, however, and its loss and reduction were observed after further heating at 973 K. Although the authors cited[35] do not point out a relationship between the observed effects and the action of water vapour, nevertheless the observed phenomenon is very similar to the analogous effects for an Ni–Ca–K–O-catalyst in the presence of water vapour.[29] The same paper also reported the unexpected deactivation of the catalyst with restoration of the activity after further heating.

IV. Influence of chlorine

In the presence of chlorine-containing compounds both in the catalyst and in the gas phase it is possible to increase considerably the yield of the products of the oxidative condensation of methane. This was first demonstrated by Otsuka and co-workers.[14,36,37] The additives LiCl, NaCl, KCl, CsCl and LiBr were deposited on MnO_x/SiO_2, NiO_y/SiO_2, and other catalysts. With a 2% $NaCl/MnO_x/SiO_2$ catalyst at 1023 K and 90 kPa, the degree of conversion of CH_4 was 46.8%, the selectivity towards C_2-hydrocarbons 66%, and the yield 31.6%, which is 8–10% greater than the yield of C_2 on the same catalyst without NaCl. It has been suggested[14] that LiCl and NaCl act as promoters as a result of the formation of chlorine atoms, which subsequently lead to the formation of additional methyl radicals

$$\begin{aligned} &LiCl + CH_4 + {}^1/_2\,O_2 \longrightarrow LiOH + CH_3Cl, \\ &CH_3Cl \longrightarrow CH_3 + Cl\,, \end{aligned} \quad (7)$$

followed by the gas-phase recombination of methyl radicals (2) and gas-phase reactions involving chlorine atoms

$$\begin{aligned} &Cl + CH_4 \longrightarrow CH_3 + HCl, \\ &Cl + C_2H_6 \longrightarrow C_2H_5 + HCl. \end{aligned} \quad (8)$$

The chlorination of methane is an important industrial process for obtaining chloro-derivatives of methane. At 1000–1200 K it takes place by a chain mechanism to give CH_3Cl, C_2H_5Cl, and ethane. The limiting stage is the removal of an H atom from CH_4 with an activation energy of 16 kJ mol^{-1}. In some experiments with chlorine-containing additives,[38] HCl was not detected in the products of the reaction of methane with chlorine. This suggested that HCl is continuously removed from the system by the reaction

$$HCl + OH = Cl + H_2O \quad (9)$$

with the regeneration of chlorine atoms, which are the active centres of the chain reaction.

The addition of ZSM-5 zeolite to MnO_x + NaCl or NiO_y + LiCl catalysts leads to the formation of aromatics.[38]

Other workers[39–43] observed an increase in the selectivity towards C_2H_6 and more particularly towards C_2H_4 when chlorides are added to oxide catalysts. The formation of chlorine is accelerated in the presence of water in the hydrolysis

$$LiCl + H_2O \longrightarrow LiOH + HCl \quad (10)$$

or the oxidative transformation on CaO + $CaCl_2$ [9]

$$\begin{aligned} &CaCl_2 + {}^1/_2\,O_2 \longrightarrow CaO + Cl_2, \\ &CaCl_2 + H_2O \longrightarrow CaO + HCl, \\ &2HCl + {}^1/_2\,O_2 \longrightarrow Cl_2 + H_2O. \end{aligned} \quad (11)$$

The introduction of water vapour into the reaction mixture on $CaCl_2$ leads to an increase in the yield of C_2-hydrocarbons and CH_3Cl, and also an increase in the ratio $[C_2H_4]/[C_2H_6]$. The high selectivity of ethylene formation is due to the high efficiency of the dehydrogenation of C_2H_6 to C_2H_4 in the presence of chlorine, compared with the dehydrogenation of C_2H_6 under the influence of O_2 alone. A decrease in the rates of the extensive oxidation of CH_4 and C_2-hydrocarbons compared with the pure oxides is also observed, making it possible to achieve a higher selectivity in the formation of ethylene. It has been shown[41] that chlorine initiates gas-phase reactions within a layer of the catalyst $SmCl_3$ or SmOCl. Reactions outside the layer increase the combustion of methane.

The introduction of C_2H_5Cl into the gas phase on $BaCO_3/\alpha$-Al_2O_3 or $BaCO_3/TiO_2$ leads to an almost two-fold increase in the yield of C_2-products. This increase in yield is due chiefly to an increase in the selectivity from 36% to 60%, while the degree of conversion decreases slightly. If C_2H_5Cl (10 p.p.m.) is added continuously to the gas stream, the yield of C_2-hydrocarbons remains constant for a long time. A very high ratio $[C_2H_4]/[C_2H_6]$ = 10.2 was obtained under these conditions on $BaCO_3/TiO_2$.[43]

A kinetic analysis of the heterogeneous–homogeneous scheme for obtaining C_2-hydrocarbons with the participation of Cl_2 showed[40] that C_2-hydrocarbons are formed preferentially at chlorine concentrations below 10^{-10} mol cm^{-3}; at a higher chlorine concentration, CH_3Cl is formed. Estimation of the concentration of CH_3 radicals based on a comparison of the experimental rates of formation of the products and the known rate constants of the elementary reactions gave high values. Increased concentrations of

the radicals possibly exist above the catalyst in a layer having a thickness of the order of the mean free path of the particles.

According to Warren,[43] chlorine has three functions in the oxidative condensation of methane: 1, it increases the conversion of CH_4 by increasing the number of active centres of the catalyst, for example by transforming surface salt centres such as carbonate, aluminate, and titanate into chlorides; 2, it decreases the number of extensive-oxidation centres; and 3, it increases the ratio $[C_2H_4]/[C_2H_6]$ (sometimes to 10). The alkali metal atoms present in the chlorides also inhibit extensive oxidation.

A particularly large number of studies have been carried out with the addition of chlorides to Mn-containing catalysts.[14,36,37,39,44–57]† In some cases a very high yield of C_2-hydrocarbons was obtained. For example, a 13% NaCl–17% MnO_x/SiO_2 catalyst at 1123 K gave a CH_4 conversion of 45.8%, and a selectivity with respect to C_2-hydrocarbons of 74.7%, that is the yield of C_2-hydrocarbons was 32% for a contact time of 0.5 s and a ratio $[CH_4]/[O_2] = 2$.[52] On an $LiCl + B_2O_3 + MnO_2$ (5:7:13) catalyst at 1023 K and a ratio $[CH_4]/[O_2] = 3:1$, the selectivity was 80%, and the yield of C_2 was 33.9%.[53]

The activity of chlorine-containing catalysts decreases during operation as a result of the loss of chlorine. It can be restored by introducing chlorine-containing additives into the gas phase: HCl,[48,51] CH_3Cl,[54] CH_2Cl_2,[40,55,56] CCl_4,[57]† Cl_2.[55] These additives restore the concentration of chlorine in the catalyst.

The phase composition of an Na–Mn–O/SiO_2 catalyst treated with a chlorine-containing reaction mixture has been studied.[58] A multi-phase oxide–halide system containing NaCl, Mn_3O_4, and MnO_2 is formed:

$$\beta\text{-}Na_{0.7}MnO_2 \xrightarrow{CH_4 + O_2 + 1\%\ HCl} NaCl + Mn_2O_3 + Mn_3O_4 + H_2O. \quad (12)$$

The phase transformations of this catalyst have been studied in detail for the oxidative dehydrogenation of ethane to ethylene by *in situ* X-ray diffraction. The initial chloride catalyst contained a phase with variable composition $NaCl.xMnCl_2$. During the $C_2H_6 + O_2$ reaction, a continuous increase in the intensity of the lines due to the NaCl phase was observed, with the appearance of oxide and the liberation of chlorine

$$3[NaCl \cdot 2MnCl_2] + 4O_2 \longrightarrow 3NaCl + 2Mn_3O_4 + 6Cl_2. \quad (13)$$

Comparison of the rates of formation of the NaCl phase (with the loss of chlorine) and ethylene showed a correspondence between these quantities. The rates, expressed in moles per minute, are fairly close to one another. Thus chlorine is generated by the redox oxidation of HCl (Deacon's process):

$$3[NaCl \cdot 2MnCl_2] + 4O_2 \longrightarrow 3NaCl + 2Mn_3O_4 + 6Cl_2 \ (\longrightarrow 12Cl),$$
$$3[4NaCl \cdot MnCl_2] + 2O_2 \longrightarrow NaCl + Mn_3O_4 + 3Cl_2 \ (\longrightarrow 6Cl),$$
$$2Cl^{\cdot} + C_2H_6 \longrightarrow C_2H_4 + 2HCl. \quad (14)$$

Ethylene is also formed in a process parallel to reaction (14), by the reaction of C_2H_6 with surface centres containing Mn^{4+}. A temperature-programmed study showed that the quantity of oxygen liberated from the oxide catalyst is four times the quantity of oxygen desorbed from the corresponding oxide halide catalyst. This weakly bound oxygen is apparently responsible for the extensive oxidation, and decreases the selectivity of the process. The selectivity increases sharply when oxygen is removed. The addition of HCl regenerates the mixed Na–Mn–Cl phase.

In some published studies, however, another opinion is found, namely that the formation of C_2H_4 on chloride catalysts is purely heterogeneous. For example, Conway and Lunsford[59] observed a selectivity in the conversion of CH_4 to ethane of 40.9% on a 65% LiCl/MgO catalyst, and selectivity in the transformation of ethane to ethylene of 70.2% for a degree of conversion of 75–79%, but the activity gradually decreased as a result of the removal of chlorine from the catalyst by its reaction with H_2O. The $LiCl/Dy_2O_3/MgO$ catalyst is even more active and stable.[60] In the opinion of the authors cited,[59,60] the presence of chlorine on the catalyst prevents the adsorption of CO_2 and alters the activity of the O^- centres in such a way that they become capable of activating the weaker C–H bond in ethane, but are still incapable of activating the stronger C–H bond in ethylene (that is for extensive oxidation).

The layer halides $MBi_3O_4X_2$, where M = Li, Na, K, Ag, Pb, Cd, and X = Cl, Br, are relatively stable under the catalysis conditions. Their activity and selectivity are not very high, however, and the yield of C_2 does not exceed 19.4%. Bromides are slightly more active than chlorides.[61,62] The so-called Arpe phases $M_{24}O_{31}Cl_{10}$, where M = Bi, La, Sm, have been studied.[63] These phases are exceptionally stable towards the removal of chlorine, and have a layer structure, but their activity is very low.

The pure chlorides of magnesium, calcium, strontium, barium, and potassium at 1023 K are selective in the formation of C_2H_6, but nonselective in the formation of C_2H_4. The mixed chlorides $LiCl/MnCl_2$ and $NiCl_2/MnCl_2$ are more selective; under the catalysis conditions they are converted into a mixture of chlorides and oxides MnO_x which is more selective.[64]

A $Bi_2O_3.MoO_3.LiCl$ melt at 1023 K gave 18% conversion, 35.8% selectivity with respect to C_2, and 6.4% yield, including only 1.4% C_2H_4. The addition of CH_3Cl to the gas phase increased the selectivity towards C_2H_4 to 100%, related to C_2-products.[65]

The aggressive nature of the halogens may prevent the practical application of reactions involving halogen-containing additives, despite the considerable increase in activity and selectivity.

V. Influence of carbon dioxide

A number of workers point out that CO_2 has a positive influence on the selectivity and a negative influence on the activity of catalysts for the oxidative condensation of methane. CO_2 forms surface carbonates on catalysts with basic properties. These carbonates decrease the number of active centres and hence decrease the activity of catalysts in oxidative condensation, but they decrease the activity in extensive oxidation to an even greater degree, so that the selectivity increases.[66,67]

Equilibrium in the decomposition of the alkaline earth metal carbonates $MCO_3 \rightleftarrows MO + CO_2$ at atmospheric pressure is established at a temperature close to that of the oxidative condensation of methane. Under the catalytic conditions, CaO was covered by a layer of $CaCO_3$,[68] and SrO by a layer of $SrCO_3$.[69] Deactivation of the catalyst with a simultaneous increase in selectivity was observed. Similar effects were observed for the Li/MgO catalyst.[70] An increase in the selectivity under the influence of CO_2 was also observed for catalysts of the oxidative dehydrogenation of ethane.[71]

† See also S Ahmed, J B Moffat *J. Catal.*, 1989, **118**(2) 281, 1190; **121**(2) 408; 1990, **125**(1) 54.

At higher temperatures, CO_2 may take part in oxidative dehydrogenation as an oxidising agent. This was first studied in detail by Aika and Nishiyama.[72] The free energies of the reactions of CO_2 with methane and ethane ΔG (kJ mol^{-1}) at 1073 K are given below:

$$CH_4 + 2CO_2 = C + 2CO_2 + 2H_2O \qquad \Delta G = -27, \qquad (15)$$

$$CH_4 + 3\,CO_2 = 4CO + 2H_2O \qquad \Delta G = -611, \qquad (16)$$

$$CH_4 + CO_2 = 2CO + 2H_2 \qquad \Delta G = -254, \qquad (17)$$

$$C_2H_6 + CO_2 = C_2H_4 + CO + H_2O \qquad \Delta G \sim 0, \qquad (18)$$

$$2CH_4 + CO_2 = C_2H_6 + CO + H_2O \qquad \Delta G = 35. \qquad (19)$$

The ΔG values are negative for the first three processes, and positive for the fifth reaction. All the reactions are endothermic. The equilibrium yield of C_2H_6 at 1073 K even according to reaction (19) should be 13%; this value is fairly high. The equilibrium yield of C_2H_4 by reaction (18) is 57%. By using a $CH_4 + CO_2 + O_2$ mixture it is possible to obtain a higher yield of C_2 and to convert the oxidative condensation of methane into a thermally neutral process, that is to solve the problem of removing heat in the oxidative condensation of methane using oxygen.

Aika and Nishiyama[72,73] studied a number of oxide catalysts of the oxidative condensation of methane. Their properties were compared in two mixtures: 1, $CH_4 + O_2$ (100:1) and 2, $CH_4 + CO_2 + O_2$ (100:100:1). A catalyst with a medium basic strength showed an even higher yield of C_2-hydrocarbons compared with the yield in a $CH_4 + O_2$ mixture. For example, on 50% PbO–MgO the yield of C_2 was 3.28% in the first case, and 4.37% in the second; on $CaO-BaO-CeO_2$ the yields were 2.2% and 3.5% respectively. From these results it was concluded[72] that the oxidative dehydrogenation of hydrocarbons involves oxygen atoms removed from CO_2

$$CO_2 \rightarrow CO + O_{ads}, \qquad (20)$$

$$2CH_4 + O_{ads} \rightarrow C_2H_6 + H_2O, \qquad (21)$$

$$C_2H_6 + O_{ads} \rightarrow C_2H_4 + H_2O. \qquad (22)$$

Experiments with labelled molecules $^{13}CO_2$ and $^{12}CD_4$ [74] showed that ^{13}CO and $^{12}C_2D_6$ appear. This means that all the CO is formed only from CO_2, and not as a result of the further oxidation of hydrocarbons. In the absence of hydrocarbon, CO_2 is completely unreactive on the catalyst. An initial quantity of ethane is necessary to initiate the reaction. The transformation of CO_2 apparently takes place by the reverse reaction to the conversion of water gas

$$CO_2 + H_2 \longrightarrow CO + H_2O \qquad (23)$$

by the action of the hydrogen formed in the gas-phase dehydrogenation of ethane, with intermediate dissociative adsorption (20). Thus in this case the mechanism of the activation of methane and ethane is the same as the mechanism of activation using oxygen alone.

The main processes are the formation of synthesis gas by reaction (17) on pure MgO, reactions (15) and (16) on PbO, and oxidative condensation (18) and (19) on PbO–MgO. The addition of O_2 facilitates reactions (18) and (19), and suppresses reactions (15) and (16). Catalysts with strong basic centres such as Li/MgO and Li/ZnO give less satisfactory results in a $CH_4 + CO_2$ mixture than in a $CH_4 + O_2$ mixture, and are rapidly deactivated.[74]

Reaction (17) takes place mainly at higher tempratures. On $Mn-BaO/Al_2O_3$ and $Mn-CaO/Al_2O_3$ catalysts, for example, this reaction takes palce above 1173 K.[75]

A study of the oxidative dehydrogenation of ethane to ethylene using CO_2 [76–78] showed that the most active and stable systems for the activation of CO_2 and the hydrocarbon are based on manganese oxides. The selectivity of the formation of C_2H_4 was 54% on a 17% MnO_x/SiO_2 catalyst; it increased to 65.4% on 5.5% Cr–17% MnO_x/SiO_2, and when 1.5% K_2O was added the selectivity increased to 76.8% for degrees of conversion of C_2H_6 and CO_2 of 82.6% and 52.3% respectively. The yield of C_2H_4 on the last catalyst was 55.7% at $C_2H_4/CO > 1$.

An *in situ* X-ray diffraction study of the phase composition of the $K-Cr-MnO_x/SiO_2$ catalyst[76,77] showed that the Mn_3O_4 phase observed initially is reduced to MnO under the reaction conditions. The same is observed for the MnO_x/SiO_2 and $Fe-MnO_x/SiO_2$ catalysts.[78] The addition of a second transition metal (iron or chormium) oxide apparently creates an inter-phase boundary which facilitates the redox process. The surface is oxidised both by CO_2 and by O_2. The oxygen capacity in the oxidative dehydrogenation using CO_2 on a $K-Cr-MnO_x/SiO_2$ catalyst was much lower (by a factor of 8) than that when O_2 was used.

The kinetics of the oxidative dehydrogenation of ethane are described by the equation

$$r = \frac{k_1 p_{C_2H_6} k_2 p_{CO_2}}{k_2 p_{CO_2} + k_3 p_{CO}}. \qquad (24)$$

With increase in the ratio $[CO_2]/[C_2H_6]$ the selectivity in the formation of C_2H_4 at first increases, and then reaches a constant value at $[CO_2]/[C_2H_6] > 2.5$. This change in selectivity differs considerably from the change in selectivity under the influence of O_2 in the oxidative dehydrogenation of CH_4 and C_2H_6, which is characterised by a decrease in selectivity with increase in p_{O_2} [see Eqn. (4)]. The increase in the extent of the oxidation of the surface with increase in p_{CO_2} possibly retards the extensive cracking of C_2H_6.

The results show that it is possible in principle to carry out the oxidative dehydrogenation of CH_4 and C_2H_6 using a mixture of the two oxidising agents O_2 and CO_2 by a thermally neutral scheme. The observed[72–74] increase in the yield of C_2H_4 in the oxidative condensation of methane using CO_2 is probably due to the continuous displacement of equilibrium (19) with the removal of ethane by reaction (18). Even higher yields of C_2H_4 than those obtained in the work cited[72–74] can be expected.

VI. Cyclic oxidation and reduction

Oxygen decreases the selectivity of the oxidative condensation of methane [see Eqn. (4)], so that many workers have tried to carry out the reaction in the absence of oxygen in the gas phase. One of the first studies[79] obtained considerable yields of C_2-hydrocarbons by the alternate reduction of the catalyst by methane and its subsequent oxidation by oxygen. Alternate reduction and oxidation also solves to a considerable extent the problem of heat removal. The most active catalyst was MnO_x/SiO_2.

The first Arco has made a detailed study of this cyclic process. The deposited oxides of manganese, indium, gallium, antimony, tin, bismuth, and praseodymium were found to be more active in the cyclic process than in the continuous process. The selectivity reached 10–15%.[80] A subsequent study[80–83] confirmed the high

activity and selectivity of manganese-containing systems and made it possible to improve them by modification. A 15% MnO_x + 5% $Na_4P_2O_7/SiO_2$ catalyst was found to be stable. Successive two-minute pulses of CH_4 and O_2 at 1123 K gave a 17% yield of C_2-hydrocarbons (77% selectivity and 22% conversion); at 1073 K and a low degree of conversion, the selectivity approached 100%.[81] Almost 30000 cycles were carried out on an Li–B–Mn–Mg–O catalyst with almost no loss of activity. Arco constructed a pilot plant based on these experiments.[84] The firm Bechtel developed an improved pilot plant for the cyclic process with reduction of the catalyst in a fluidised bed.[85]

The $Mn-O/Al_2O_3$ catalyst was much less selective than $Mn-O/SiO_2$.[85] Its phase composition changes continuously on oxidation and reduction. In the reaction of MnO_x/SiO_2 with CH_4, the reduction of Mn_3O_4 to MnO was observed, corresponding to the removal of 0.33 g-atom of oxygen per g-atom of manganese.

A study of the reduction of PbO/Al_2O_3 and PbO/MgO catalysts under cyclic conditions showed that in the reduction, up to 23% of the oxygen of PbO is removed, and the metallic lead remaining converts CH_4 mainly into C_2H_6.[86] This result to some extent contradicts X-ray photoelectron spectroscopic data,[87] according to which a Pb phase is not formed on 0.4% PbO/MgO, and also other published data,[33] which show that the reduction of PbO to Pb leads chiefly to the oxidation of CH_4 to CO_2.

4% Na/Pr_6O_{11} was also an active catalyst in the cyclic process.[84] At 1073 K it gave 21% conversion and 76% selectivity. The selective preparation of C_2-hydrocarbons in a cyclic process was carried out on an $Li/NiO/TiO_2$ catalyst; on Li/TiO_2, however, only CO and CO_2 were obtained.[88] The pure oxides Mn_2O_3 and MnO_2 function effectively under cyclic redox conditions, but the addition of even small quantities of oxygen to methane leads to extensive oxidation.[5] Relatively high yields of C_2-hydrocarbons were also obtained under cyclic conditions on an Li/MgO catalyst.[89]

The best catalysts for cyclic redox conditions are systems containing the oxides of transition metals and reducible lanthanide oxides. Their capacity with respect to oxygen is apparently fairly high, while the absence of weakly-bound oxygen on the surface prevents extensive oxidation.

The selectivity of catalysts such as In_2O_3, Bi_2O_3, La_2O_3, and Li/MgO under cyclic conditions is also fairly high, but the capacity with respect to oxygen is much lower.[5,79,81,90]

The oxidative dehydrogenation of CH_4 [75] and C_2H_6 [76,77] using CO_2 has also been studied under cyclic alternating conditions. The selectivity is higher, but the oxygen capacity much lower, than in the case where oxygen is used as oxidant. The rate of the oxidative dehydrogenation on a $K-Cr-MnO_x/SiO_2$ catalyst increases when chromium is introduced. According to the authors cited,[76,77] the inter-phase boundary between MnO_x and CrO_y facilitates the re-oxidation of the catalyst.

One form of separated process involves the use of membranes permeable to oxygen. An advantage of this process may be the possibility of condensation in the absence of oxygen or at a low oxygen pressure.

The formation of ethane on a silver membrane with O_2 on one side of the membrane and CH_4 on the other was observed even at 743 K.[91] 100% selectivity was obtained with a low conversion (0.02%). Increase in temperature to 953 K increased the conversion to 40% for a selectivity of about 40%. C_2H_4 also began to appear in the products at 823 K. The active species is atomic oxygen, which diffuses to the silver surface through the membrane and takes part in the formation of C_2-hydrocarbons. The diffusion is apparently the limiting stage; this is confirmed by the similarity in the rate of formation of the C_2-products and the rate of diffusion of oxygen through silver. The observed activation energy of the formation of C_2-hydrocarbons is 150 kJ mol^{-1}. The authors cited[91] consider the C_2-hydrocarbons may be formed as a result of the reaction of CH_4 with atomic oxygen in the gas phase.

Membranes of PbO or MgO on Al_2O_3,[92] PbO/MgO/dynacerum (ceramic),[93] or Pd/MgO/ceramic[94] have also been studied. In the last case the catalysis took place at a low temperature, 553–683 K; 38% selectivity with 0.45% conversion was observed even at 523 K.

The separated cyclic process can be modified by the sectional introduction of oxygen into the reactor. For example, oxygen has been introduced in portions into four successive reactors.[95] This gave a much higher selectivity of up to 80% at 1103 K and 20% conversion on an La/MgO catalyst when oxygen was introduced in equal quantities into each of the four sections. A selectivity of 62% was obtained for 35.7% conversion.

Finally, an electrochemical version of the process is possible. An electrochemical cell with 80% Y_2O_3/ZrO_2 solid electrolyte, a silver anode, and an Ag/Bi_2O_3 cathode was first used by Otsuka and co-workers.[96] A CH_4 + O_2 mixture was passed over the anode. The selectivity was higher than in the continuous gas-phase process.

Other authors[97–102] carried out the electrochemical process at 1023–1123 K using the same solid electrolyte Y_2O_3/ZrO_2. The electrodes used were the catalysts $La_{0.89}Sr_{0.10}MnO_3$,[97,100] Au, Pd, Ag/Bi_2O_3,[98] Cu, Ag–Pd, La–Li–O,[101] and $LaCoO_3$.[102] The reaction rates were low, however. The electrochemical version is still far from the stage of practical application.

References

1. J R Anderson *Appl. Catalysis*, 1989, **47**(2) 177
2. J H Lunsford *Langmuir*, 1989, **5**(1) 12
3. M Yu Sinev, V N Korchak, O V Krylov *Usp. Khim.*, 1989, **58**(1) 38 [English translation in *Russ. Chem. Rev.*, 1989(1)]
4. Y Amenomiya, V T Birss, M Goledzinowski, et al. *Catal. Rev.*, 1990, **32**(3) 163
5. J H Lunsford *Catalysis Today*, 1990, **6**(1/2) 235
6. J L Duboix, C J Cameron *Appl. Catalysis*, 1990, **67**(1) 49
7. J C Mackie *Catal. Rev.*, 1991, **33**(1/2) 169
8. J A Labinger, K C Ott *J. Phys. Chem.*, 1987, **91**(11) 2682
9. J G McCarty *New Developments in Selective Oxidation (Rimini, Italy, 1989): Proc. I World Congress*, Elsevier, Amsterdam, 1990, p. 393
10. H Chen *Chinese J. Natural Gas Chem.*, 1990, **4**(1) 13
11. K Machida, M Enyo *J. Chem. Soc., Chem. Commun.*, 1990, (2) 1639
12. Y In *Acta Physicochim. Sinica*, 1990, **6**(6) 845–848
13. M Yu Sinev, V N Korchak, O V Krylov *Kinet. Katal.*, 1987, **28**(5) 1376
14. K Otsuka, M Hatano, Q Lin, A Morikawa *Proc. 8th Japan–USSR Catalysis Seminar*, Tokyo, 1986, p. 1
15. A Ekstrom, J A Lapszewicz *J. Phys. Chem.*, 1989, **93**(13) 5230
16. J A Roos, S J Korf, J J Biermann, et al. *Proc. I World Congress "New Developments in Selectivation Oxidation" (Rimini, Italy, 1989)*, Elsevier, Amsterdam, 1990, p. 381
17. V A Seleznev, Yu P Tyulenin, A A Kadushin, et al. *Proc. Workshop Meeting for C_1-C_3 Hydrocarbons Conversion*, Krasnoyarsk, 1991, p. 20

18. Yu P Tyulenin, V A Seleznev, A A Kadushin, et al. *Kinet. Katal.*, 1991, **32**(4) 1023
19. J S Tsay, N Davydova, M Traykova-Kolchova *Proc. 7th Intern. Symp. on Heterogeneous Catalysis (Burgas, 1991)* (Edited by L Petrov), 1991, Vratza, p. 273
20. O V Buevstaya, S M Aliev, V D Sokolovskii *Proc. 7th Intern. Symp. on Heterogeneous Catalysis (Burgas, 1991)* (Edited by L Petrov), 1991, Vratza, p. 703
21. O V Krylov *Kinet. Katal.*, 1992, **33**
22. E Iwamatsu, K Aika *J. Catal.*, 1939, **117**(2) 416
23. V R Choudhary, A M Rajput, D B Akolekar, V A Zeleznev *Appl. Catalysis*, 1990, **62**(2) 171
24. M Matsukata, E Okanari, K Komori, et al. *Proc. Symp. on Methane Activation Intern. Congress on Pacific Basin Soc.*, Honolulu, 1989, p. 52
25. S V Adel'son, T A Vorontsova, E E Bobkovskaya *Neftekhimiya*, 1991, **31**(6) 848
26. O V Buevskaya, M P Vanina, N F Sapatina, V D Sokolovskii *Proc. Workshop Meeting for C_1-C_3 Hydrocarbons Conversion*, Krasnoyarsk, 1991, p. 61
27. Z Zhang, M A Baerns *Appl. Catalysis*, 1991, **75**(2) 239
28. P Pereira, S H Lee, G A Somorjai, H Heinemann *Catalysis Lett.*, 1990, **6**(3/6) 255
29. J Rasco, P Pereira, G A Somojai, H Heinemann *Catalysis Lett.*, 1991, **9**(5/6) 395
30. P Pereira, R Csencsits, G A Somorjai, H Heinemann *J. Catal.*, 1991, **123**(2) 463
31. C E Mooney, L C Anderson, J H Lunsford *J. Phys. Chem.*, 1991, **95**(16) 6070
32. A F Carley, P R Davies, M W Roberts, K K Thomas *Surf. Sci.*, 1990, **238**(1/3) 2467
33. M Yu Sinev, V Yu Bychkov, V N Korchak, et al. *Kinet. Katal.*, 1989, **30**(5) 1137
34. H Matsuhashi, T Hisazaki, K Aratu *Proc. 9th Soviet–Japanese Seminar on Catalysis (1990, Yuzhno-Sakhalinsk)*, 1990, p. 33
35. A V Annapragada, E Gulari *J. Catal.*, 1990, **123**(1) 130
36. K Otsuka, K Jinno, A Morikawa *Chem. Lett.*, 1985, (5) 467
37. K Otsuka, T Komatsu *J. Chem. Soc., Chem. Commun.*, 1987, (5) 388
38. T R Baldwin, R Burch, G D Squire, S C Tsang *Appl. Catalysis*, 1991, **75**(1) 153
39. A N Shigapov, M A Novozhilova, S N Vereshchagin, et al. *React. Kinet. Catal. Lett.*, 1988, **37**(2) 367
40. R Burch, G D Squire, S C Tsang *Appl. Catalysis*, 1988, **43**(1) 109
41. R Burch, S Chalker, P Louder, et al. *Appl. Catalysis*, 1991, **A/79**(2) 203
42. K Fujimoto, S Hashimoto, K I Asami, H Tominaga *Chem. Lett.*, 1987, (11) 2157
43. B Warren *Catalysis Today*, 1992, **13**(3) 311
44. Kh M Minachev, N Ya Usachev, Yu S Khodakov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, (7) 1686
45. J Wang, K Zhen, Y L Bi, Q Wei *Proc. Symp. on Methane Activation. Intern. Congress on Pacific Basin Soc.*, Honolulu, 1989, p. 68
46. H Yang, F C Thyrion *Catalysis Today*, 1990, **6**(3/6) 611
47. I A Guliev, S A Dzhamalova, I A Timakova, A Kh Mamedov *Trudy 9-i Vsesoyuznoi Konferentsii po Okislitel'nomu Katalizu* (Proceedings of the Ninth All-Union Conference on Oxidative Catalysis), Baku, 1988, p. 64
48. A Kh Mamedov, I A Guliev, M K Guseinova, V S Aliev *Trudy 4-i Vsesoyuznoi Konferentsii po Kinetike Kataliticheskich Reaktsii* (Proceedings of the Fourth All-Union Conference on the Kinetics of Catalytic Reactions), Yaroslavl', 1987, p. 151
49. A Kh Mamedov, S R Mirzabekova, S A Dzhamalova, I A Guliev *Trudy 5-i Vsesoyuznoi Konferentsii po Mekhanizmu Kataliticheskikh Reaktsii* (Proceedings of the Fifth All-Union Conference on the Mechanisms of Catalytic Reactions), Nauka, Moscow, 1990, p. 105
50. I A Guliev, S A Dzhamalova, M K Guseinova, A Kh Mamedov *Kinet. Katal.*, 1990, **31**(5) 1214
51. I A Guliev, A Kh Mamedov *Neftekhimiya*, 1988, **28**(6) 786
52. S A Dzhamalova, I A Guliev, S R Mirzabekova, A Kh Mamedov *Neftekhimiya*, 1984, **28**(5) 780
53. J Wang, Q Lin *C_1 Chemistry and Chem. Industry*, 1990, **4**(3) 401
54. D I Bradshaw, P T Coolen, R W Judd, C Komodromos *Catalysis Today*, 1990, **6**(4) 427
55. C Komodromos, quoted in G Hutchings *Appl. Catalysis*, 1988, **42**(1) 190
56. T Ohno, J B Moffat *Catalysis Lett.*, 1991, **9**(1) 20
57. S Ahmed, J B Moffat *Catalysis Lett.*, 1989, **2**(3) 249
58. A Kh Mamedov, I A Guliev, P A Shiryaev, D P Shashkin *Kinet. Katal.*, 1990, **31**(5) 1214
59. S J Conway, J H Lunsford *J. Catal.*, 1991, **131**(2) 513
60. S J Conway, D J Wang, J H Lunsford *Appl. Catalysis.*, 1991, **79**(1) 1
61. W Ueda, J M Thomas *Proc. 9th Intern. Congress on Catalysis* (Edited by M J Phillips, M Ternan), Chem. Inst. Canada, Calgary, 1988, Vol. 2, p. 960
62. W Ueda, T Isozaki, Y Morikawa, J M Thomas *Chem. Lett.*, 1989, (12) 2103
63. W Ueda, F Sakyu, T Isozaki *Catalysis Lett.*, 1991, **10**(1) 83
64. T R Baldwin, R Burch, E M Craft, et al. *Appl. Catalysis*, 1989, **59**(2) 219
65. Y Ohtsuka, M Kawabata, A Tomita *Appl. Catalysis*, 1989, **47**(2) 307
66. S J Korf, J A Roos, N A de Bruijn, et al. *J. Chem. Soc., Chem. Commun.*, 1987, (19) 1433
67. G J Hutchings, M S Scurrell, J R Woodhouse *Catalysis Today*, 1990, **6**(3) 394
68. X D Peng, P C Stair *J. Catal.*, 1991, **128**(2) 264
69. K Aika, K Aono *J. Chem. Soc., Faraday Trans.*, 1991, **87**(8) 1277
70. J X Wang, J H Lunsford *J. Phys. Chem.*, 1986, **90**(22) 5883
71. R G Gaziev, A A Ukharskii, Z T Fattakhova, et al. *Proc. 6th Intern. Symp. on Heterogeneous Catalysis*, BAN, Sofia, 1987, p. 228
72. K Aika, T Nishiyama *J. Chem. Soc., Chem. Commun.*, 1988, (1) 70; *Proc. 9th Intern. Congress on Catalysis* (Edited by M J Phillips, M Ternan), Chem. Inst. Canada, Calgary, 1988, Vol. 2, p. 907
73. K Aika, T Nishiyama *Catalysis Today*, 1989, **4**(2/4) 271
74. T Nishiyama K Aika *J. Catal.*, 1991, **122**(2) 346
75. A Kh Mamedov, S R Mirzabekova, Sh A Nuriev, et al. *Neftekhimiya*, 1990, **30**(1) 30
76. A Kh Mamedov, P A Shiryaev, D P Shashkin, O V Krylov *Proc. I World Congress "New Developments in Selective Oxidation" (Rimini, Italy, 1989)*, Elsevier, Amsterdam, 1990, p. 477

77. A Kh Mamedov, P A Shiryaev, D P Shashkin, O V Krylov *Kinet. Katal.*, 1991, **31**(3) 625
78. A Kh Mamedov, S R Mirzabekova, Sh A Nuriev, et al. *Trudy 5-i Vsesoyuznoi Konferentsii po Mekhanizmu Kataliticheskikh Reaktsii* (Proceedings of the Fifth All-Union Conference on the Mechanisms of Catalytic Reactions), Moscow, 1990, p. 185
79. G F Keller, B Bhasin *J. Catal.*, 1982, **73**(1) 9
80. J A Sofranko, J J Leonard, C A Thomas *J. Catal.*, 1987, **103**(2) 302
81. C A Jones, J J Leonard, J A Sofranko, US P. 4 433 644
82. C A Jones, J J Leonard, J A Sofranko *J. Catal.*, 1987, **103**(2) 311
83. J A Sofranko *J. Catal.*, 1988, **114**(1) 472; *Proc. Symp. on Methane Activation, Intern. Chem. Congress on Pacific Basin Soc., Honolulu*, 1989, p. 34
84. A M Gaffney, C A Jones, J J Leonard, J A Sofranko *J. Catal.*, 1988, **114**(2) 422
85. J M Fox, T P Chen, B D Degen *Chem. Eng. Progr.*, 1990, **86**(1) 42
86. K Asami, S Hashimoto, T Shikada, et al. *Chem. Lett.*, 1986, (7) 1233
87. Y K Agarwal, R A Migone, G Marcelin *J. Catal.*, 1990, **121**(1) 110
88. Z Kalenik, E Miro, J Santamaria, E E Wolf *Proc. Symp. on Methane Activation, Intern. Chem. Congress on Pacific Basin Soc.*, Honolulu, 1989, p. 109
89. V R Choudhary, S D Sansare, A M Rajput, D B Akolekar *Appl. Catalysis*, 1991, **69**(1) 187
90. Z G Osipova, L M Plyasova, V D Sokolovskii *Trudy 9-go Sovetsko–Yaponskogo Seminara po Katalizu* (Proceedings of the Ninth Soviet–Japanese Seminar on Catalysis), Yuzhno-Sakhalinsk, 1990, p. 41
91. A G Anshits, A N Shigapov, S N Vereshchagin, B A Shevnin *Kinet. Katal.*, 1990, **30**(5) 1260
92. J Haggin *Chem. Eng. News*, 1990, **68**(1) 36
93. K Omata, S Hashimoto, H Tominaga, K Fujimoto *Appl. Catalysis*, 1989, **52**(1) 1
94. N Mouaddib, K R Thampi, A J Mc Evoy, J Kiwi *Catalysis Lett.*, 1990, **4**(3) 285
95. V R Choudhary, S T Chaudhari, A M Rajput, V H Rane *J. Chem. Soc., Chem. Commun.*, 1989, (20) 1526
96. K Otsuka, S Yakayama, A Morikawa *Chem. Lett.*, 1984, (3) 339
97. S F Sammells, K Q Frese, V Kirst *Proc. Symp. on Methane Activation, Intern. Congress on Pacific Basin Soc.*, Honolulu, 1989, p. 34
98. D W Eng, P P Shiang, M Stoukides *Proc. Symp. on Methane Activation, Intern. Congress on Pacific Basin Soc.*, Honolulu, 1989, p. 54
99. K Otsuka, K Suga, I Yamanaka *Catalysis Today*, 1990, **6**(4) 587
100. L S Vol'dman, V D Sokolovskii *Catalysis Lett.*, 1991, **8**(1) 6
101. V D Belyaev, O V Bazhin, V A Sobyanin, V N Parmon *Proc. Intern. Congress "New Developments in Selective Oxidation" (Rimini, Italy, 1989)*, Elsevier, Amsterdam, 1990, p. 469
102. I T Nagamoto, K Hayashi, M Inoue *J. Catal.*, 1990, **126**(2) 671

Received 8th April 1992

Translated from *Uspekhi Khimii* **61** 1564–1593 (1992) U.D.C. 542.91:547.92

Progress in the field of physiologically active lanosterol compounds

I G Reshetova, R K Tkhaper, A V Kamernitskii
Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences

ABSTRACT. This review correlates the studies (up to 1991) on the isolation, structural determination, biological activity, and synthesis of physiologically active polyoxidised lanosterol derivatives of vegetable (inotodiol, ganoderic acids) and animal (seychellogenin) origin. The cytotoxic, cardiovascular, and other forms of activity of compounds of this type are of considerable interest in relation to their medical use. It is noted that the functionalised side chain (in an open form or containing lactones, lactols, etc.) is generally responsible for the activity exhibited by lanosterol derivatives. Two basic approaches to the derivation of these structures are defined: either by complete reconstruction of the side chain of lanosterol (degradation and rebuilding with oxygen-containing residues) or by progressive functionalisation of the Δ^{24}-side chain of lanosterol. The syntheses of the known anticancer compound "inotodiol", seychellogenins, ganoderic acids, and other compounds are described.

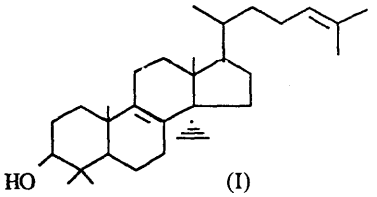
The bibliography includes 105 references.

Contents

I. Introduction 859
II. Natural derivatives of lanosterol 859
III. Synthetic approaches to lanosterol derivatives with a functionally substituted side chain 865

I. Introduction

Triterpenoids of natural origin with polyfunctional side chains at C(17) and C(20) and with the lanostane skeleton (I) [also known as 4,4,14-trimethylpregn-5α-8(9)-ene or -7,9(11)-diene] have attracted considerable attention[1] from research workers because of their high and varied biological activity.



(I)

Their occurrence in nature, in particular in the plant world and fungi, forms the subject of a number of reviews[2–4] covering the literature up to 1977. It has been established that the main responsibility for their biological activity is borne by the functionalised side chain of lanosterol containing hydroxyl, carbonyl, and other groups, right up to an 18,20-lactone ring, which imparts antifungal and carcinolytic properties to lanostane derivatives. These lactones make up a separate group of triterpenoids—the holothurigenins.[5,6] The regulatory effect on the biosynthesis of cholesterol, when the presence of an O-functional group adjacent to the skeleton [8(9) double bond] is important, constitutes the only exception.[7]

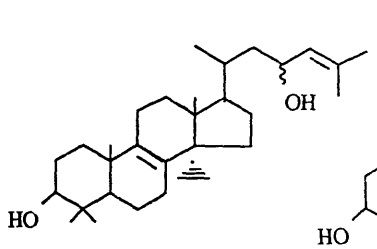
In the present review we have assumed the task of focusing attention on an analysis of the structural features of polyoxidised lanosterol derivatives that have been isolated up to 1991, monitoring the effect of their structure on cytotoxic, antisclerotic, and other types of biological activity, and discussing the most promising synthetic methods. The material has been classified and arranged in an order corresponding to an increase in the degree of oxidation of the side chain of lanosterol. Studies relating to skeletal rearrangements of lanosterol that lead to cucurbitane and fusidic acid have not been covered in this review.[8,9]

II. Natural derivatives of lanosterol

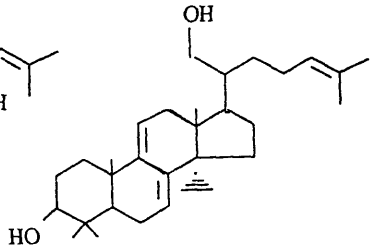
1. Natural derivatives of lanosterol with open side chains containing oxygen functional groups

Of the monohydroxy derivatives of lanosterol, 23ξ-hydroxylanosterol (II) was first isolated in1968 as a metabolite of the fungal mycelium of *Scleroderma aurantium* Pers.[10–12] The absolute configuration at C(23) in natural 23-hydroxylanosterol was determined by correlation of the sign of its molecular rotation with that of known (*R*)(–)- and (*S*)(+)-4-methylpent-3-en-2-ols. The difference between M_D for the natural (23*S*)-23-alcohol and lanosterol is positive while for the synthetic (23*R*)-23-alcohol there is a negative difference.[11] It was subsequently established that this allylic alcohol is unstable and undergoes dehydration during chromatographic separation.[13] The 21-hydroxy derivatives with a

lanosta-7,9(11),24-triene and -8,24-diene skeleton (IIIa, b) were also isolated.[14]

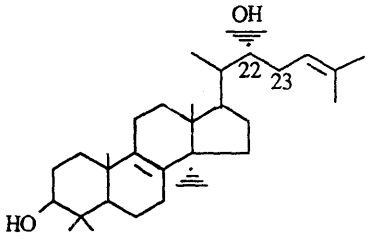


(II)



a: $\Delta^{8(9)}$
b: $\Delta^{7,9(11)}$

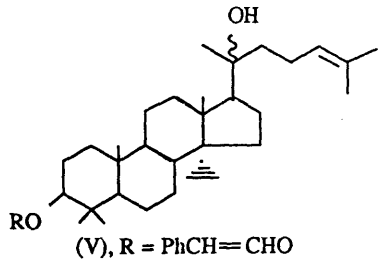
(III)



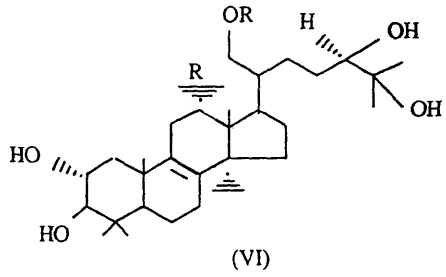
(IV) inotodiol

The 22- and 24-hydroxy derivatives were isolated from the fungus *Inonotus obliquus* and plant *Euphorbius corollatta*,15,16 and the most interesting of these is (22*R*)-hydroxylanosterol (IV)—the so-called inotodiol—a compound which is highly active towards cancer cells grown *in vitro*. It inhibits the growth of sarcoma 180 and carcinoma 755.[17] The 22-hydroxylanosterin derivative with a 4-carboxyl group, which is similar in structure to inotodiol, was isolated from the fungus *Fomes senex*.[18] 25-Hydroxylanosterol was isolated by Japanese researchers.[19] Lanostane with a shortened 22-hydroxy side chain has been isolated from the fungus *Verticillium lecanii*.[20]

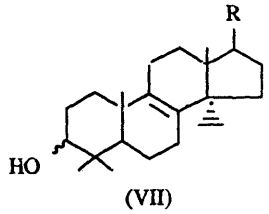
The Indian plant *Euphorbia antiquorum* L has proved to be a very abundant source of 20-hydroxylanosterol (V). Its gum has diuretic, laxative, and toxic properties.[21] It is used in stomatology, in the treatment of nervous disorders, and for treatment of wounds. In the isolation of the active principle, the cinnamic ester of 20-hydroxylanosterol (V), known as anticulol A, was obtained. Its mass spectrum did not exhibit a peak due to the molecular ion but a peak from the dehydrated form with *m/z* 556 occurred. The position of the 20-hydroxy group was confirmed by the ^{13}C NMR spectroscopic data (δ 75.4 ppm). In the PMR spectrum, in addition to the chemical shifts (δ) corresponding to the protons of cinnamic acid, signals from the 21-CH_3 group on C(20)—OH (δ 1.15 ppm) and from C(18)—CH_3 (0.98 ppm) were recorded. The skeletal structure of 8(9)-dihydrolanostane was confirmed by analysis of the ^{13}C and ^1H NMR spectra. Japanese scientists isolated 2α,3β,21,24,25-pentahydroxy derivatives of lanosterol (VI)—the so-called fasciculols, which are novel plant growth inhibitors—from the plant *Naemotoloma fasciculara*.[22] The 22,24-, 22,25-, and 22,23-dihydroxy derivatives of lanosterol (VIIa—d) were isolated from *Pisolithus tinctorius* fungi.[23] These compounds exhibited appreciable cytotoxic activity on hepatoma and tinoma cells *in vitro*. The structure of the side chains, in particular the position of the OH groups has been demonstrated by a combination of known phyiscal methods, including the nuclear Overhauser effect (NOE) and the formation of derivatives.



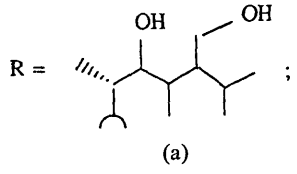
(V), R = PhCH=CHO



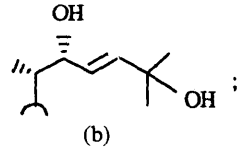
(VI)



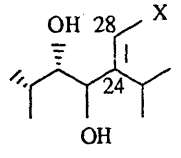
(VII)



(a)



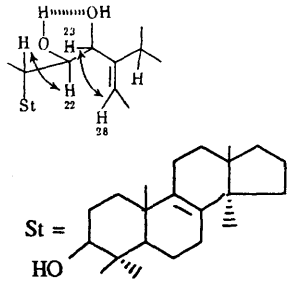
(b)



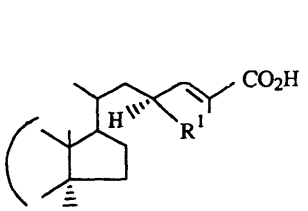
, X = H (c) CH_3 (d)

Thus, the presence of the C—CH=CX group (where X = CH_3) was confirmed from the signals at δ 1.47 ppm (3H, d, *J* 6 Hz) and δ 5.63 ppm (1H, q, *J* 6 Hz) while the secondary OH groups were identified from the multiplets at δ 3.98 ppm (1H, *J* 9 Hz) and δ 3.62 ppm (1H, *J* Hz) due to the protons attached to the carbon atoms bearing these OH groups. Their 22-acetates give chemical shifts at lower field (δ 5.2 and 4.2 ppm). The mass spectra were characterised by fragments corresponding to loss of a single proton from the side chain of the molecule, which indicates that all of the compounds differ only in the degree of substitution of the steroid side chain. The double bond in the side chain was confirmed by oxidation of glycol (VIId) to the 22-aldehyde and 3-methyl-2-methylenebutanal isolated as its dinitrophenylhydrazine derivative. The stereochemistry of the substituents in the side chain of the steroid was demonstrated by means of NOE experiments in the PMR spectra. Thus, a *Z*-configuration was assigned to the 24(28)-olefin because of the interaction of H(28) with H(22) and H(23) rather than with H(25).

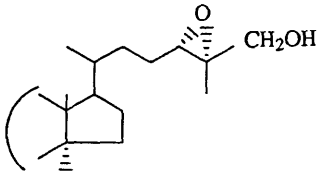
The existence of an intramolecular hydrogen bond was demonstrated.



Extracts from the fungal mycelium of *Ganoderma lucidum* proved extremely interesting in terms of their biological properties.[24] A pharmacological study demonstrated their effect on the cardiovascular system (decrease in blood pressure). Lanostane alcohols and acids—24,25,26-triols and 23-hydroxy-26-acids[25]—were isolated from the mycelium and fruit body of this fungus, and an (*S*)-configuration of the 23-centre was established for the latter by measurement of the Cotton effect (CE) of the 23-monodimethyl-*p*-aminobenzoate.



(VIII), R^1 = $OH, OCOC_6H_4NH_2$,

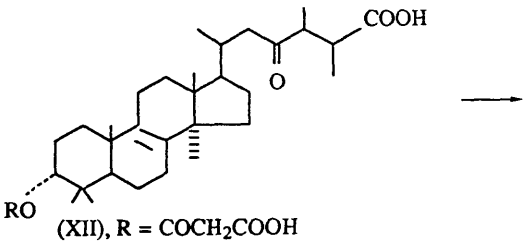


(IX)

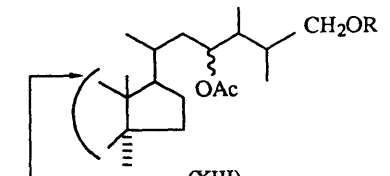
The 24,25-epoxy derivative of the 26-alcohol (IX) was isolated from the same fungus,[26] and the configuration of its oxide ring was established from NOE data and by a method described by Dillon and Nakanishi,[27] which involved the reduction of the α-epoxide with lithium aluminium hydride and determination of the sign of the Cotton effect in the circular dichroism spectrum in the presence of $Pr(dpm)_3$ according to the empirical rule of Nakanishi.[27]

The 21-carboxy derivatives of lanosterol (X), known as trametenolic acids, were isolated by several groups of scientists[28,29] from *Polyporaceae Fomes Hartigii* Allescher fungi; some of these were subsequently called eburicoic acids.[4] The lanosta-7(8),9(11),24-triene-21-acid[30] and lanosta-17(20),24-diene-21-acid substituted at C(6), C(7), and C(11) [31] were also isolated. The 26-acids, so-called polyporenic acids (XI), occur widely in nature.[4] The novel 23-keto-26-acid (XII), known as carboxaquercinic acid, was isolated as its 3-malonate from fungal metabolites of *Daedalea quercina*.[32]

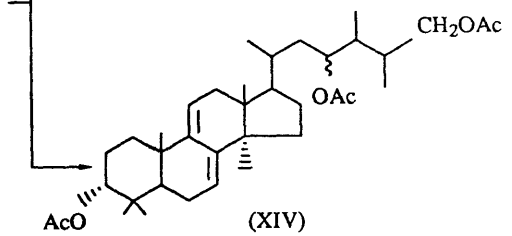
Its structure was demonstrated by a combination of PMR and mass spectrometry data as well as by chemical conversions to the dihydroxy derivatives (XIII) and (XIV).



(XII), R = $COCH_2COOH$

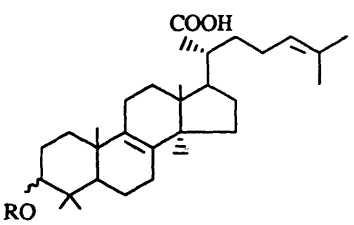


(XIII)

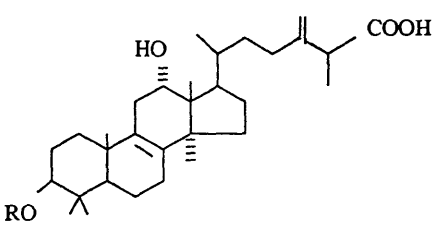


(XIV)

Lanostane 26-acids differing in the configuration of substituents at C(3) have been isolated from Chinese[33] and Mexican[34] plants. A large group of triterpenoids isolated from the fungal mycelium of *Ganoderma lucidum* was made up by 26-acids with a functionalised lanostane skeleton (XV).[35] The useful biological properties of the "ganoderic" acids, in particular their cytotoxicity towards hepatoma cells[36–40] acted as a stimulus for detailed studies on the extracts from fungi used in Chinese, Indian, and Korean popular medicine as anodynes. To date more than 30 studies[35] in which the isolation of ganoderic and ganoderenic acids (labelled with the letters of the alphabet from A to T) is reported to have been published. They have been isolated from a chloroform–ethanol extract by chromatography on silica gel columns. In some cases separation is more effective after conversion of the acid mixtures to their methyl esters. Ganoderic acids differ in the degree of oxidation of the side chain. Thus, the distinctive group fo the 23-keto-26-acid[40,43] and 22-hydroxy-26-acid[40] has been detected. The $\Delta^{20(22)}$-23-keto-26-acid (XV) and 20-hydroxy-23-keto-26-acid (XVI) with the same

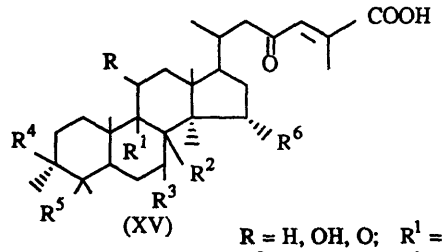


3α– or 3β–(X)



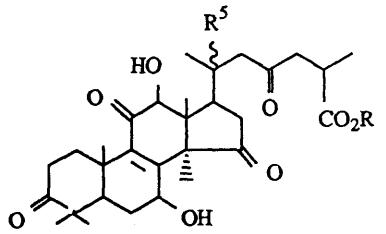
(XI)

functionality in the skeleton, known as ganoderenic acids[44,45] and 21,26-acids,[46] have been isolated from *Ganoderma lucidum* Karst. The amide of the 26-acid (XVII) has also been isolated.[47]

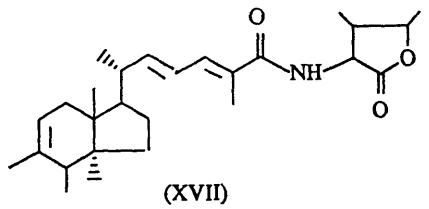


(XV)

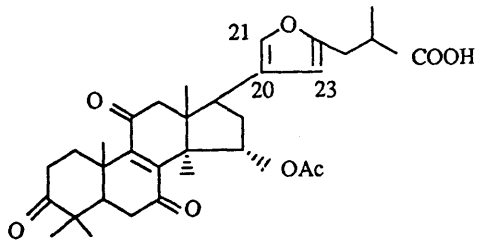
R = H, OH, O; R^1 = H; R^1, R^2 = Δ; R^3 = H, α-OH; R^4, R^5 = O; R^4 = OH; R^5 = H, OH; R^6 = H, OH.



(XVI), R^5 = H, OH; $\Delta^{20(22)}$



(XVII)

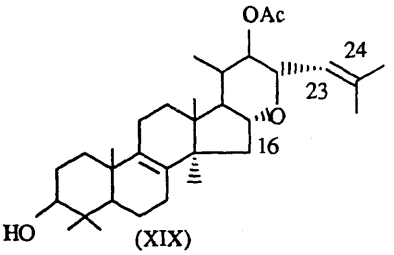


(XVIII)

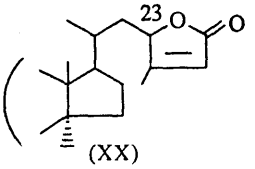
The furanoganoderic acid (XVIII) was isolated by Nishitoba et al.[35] The identification and structural assignment of ganoderic acids was based on an analysis of their ^{13}C and ^1H NMR spectra and the fragmentation in their mass spectra. A structural feature of their skeleton is the presence of the cross-conjugated 7,9(11)-diketo system, in some cases a 7β-hydroxy group and 3-carbonyl, and in certain instances a variable configuration of the 3-hydroxy group. It was noted by Lobo et al.[23] that the variation in the configuration of the substituent at C(3) in ganoderic acids is dependent on the source from which they are isolated — the fruit body of the fungus (3β-hydroxy) or from a culture of mycelium (3α-hydroxy). This finding is interesting in relation to the possible biosynthetic pathways of triterpenoids in *Ganoderma lucidum*. By studying the biosynthesis of ganoderic acids in a culture of mycelium using labelled squalene (1,2-^{13}C)-acetate, Tiasen and Meifen[33] found that ganoderic acid T, for example, is formed from (3*S*)-oxidosqualene via the 3-keto compound by the same route as that which occurs in higher plants with formation of the 3α-hydroxy substituent. All of the ganoderic acids have signals corresponding to the 4,4,14,18,19-CH_3 groups. The presence of double bonds is reflected in the appearance of signals from olefinic protons in the region of 5–6 ppm. Conjugated keto groups are demonstrated by the absorption in the UV spectra. In some cases the presence of a double bond in the molecule of a natural acid can be confirmed by ozonisation and identification of the resulting products. The configuration of the hydroxide at C(3) is determined from the PMR spectroscopic data; 3β-OH appears as two doublets at δ 3.5 ppm with *J* 10.5 Hz while 3α-OH has a lower spin–spin coupling constant. In the PMR spectrum of furanoganoderic acid (XVIII) there was no signal at 2.2 ppm due to a 21-CH_3 group but two signals due to olefinic protons appeared as singlets at δ 6.90 and 5.77 ppm. From these data together with the signals in the ^{13}C NMR spectrum at δ 107.7 and 138.4 ppm (from two methine olefinic carbons) and δ 153.2, 153.6, 150.9, and 124.9 ppm (from four tertiary olefinic carbons), De Bernardi et al.[53] could establish the presence of a 2,4-substituted furan ring in the side chain of this novel ganoderic acid. The structure of furanoganoderic acid — 21,23-epoxy-15α-hydroxy-3,7,11-triketo-5α-lanosta-8,20(21),22-trien-26-oic acid (XVIII) — corresponds to its biogenesis.

2. Natural lanosterol derivatives with lactone, lactol, and furan rings in the side chain

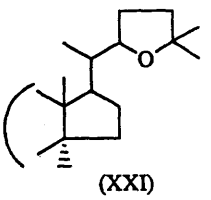
Compounds with a lanostane skeleton and a heterocyclic structure in their side chains have been found amongst natural polyhydroxytriterpenoids.[18,48–51] It has been argued, however, that they may be secondary products formed during isolation as a result of the condensation of hydroxy and keto acids.[32] Echinodol (XIX) [49] and abieslactone (XX) [51] are amongst such compounds. Echinodol was isolated from *Echinodontium tsugicola*[52] fungi and from plants having anticancer activity. The structure of (XIX) was demonstrated by a sequence of reactions, including dehydration, acid hydrolysis, Jones oxidation, and Wolff–Kishner reduction, giving lanosterol, and it was also supported by the PMR spectroscopic data.[52] The structure of abieslactone (XX) was established by X-ray diffraction analysis. It is (23*R*)-3α-methoxy-5α,9β-lanosta-7,24-dien-23,26-olide. Senexenol (XXI) isolated from *Fomes senex* fungi contains a 22,25-tetrahydrofuran residue.[18]



(XIX)



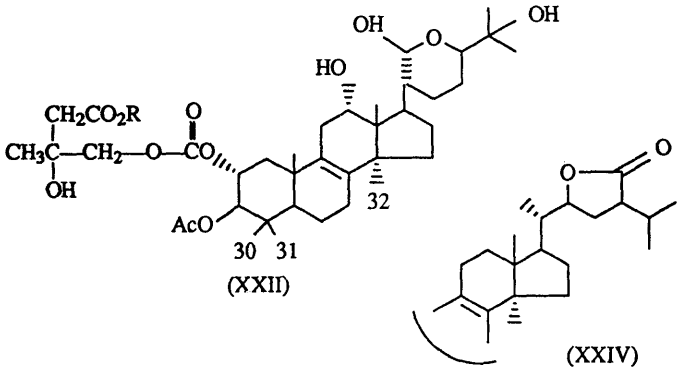
(XX)



(XXI)

3β-Acetyl-2α-(3′-hydroxy-3′-methyl)glutarylcrustulinol (XXII), which is active against leukaemia, was isolated from *Hebeloma species* fungi.[53] The molecular structure of (XXII) was determined

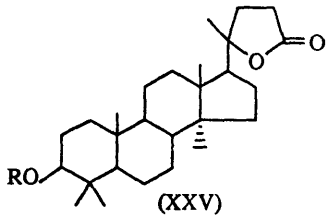
from its ^{13}C NMR data. The three acetyl carbons give signals in the region of δ 170–174 ppm; the methines attached to two oxygen atoms appear at δ 93.2 and 5.48 ppm. The tetrasubstituted 8(9)-double bond gives signals at δ 135.8 and 132.7 ppm. Oxidation of the hemiacetal (XXII) with Fetizon reagent—silver acetate on Celite—gave a δ-lactone (XXIII). The conformation of the tetrahydropyran ring in (XXII) existing in the boat form was established from PMR spectroscopic data. The anomeric OH group and isopropyl group have a pseudoaxial conformation. The γ-lactone (XXIV), which is similar in structure to hemiacetal (XXII), was isolated from the fungus *Pisolithus*,[23] and it also exhibited appreciable cytotoxic activity. Lobo et al.[54] noted that this was the first natural example of a triterpene carboxylic acid derivative. Its structure was demonstrated by elemental analysis and the data of NMR and mass spectrometry. Thus, 4 signals (δ 0.72, 0.97, 0.81, and 0.88 ppm) are attributed to those from the CH_3 groups at C(18), C(19), C(30), and C(31). The groups at C(21), C(26), and C(27) appear as singlets at δ 1.66, 1.02, and 0.94 ppm. The mass spectrum is characterised by a fragment with *m/z* 155 ($C_9H_{15}O_2$), which corresponds to cleavage between the steroid skeleton and side chain. The structure and configuration of (XXIV) was confirmed conclusively by X-ray diffraction analysis.



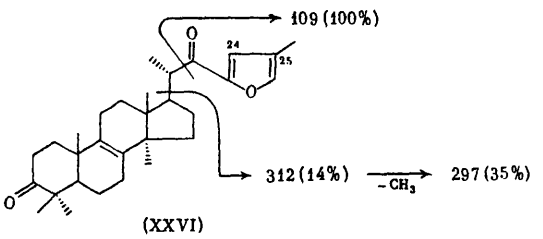
(XXII) (XXIV)

A γ-lactone on C(20) of the side chain of lanostane was isolated[55] from the leaves of the Indian plant *Lansium* qn Bedd and was given the name lansilactone. The structure of (XXV) was established from its ^{13}C and ^{1}H NMR data, and the point of attachment of the lactone ring was determined from the nature of fragmentation in the mass spectra.[55]

The novel furanoid triterpenoid pomacerone (XXVI) [56] was isolated from the fungus *Phellinus pomaceus*.

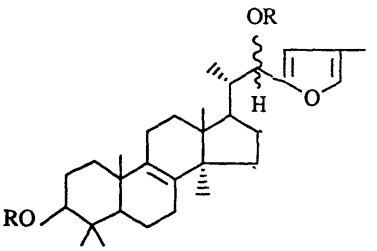


(XXV)

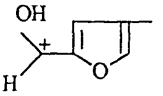


(XXVI)

The presence of a furan residue was confirmed from the absorption in the UV spectrum with λ_{max} at 234, 245, and 292 nm and by the absorptions in the IR spectrum at 1660 and 1600 cm^{-1}. The main fragment in the mass spectrum corresponds to cleavage of the C(20)–C(22) bond (*m/z* 109, 100%). The PMR spectrum of (XXVI) is characterised by signals due to the angular CH_3 groups at δ 0.81, 0.92, 1.05, 1.07, and 1.1 ppm and the one secondary CH_3 group as a doublet at δ 1.17 ppm, which is characteristic of a CH_3 group at C(21). The side chain exhibits the following signals: δ 2.07, 3.22 (1H dq., *J* 6.8, 10.5 Hz), 7.04 (1H, br. s.), and 7.35 (1H, br. s.), corresponding to the protons on C(27), C(20), C(24), and C(26). The signals that appear between δ 2.50 and 0.90 ppm correspond to the two methine protons and eight methylene protons (one of which is at an α-position relative to the carbonyl group at δ 2.45 ppm). With double resonance the symmetric quartet due to H(17) is converted to a triplet by irradiation on the H(20) nuclei at δ 3.22 ppm. This suggests that the coupling constant between H on C(16) and C(17) is of the same order as that between H on C(17) and C(20) and is consistent with the Karplus equation for structure (XXVI). At the same time the *J* values between the protons on C(20) and C(21) (6.8 Hz), C(24) and C(26) (9.9 Hz), C(16) and C(17) (10.0 Hz), C(17) and C(20) (10.5 Hz), and C(26) and C(27) (1.5 Hz) were determined. Thus, on the one hand, interaction between the protons on C(24), C(26), and C(27) is confirmed as is that between the proton on C(20) and the methine proton on H(17) and the protons on H(21), on the other hand. Compound (XXVI) was reduced with lithium aluminium hydride. The resulting 3,22-tetrahydropomacerone (XXVII) displayed signals in its PMR spectrum due to the furan protons at δ 6.10 and 7.15 ppm and at δ 3.20 and 4.72 ppm from the H(3) and H(22) protons that are geminal relative to both OH groups. These signals do not appear when lithium aluminium deuteride is used for reduction. Acetylation of derivative (XXVII) gave 3,22-diacetoxy-23,26-oxidolanosta-8(9),23,25-triene (XXVIII), in whose PMR spectrum the signals due to the H(24) and H(26) furan protons are shifted to δ 6.14 and 7.15 ppm while the signals from H(3) and H(22) occur at δ 4.55 and 5.84 ppm. The mass spectrum of (XXVIII) has a fragment with *m/z* 111 ($C_6H_7O_2$).



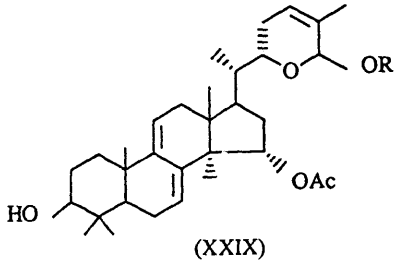
(XXVII), R = H;
(XXVIII), R = Ac



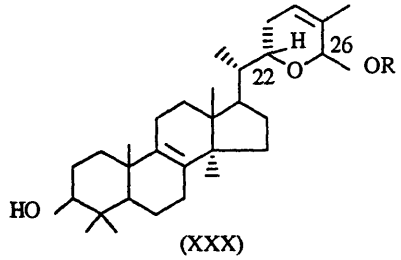
m/z 111

Triterpenoids with a six-membered hemiacetal residue in the side chain—the so-called perenniporiols—were first isolated from the mycelium of the higher fungi *Perennipria ochroleuca*. These compounds with the same structural characteristics as the group of nautral vitanolides[57–60] are of interest because of their high diverse biological activity. Vitanolides with a lanostane skeleton have been isolated in small quantities.[61,62] The structure and configuration of the diaxially interacting (22*S*,26*S*)-sites in (XXIX) have been established by comparision of the ^{13}C NMR spectroscopic data with the results of X-ray diffraction analysis, and the compound has been

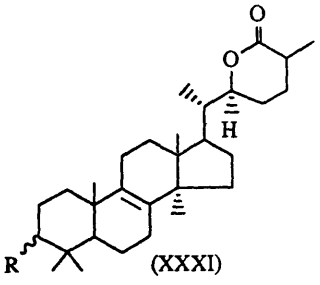
identified as (22*S*,26*S*)-15α-acetoxy-22,26-epoxy-3,26-dihydroxylanosta-7,9(11),24-triene (perenniporiol). The 15-desacetoxy-7,11-dihydroperenniporiol (XXX) was also isolated. The configuration of the lactol rings in both compounds was confirmed by comparison of the PMR spectroscopic data—the *J* values and position of the signals due to H(22) at δ 3.95 ppm (dd. *J* 12 and 2.5 Hz) and δ 5.16 ppm (d. *J* 4.9 Hz).



(XXIX)



(XXX)

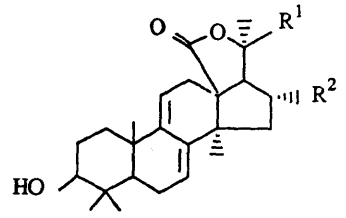


(XXXI)

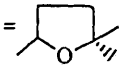
R = α-H, β-OH (a)
β-H; α-OH (b)

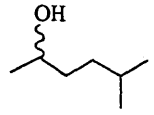
The δ-lactone astrahygrol (XXXI), which has a similar structure, was isolated from the fruit body of the fungus *Astraeus hygrometricus* (Pers) Morgan (*Gasteromycetes*), familiar in Chinese popular medicine as a haemostatic agent.[62] The presence of two secondary and five tertiary CH_3 groups in the PMR spectrum of the molecule of (XXXI) provided support for a lanostane skeleton, and the fragment with *m*/*z* 314, corresponding to loss of the side chain from the molecular ion in the mass spectrum confirmed the presence of a δ-lactone ring in the side chain. The ^{13}C NMR data attested to the presence of a double bond between rings. The structure of the side chain as a δ-lactone was also clearly demonstrated by the respective signals in the PMR spectrum—a single-proton doublet of doublets at δ 4.3 ppm with *J* 11.6 and 3.0 Hz due to the proton on C(22) proton, a single-proton doublet of quartets at δ 2.61 ppm with *J* 10 and 7 Hz due to H(25), and a single-proton doublet at δ 0.99 ppm with *J* 6.3 Hz due to H(21).

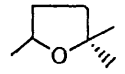
Triterpenoids with a 18,20-γ-lactone ring and a double bond at the 8(9)-position or double bonds at the 7(8)- and 9(11)-positions have been isolated from sea cucumbers (holothurians) as glycosides and consequently have been called holothurigenins or seychellogenins. In some cases they contain oxygen substituents at C(16), C(23), and other positions.[7,63–67] These compounds act as powerful growth inhibitors of pathogenic fungi and have significant carcinostatic activity.

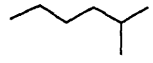


(XXXII)

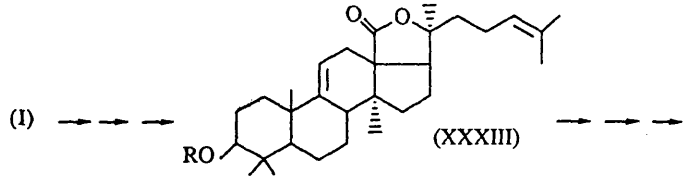
R^1 =  , R^2 = H, 17-desoxy-22,25-oxidoholothurinogenin;

R^1 =  , R^2 = OH, griseogenin;

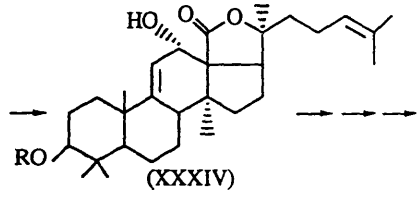
R^1 =  , R^2 = OH 22,25-oxidoholothurinogenin;

R^1 =  , R^2 = H seychellogenin

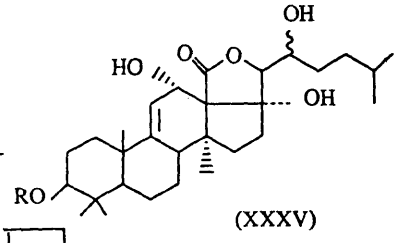
It is assumed that holothurinogenins are formed as a result of bioconversions involving the oxidation of lanosterol according to the scheme shown below. In the majority of cases the 8(9)-double bond of the precursors migrates to the 7(8)-position. Subsequent hydroxylation, acetylation, and saturation of the 24(25)-double bond gives a compound with the general formula (XXXIII). Oxidation of the side chain leads to derivatives (XXXIV)–(XXXVI), etc.



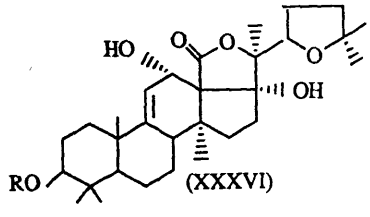
(XXXIII)



(XXXIV)



(XXXV)



(XXXVI)

Thus, it can be seen that natural sources provide a substantial number of compounds that are functionalised both on the lanostane skeleton and in the side chain of the molecule. The existing, generally fragmentary data on their biological activity, in particular on the medicinal properties of the plants and fungi containing these compounds that are frequently used in popular medicine, especially in countries of the East, suggest the possibility of finding interesting and promising drugs amongst them and their analogues. However, the "active principles" are present in extremely small quantities and sometimes undergo unwanted conversions during isolation. Therefore, the synthesis of these complex structures and their biological study have been and remain an important task.

III. Synthetic approaches to lanostane derivatives with a functionally substituted side chain

One of the possible courses in the modification of lanosterol aimed at yielding biologically active derivatives is the introduction of oxygen-containing substituents into the side chain. There are a number of examples in the literature on this type of approach.

The introduction of oxygen substituents into the lanosterol molecule has been carried out without disruption of the C(18)-side chain using the existing 24(25)-double bond of 3β-hydroxylanosta-8,24-diene (I). An alternative route is degradation of the side chain to C_2-C_4 and its reconstruction.

1. Partial conversions of the side chain of lanosterol

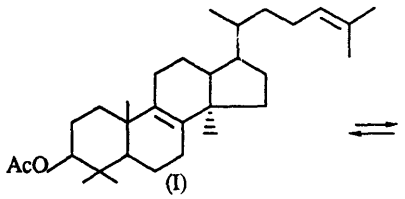
Oxidised sterols are potential inhibitors of the demethylation of lanosterol to cholesterol. It has been proposed that lanosterol derivatives with an oxidised side chain may be converted to metabolites that have the ability to inhibit the biosynthesis of cholesterol.[5,68] In order to study this problem, mono- and poly-oxidised derivatives of lanostane—22ξ-hydroxy-, 24-hydroxy-, 25-hydroxy-, and 26-hydroxy-lanosterols were synthesised and the following series of decreasing activity was drawn up: 26-hydroxy- > 25-hydroxy- > (24*R*)- and (24*S*)-hydroxy-24,25-dihydrolanosterol > (22*R*)- and (22*S*)-hydroxylanosterol.[5,68]

The synthesis of 25-alcohols is the simplest to carry out.[69] Several methods, such as direct hydration of the Δ^{24}-bond and the use of an intermediate 24,25-epoxide, have been developed.

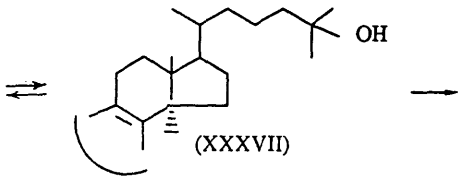
Hydration of the Δ^{24}-bond leading to 25-hydroxydihydrolanosterol was used by Rodewald and Jagodzinski[70–74] as a method for the synthesis of 25-alcohols and for selective protection of this bond for the isolation of analytically pure lanosterol from a mixture also containing dihydrolanoserol and dihydroagnosterol in a commercial product.

In fact, all methods for the isolation of pure lanosterol that were developed in the 1960s involve the selective addition of bromine to the side chain, crystallisation of the mxiture of bromides, and reduction of the resulting 24ξ,25-dibromo derivative with zinc in acetic acid to the 24-ene. These yield the required starting material in low yield. A method for selective hydration using a hydroxymercuration—demercuration reaction has been proposed. For this purpose a mixture was treated with mercuric acetate in a water–THF mixture[70] and the resulting organomercury compound was reduced with sodium borohydride. Separation on a silica gel column gave the analytically pure 25-alcohol (XXXVII) in quantitative yield. The Δ^{24}-bond may be regenerated as required by refluxing in a mixture of acetic anhydride and acetic acid. Thus, the total yield of pure 8,24-diene is more than 70% based on the commercial product. The same 25-alcohol (XXXVII) was obtained by low-temperature epoxidation of the Δ^{24}-bond, reduction with lithium aluminium hydride, and acetylation of the 3β-hydroxy group.

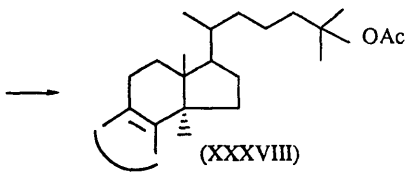
25-Hydroxylanosterol is itself of interest as a possible precursor of vitamin D analogue. The use of 25-hydroxylation as a means of protecting the double bond was investigated in the oxidation of the 8(9)-double bond of lanosterol to give seco derivatives.[71] It was shown that the alcohol is stable during oxidation with chromium trioxide and during alkali treatment. However, under acidic conditions dehydration in the side chain occurs. In order to prevent the occurrence of side reactions, the 25-hydroxy group in (XXXVIII) is acetylated with isoprenyl acetate. The 25-acetate is stable towards elimination in an acid medium.



(I)



(XXXVII)

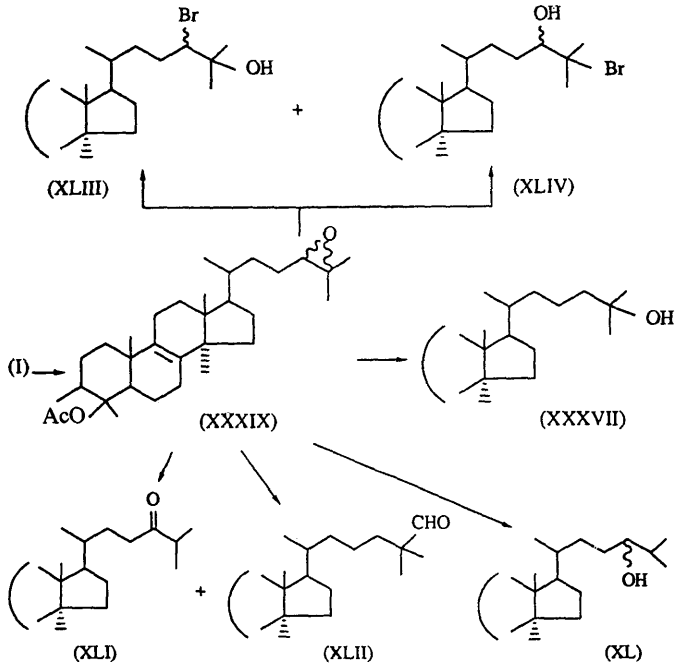


(XXXVIII)

The 25-alcohol is also formed on opening of the 24,25-epoxide (XXXIX) with HBr followed by removal of bromine. The absolute configuration of 24ξ,25-epoxylanostanes was established by converting them to the corresponding 24ξ-alcohols (XL) through reduction with diborane oxide and sodium borohydride, without affecting the C(24)–O bond. The configuration of the 24-alcohols was established by the method of Horeau.[75,76]

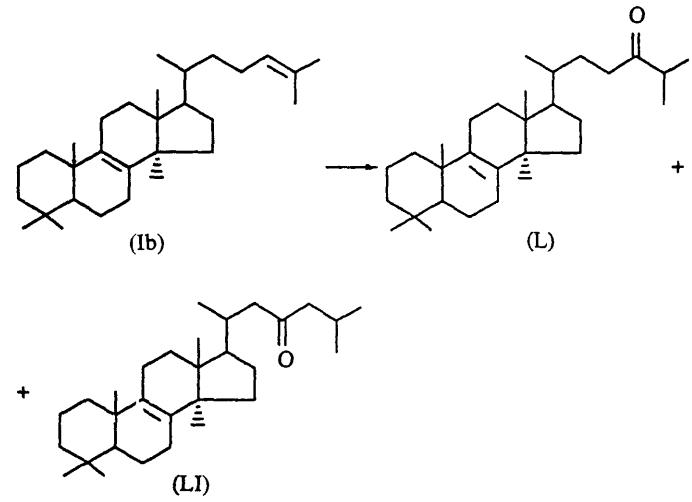
24-Hydroxy derivatives may also be obtained by isomerisation of the 24,25-epoxide on treatment with boron trifluoride etherate followed by reduction of the corresponding ketone (XLI).[77] However, in this reaction isomerisation of the oxide (XXXIX) to the

24-aldehyde (XLII) occurs together with formation of the 24-ketone (XLI).[77,78]

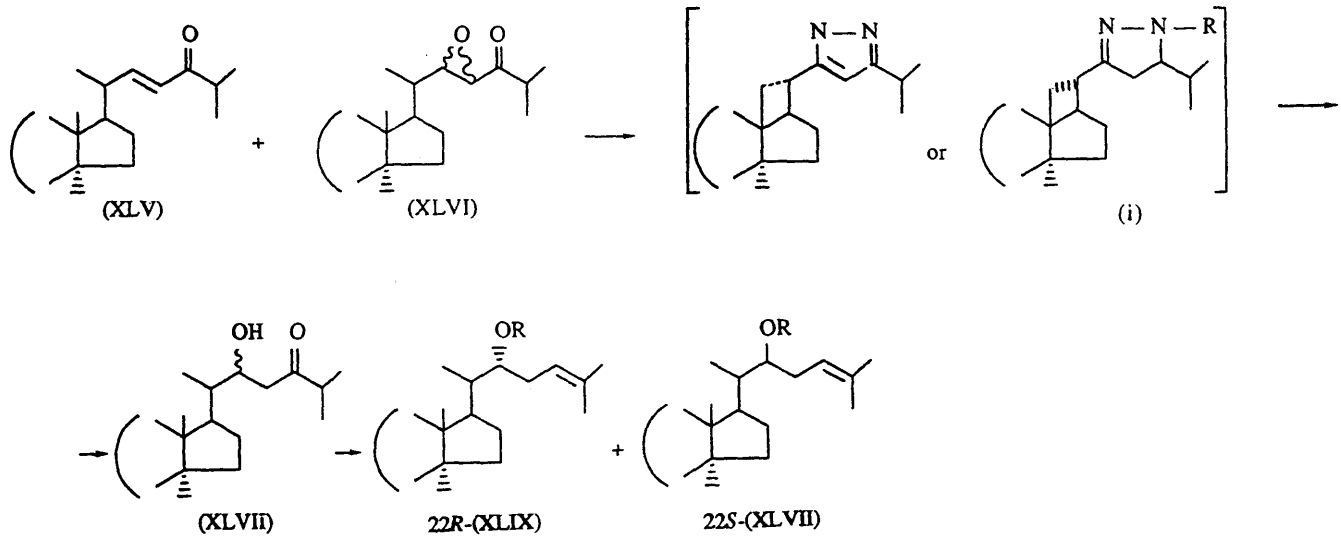


On dehydrogenation of the 24-ketone (XLI) using selenium dioxide,[77] the α,β-unsaturated 24-ketone (XLV) was obtained, albeit in low yield. It was epoxidised with hydrogen peroxide in an alkaline medium. The resulting predominant isomer of the 22,23-epoxyketone (XLVI), gave an intermediate of the type (i) when a Wolff–Kishner reduction was attempted, and this was then converted by decomposition of the diimide with alkali to give a mixture of C(22)-isomers of 22-hydroxy-24-ketosteroids (XLVII). Subsequent acetylation, reduction of the 24-keto group with sodium borohydride, dehydration on treatment with $POCl_3$, and hydrolysis gave (22*S*)- and (22*R*)-hydroxylanosterols (XLVIII) and (XLIX) in the ratio 2:1.[79]

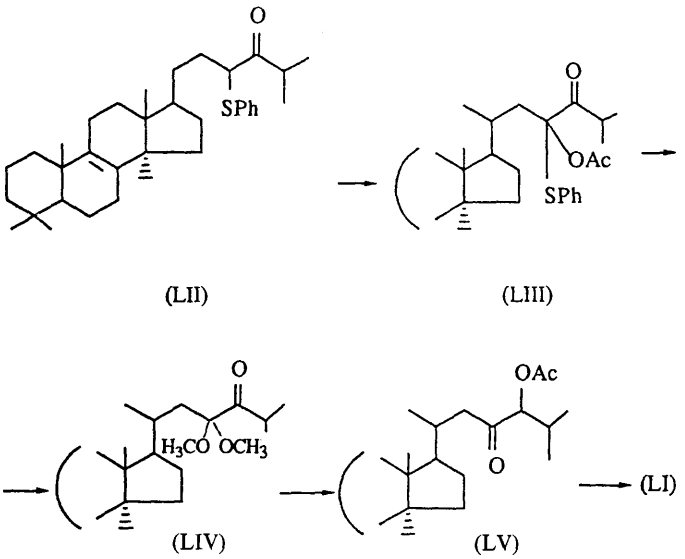
The 24-ketone of 3-desoxylanostane (L) was synthesised by Yamashita et al.[80] by hydroboration of the Δ^{24}-bond followed by oxidation of the resulting 24-alcohol. The authors found that, depending on the reaction conditions (hydroboration directly with diborane or with sodium borohydride in the presence of boron trifluoride etherate), very small quantities of the 23-derivative (LI) were formed together with the expected product. The mechanism of formation of 23-ketodihydro-3-desoxylanosterol (LI) is not clear; it was assumed to be a rearrangement product and it was detected using high-resolution liquid chromatography.



The presence of additional methyl groups at C(4) and C(14) in the lanostane skeleton compared to steroids results in a considerable steric effect on the reactivity of the α-carbon atoms relative to the 24-ketone in the side chain. The difficulty in enolisation at the C(23) position and its preferred route on C(25) has been attributed to this.[81] Numerous attempts to functionalise the 23-position of 24-keto-3-desoxylanostane proved unsuccessful. Regioselective sulphenylation at C(23) was achieved[82] in the case of the 24-ketolanostane (L) only under kinetically controlled conditions by the addition of (L), lithium isopropylamide, hexametapol, and THF



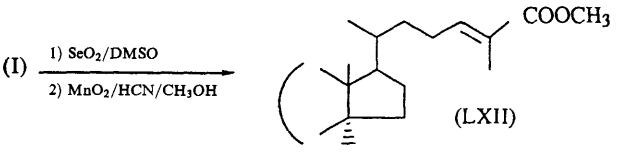
at −78 °C to a solution of diphenyl disulphide. The key sulphur-containing compound (LII) after treatment with lead tetraacetate was converted to a mixture of diastereomers at C(23) (LIII). Subsequent treatment with methanol and iodine gave the 23-dimethylacetal (LIV), and reduction of the 24-carbonyl group, removal of the acetal protecting group, and acetylation yielded the 24-acetoxy-23-ketone (LV). Hydrogenolysis of the 24-acetate using calcium in liquid ammonia gave the 23-ketolanostane (LI).



The successive introduction of hydroxy groups into the C(8)-side chain of lanosterol to obtain 26-hydroxy and 24,25,26-trihydroxy derivatives has been reported by Sato et al.[77,83] The 26-alcohol (LVI) was obtained by the allylic oxidation of lanosterol with selenium dioxide. Epoxidation of its acetoxy derivative (LVII) with peroxyacetic acid in the presence of concentrated sulphuric acid[84] gave the 24ξ,26-diacetoxy-25ξ-hydroxy derivative (LVIII), and hydrolysis of its acetoxy groups led to the formation of 24ξ,25ξ,26-trihydroxylanosterol (LIX). 24ξ,25-dihydroxylanosterol (LX) was obtained by reduction fo the 25-hydroxy-24-ketone (LXI) with sodium borohydride. The latter ketone was detected[77] amongst the products of the oxidation of lanosterol with the oxide system $KMnO_4-NaIO_4$. These polyoxidised lanosterol derivatives exhibited considerable anticholesterolemic activity.

The vicinal 24,25-diol (LX) is a convenient starting compound for the preparation of the 24-aldehyde, which is used to extend the side chain by the Wittig reaction.[85]

By applying more severe conditions in the allylic oxidation of lanosterol it is possible to obtain 26-acids of the polyporenic type (LXII).[4]



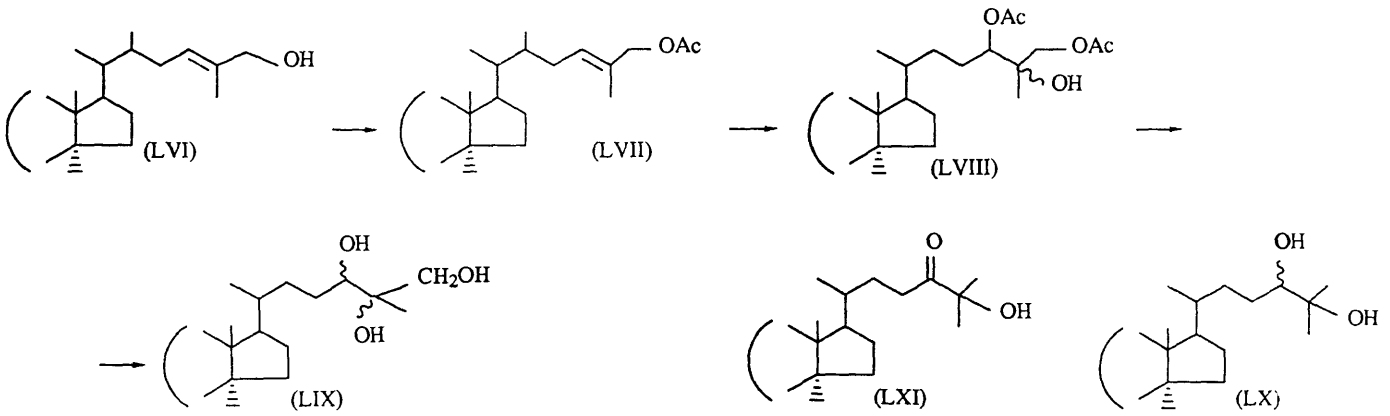
2. Chemical methods for degradation of the side chain of lanosterol

All the methods described in the literature for degradation of the side chain of lanosterol are essentially based on preparation of key 17(20)-, 20(22)-, and 22(23)-olefins. Their successive epoxidation, hydroxylation or direct ozonisation can give the required or intermediate epoxides, aldehydes or ketones (with a shortened side chain).

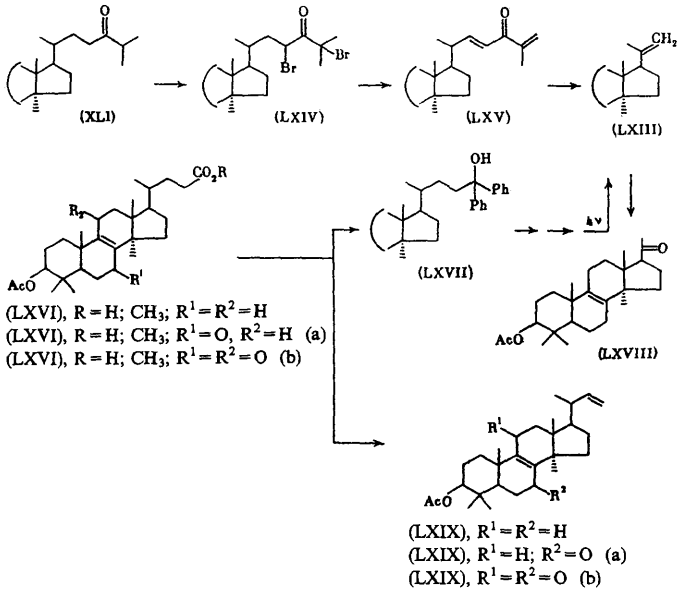
It should be noted straight away that degradation of the side chain of 3β-hydroxylanosta-8,24-diene is not always simple since by-products that are highly oxidised in the skeleton are often formed.

Several schemes for degradation of the side chain of lanosterol using chemical methods have been developed. These are all generally multistage processes and differ in the number of stages and chosen sequence of reactions, and the yields are low.

Thus, three main methods for the preparation of the 20(22)-olefin (LXIII) have been reported. The first (with the greatest number of stages and the least effective)[78] involves the bromination of the above-mentioned 24-ketolanosterol (XLI) to the dibromide (LXIV), its dehydrobromination, and subsequent irradiation. Another scheme[87] involves cleavage of the Δ^{24}-bond in lanosterol to the 24-acid (LXVI). Conversion of (LXVI) with phenylmagnesium bromide to the tertiary alcohol (LXVII), its subsequent isomerisation, and irradiation of the keto derivative afford (LXIII). The third,[88] most effective method of preparing the 20(22)-olefin (LXIII) involves the treatment of the 24-acid (LXVI) with carbonyldiimidazole followed by irradiation at λ_{max} 220 nm.[89]



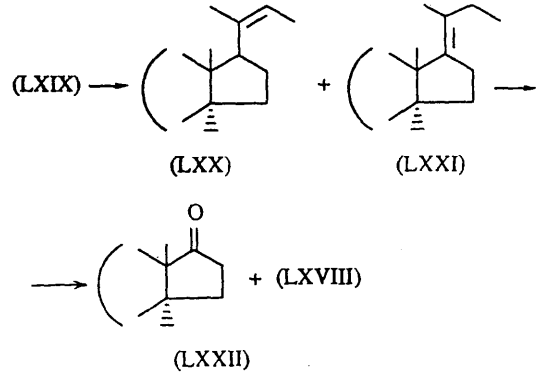
Hydroxylation of olefin (LXIII) accompanied by oxidation with periodic acid, gives the pregnenolone analogue (LXVIII) with a lanostane skeleton.[87]



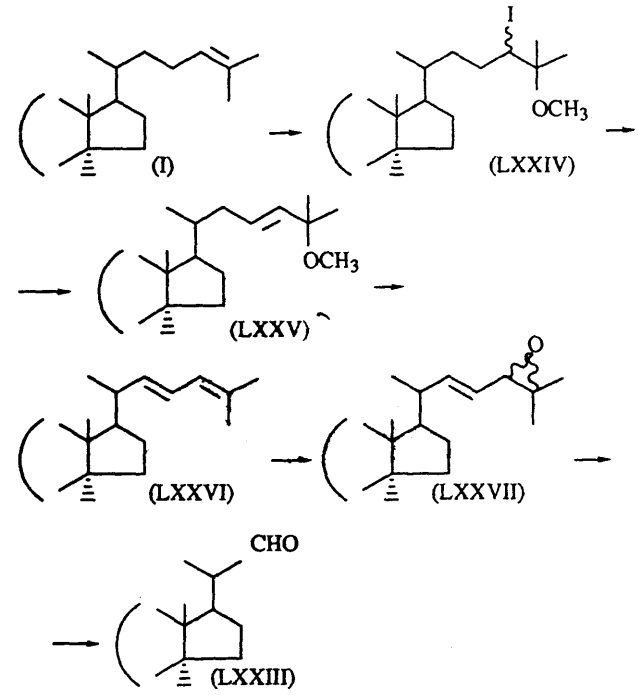
Key lanostane olefins with the double bond at a position other than 20(22) have been obtained by decarboxylation of the 24-acids. It was shown by Reshetova et al.[90] that the Δ^8-7-keto acid (LXVIa) and Δ^8-7,11-diketo acid (LXVIb) were formed in addition to the Δ^8-acid (LXVI) on oxidation of lanosterol by the method of Lumé–von Rudolf. Decarboxylation of these keto acids gave 24,25,26,27-tetranor-Δ^8-7-keto- and 24,25,26,27-tetranor-Δ^8-7,11-diketo-lanosta-8,22(23)-dienes (LXIX)–(LXIXb), which act as intermediates in the stereospecific introduction of oxygen functions into the lanosterol molecule.[91]

In two studies[77,92] the initially formed terminal 22(23)-olefin (LXIX) was isomerised on treatment with lithium in ethylenediamine to the 20(22)-olefin (LXX) and 17(20)-olefin (LXXI).

In most studies all of the olefins described were primarily used for preparing 17- or 20-ketolanostanes or aldehydes. However, ozonisation generally has low selectivity and gives mixtures of highly oxidised analogues of 17-ketones, 17-acids, etc.[77,92]



A more effective method than that of Sato and Sonoda[77] was degradation of the side chain of lanosterol to obtain the 22-aldehyde (LXXIII) by means of the electrophilic addition of methoxyiodide to the Δ^{24}-bond.[93] The subsequent elimination of hydriodic acid from (LXXIV) using potassium t-butoxide accompanied by the elimination of methanol on treatment with acetyl chloride and sodium iodide in a mixture of acetonitrile and methylene dichloride resulted in the formation of the 22,24-diene (LXXVI).[94] In a study of the ozonisation of this diene it was shown that both the C(22)- and C(24)-aldehydes are formed, with the latter in slight excess. Further ozonisation of the 24-aldehyde does not give the required 22-aldehyde. Consequently, the regioselective epoxidation of diene (LXXVI) was carried out with a complex of *m*-chloroperoxybenzoic acid and KF, which gave the 24,25ξ-monoepoxide (LXXVII). Ozonisation of the epoxyene (LXXVII) gave the 22-aldehyde (LXXIII) in high yield (~60%).



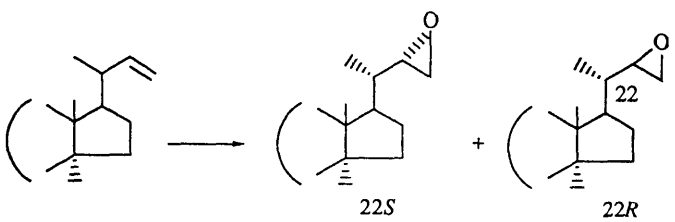
The lanostane derivatives with C_2- and C_3-side chains that are synthesised in this manner have been used in many studies in nucleophilic addition reactions to create novel polyfunctional lanosterol analogues.

3. Formation of oxygen-containing side chains in lanosterol

Many methods have been developed for the stereospecific building of polyfunctional side chains in steroid compounds.[95] However, as demonstrated in compounds simulating the *C/D* rings of lanostane,[96] these cannot be directly transferred and adapted to triterpenoids and 14α-methylsteroids, especially in those cases where the reactions occur in the vicinity of ring *D*, where the α-region is equally or more hindered than the β-region of the molecule. That is probably the reason for the comparatively small number of studies on building up the side chains. There are virtually no studies on the construction of side chains on 17-ketolanostanes

Methods for building the side chains of triterpenoids have been developed with terminal olefins[97] of the type (LXIX) and (LXIII), formed by decarboxylation of 24-acids (as described above), 20-ketones,[98] 22-aldehydes,[9,97] and 24-aldehydes[85,99] as starting materials.

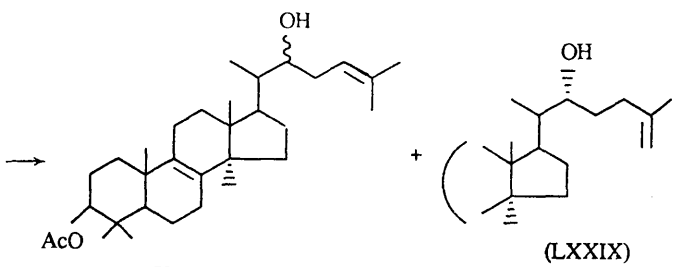
The strategy of Poyser et al.[97] for using 22,23-olefins involved their conversion to the corresponding epoxides and including the latter in a Grignard reaction with a suitable alkyl halide. However, it was demonstrated right at the beginning in studies on this route[97] that epoxidation with peroxyacids under normal conditions usually has an effect on the intraring 8(9)-double bond, with the result that a whole range of reaction by-products is formed. Therefore, the preparation of 22,23-epoxides (LXXVIII) was carried out via bromohydrins followed by dehydrobromination. This procedure, however, gave a mixture of isomeric (22*S*)- and (22*R*)-epoxides.



(LXIX) 22*S* (LXXVIII) 22*R*

Hence a Grignard reaction with isobutenylmagnesium bromide gave a mixture of (22*S*)- and (22*R*)-22-hydroxylanosterols (XLVIII) and (XLIX) that was difficult to separate. Furthermore, the terminal olefin (LXXIX) — a product of isomerisation of the double bond during reaction — was formed. An attempt to oxidise the mixture of 22-alcohols to the ketone followed by reduction with lithium aluminium hydride did not have favourable results.[97]

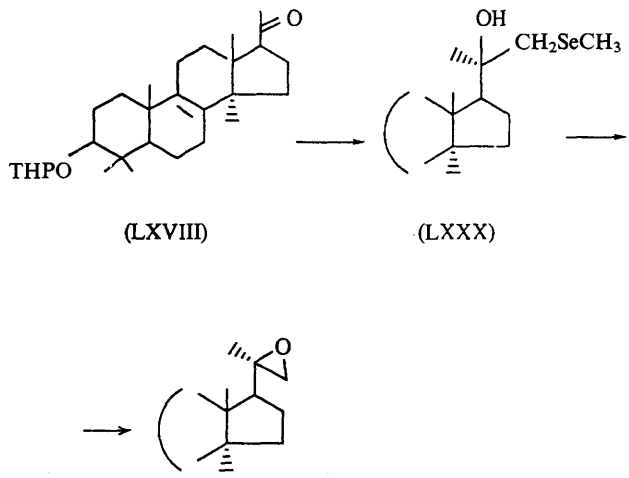
(LXXVIII) →



(XLVIII) + (XLIX) (LXXIX)

Epoxides are known to react with organomagnesium reagents in different ways. Depending on the nature of the reagents and the reaction conditions they give alcohols formed by nucleophilic ring opening (with no change in configuration, as described above) or rearranged alcohols formed by attack of the reagent on an aldehyde intermediate.

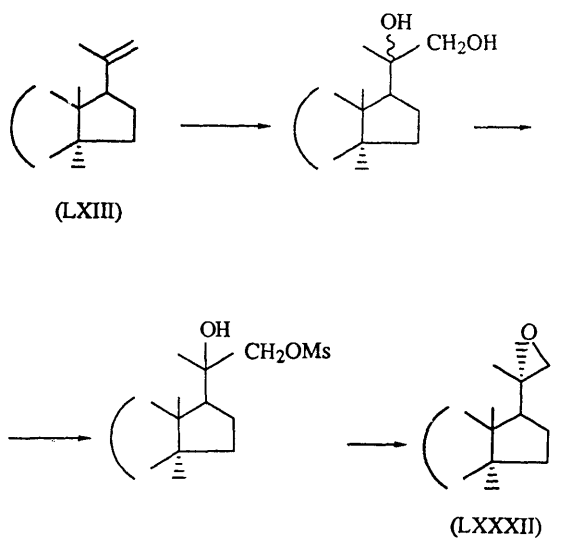
Thus, 22-hydroxy-substituted lanosterols may be obtained from 22-aldehydes that are formed, as we have described above, from a 20(22) olefin or during rearrangement of 20(22)-oxides. At the same time the conditions for stereospecific formation of a chiral centre at C(20) can be selected. The problem of stereoselective synthesis of lanostane 20(22)(*R*)- and (*S*)-epoxides was solved by Schauder and Krief[98] through the use of the reaction of 3-tetrahydropyranyloxy-20-ketolanostane (LXVIII) with methylselenomethyllithium. The resulting 20-alcohol (LXXX) on treatment with base gave the (20*R*)-epoxide (LXXXI) in 60% yield.



(LXVIII) (LXXX)

(LXXXI)

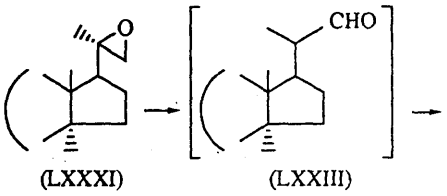
At the same time the (20*S*)-epoxide (LXXXII) was obtained from the 20(22)-olefin (LXIII) by hydroxylation of the latter with osmium tetroxide, mesylation of the 22-hydroxy group, and elimination of methanesulphonic acid on treatment with alkali:



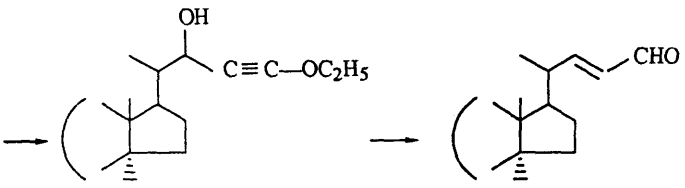
(LXIII) (LXXXII)

Schauder and Krief[98] made a detailed study of the synthesis of 22-alcohols that was stereoselective with respect to C(20) by varying the conditions of a Grignard reaction with ethoxyethynylmagnesium bromide. Moreover, this reagent was used instead of isobutenylmagnesium bromide so as to avoid the formation of regioisomeric by-products (with respect to the position of the double bond in the side chain). It was found that the solvent plays a decisive role in a controlled reaction of the magnesium salt with epoxides.

By conducting the reaction in ether at 20 °C, high yields of the acetylenic alcohol (LXXXIII) (via the 22-aldehyde) were achieved.



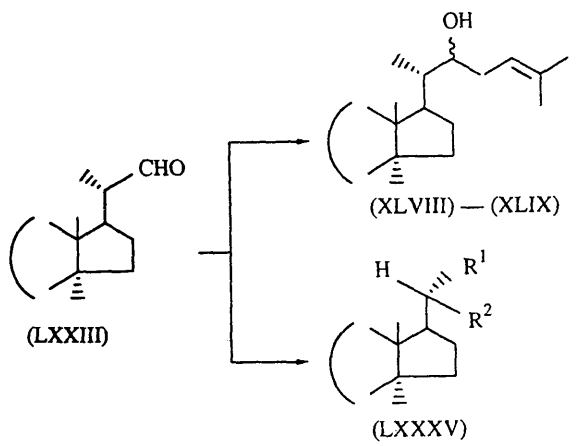
(LXXXI) (LXXIII)



(LXXXIII) (LXXXIV)

Reduction of the ynol ether (LXXXIII) with lithium aluminium hydride and subsequent acid hydrolysis of the resulting γ-hydroxy-enol ether gave the (*E*)-α,β-unsaturated aldehyde (LXXXIV), consisting mainly of the (20*R*)-isomer (98%), which is a precursor in the synthesis[98] of (20*R*)-lanosterol (after hydrogenation of the aldehyde and its Wittig reaction with isopropylidenetriphenylphosphorane). Schauder and Krief[98] obtained (20*S*)-lanosterol with the same sequence of reactions. This scheme appears to have realised its full potential in the synthesis of functional derivatives of (20*R*)- and (20*S*)-lanostane.

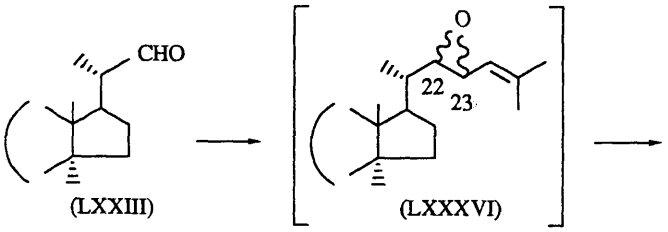
In order to build up the side chain, the 22-aldehyde may be obtained by ozonisation of the olefin or by hydroboration[99] followed by mild oxidation. The use of (LXXIII) in a Wittig reaction[99] or reaction with the Grignard reagent from 4-chloro-2-methylbut-2-ene provided the authors with novel functional lanostane side chains.



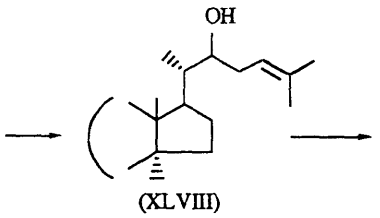
(LXXIII) (XLVIII) — (XLIX) (LXXXV)

$R^1 = CH_3$, $R^2 = C_6H_{11}$, CH_2OH, $CH=CH_2$, $(CH_2)_2CHO$, etc.

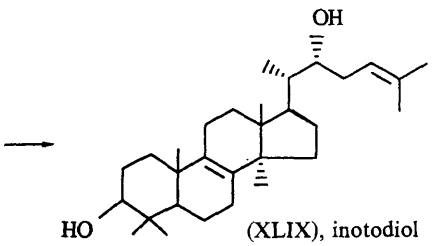
However, a detailed study[93] of the reaction conditions with the 22-aldehyde for formation of a 22-hydroxy-$\Delta^{24(25)}$ residue showed that neither a Grignard reagent nor a sulphur ylide can be used successfully. As was mentioned above, the dimethylallyl residue undergoes rearrangement. If an α-anion of a sulphone is condensed with aldehyde (LXXIII), a sulphinate residue is not eliminated in the latter. Amann et al.[93] solved this problem by using an arsenic ylide obtained from (3-methylbut-2-enyl)triphenylarsonium tetrafluoroborate[100] and n-butyllithium. Condensation of this ylide with the 22-aldehyde (LXXIII) gave the 22,23-epoxy-24(25)-ene intermediate (LXXXVI), and it was reduced with lithium triethylborohydride stereoselectively to give (22*S*)-22-hydroxylanosta-8,24-diene (XLVIII). In order to invert the 22*S* configuration to 22*R*, which is characteristic of the biologically active inotodiol, Amann et al. used the method of Corey—mesylation in pyridine followed by treatment with KO_2 and 18-crown-6 in a mixture of DMF and DMSO. Thus, the overall yield of inotodiol by this synthetic route was about 30%.



(LXXIII) (LXXXVI)



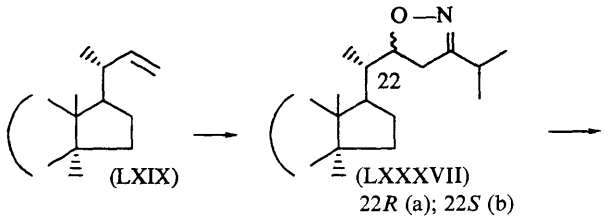
(XLVIII)

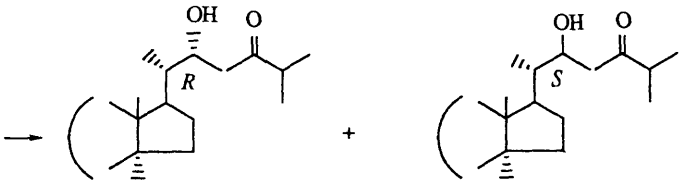


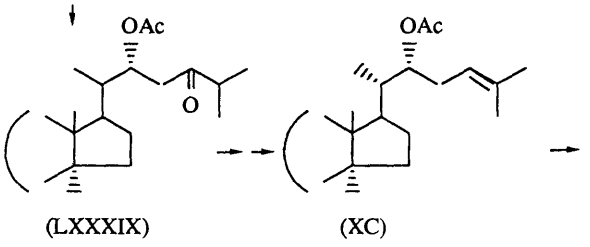
(XLIX), inotodiol

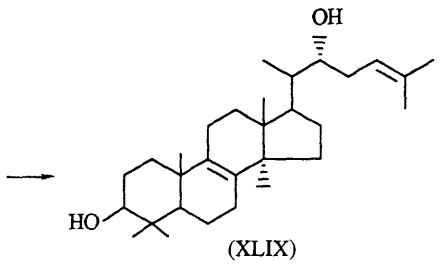
Key intermediates in the stereospecific introduction of oxygen functional groups into the C(22)-position of lanosterol were the 22(23)-terminal olefins (LXIXa, b), obtained by decarboxylation of lanostane 24-acids, by involving them in a 1,3-dipolar cycloaddition reaction.[101,102] Cleavage of the isopropylisoxazolinolanostanes (LXXXVIIa, b) in an atmosphere of hydrogen in the presence of boric acid after resolution of the 22-epimers followed by acetylation provided a route to (22*R*)-3β,22-diacetoxylanost-8-en-24-one (LXXXIX). This isomer was successfully used in a highly effective novel stereoselective synthesis of inotodiol (XLIX),[101–103] which differs from that described above by virtue of its simple operation, greater accessibility of reactants, and lower number of stages. The

yield of required product was about 26% and could be increased if the Corey isomerisation of the (22*S*)-isomer was used.[93]



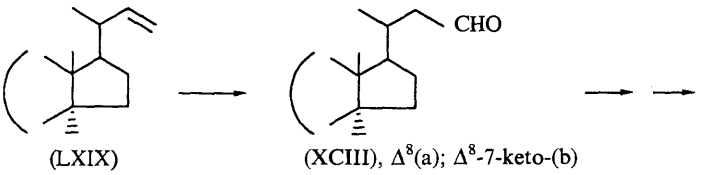


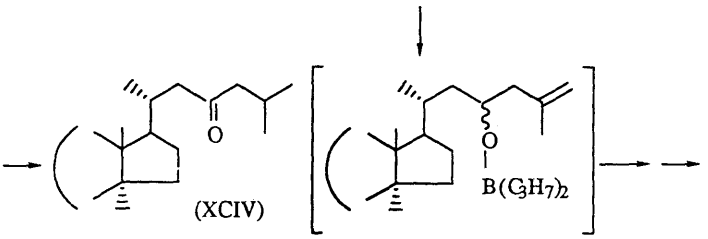


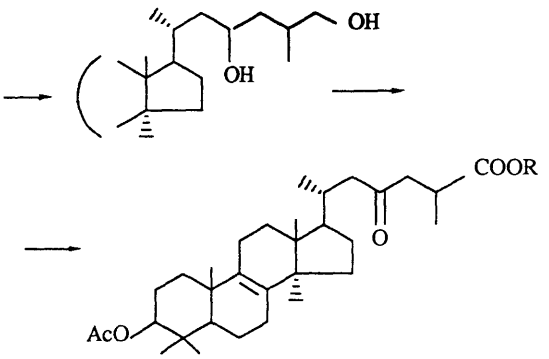


Use of the same diacetate (LXXXIX) in a Reformatsky reaction with ethyl bromoacetate followed by dehydration gave the δ-lactone of (22*R*)-3β-acetoxy-22-hydroxylanosta-8,24(31)-dien-32-oic acid (XCII), which was the first lanostane analogue of the sex hormone of *Achlya* marine fungi[101]

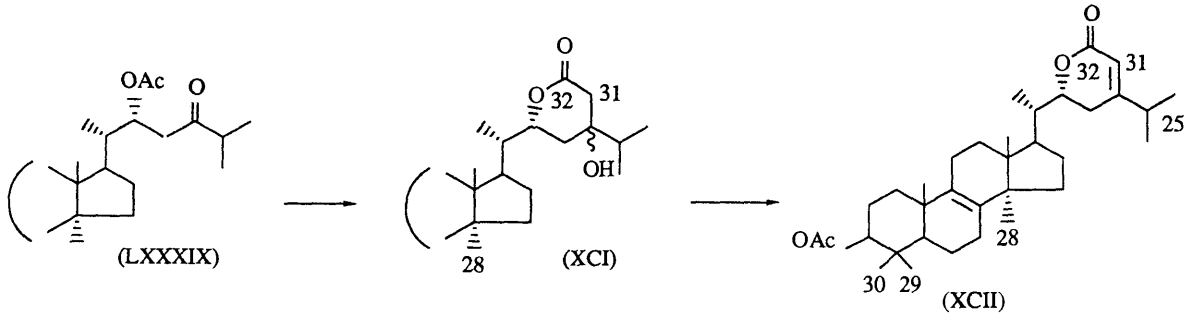
Conversion of 22(23)-olefins to 23-aldehydes (XCIIIa, b) by hydroboration[91] followed by oxidation made the 23-aldehyde (XCIIIa) a convenient starting material for the synthesis of 23-keto-lanostanes (potential cardiotonics) (XCIV).[102] The first two-stage synthesis of 3β-acetoxylanost-8-en-23-keto-24-oic acid (XCV)—a ganoderic acid analogue—was achieved by reaction of allylborane with the 23-aldehyde (XCIIIa) together with the subsequent hydroboration and oxidation in a single stage.[91]





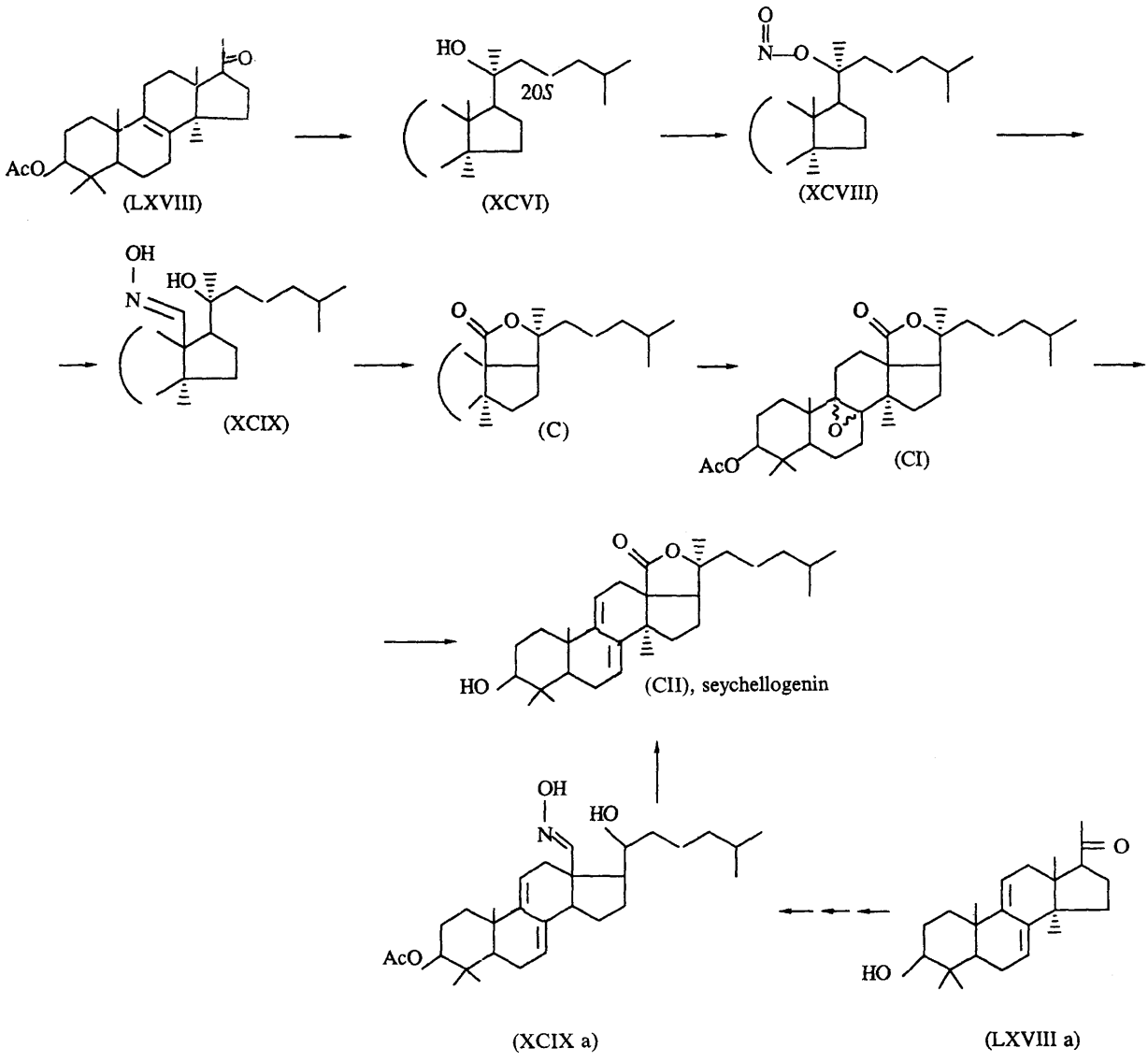


Seychellogenins have various useful biological properties. In view of their limited availability from natural sources, considerable attention has been given to their synthesis. After methods had been developed for dehydrating the side chain of lanosterol and converting it to the 20-ketone (LXVIII),[78] attempts to functionalise the 18-methyl group were initiated. The original scheme for the

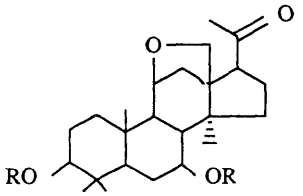


synthesis of seychellogenin[104] involved conversion of the 20-ketone (LXVIII) by a Grignard reaction with isohexylmagnesium bromide to give (20*S*)-dihydrolanost-8-ene, which was converted on treatment with nitrosyl chloride to the nitroso derivative (XCVIII). Photoisomerisation of the latter to the oxime (XCIX) occurred with a yield of 8%, and this governed the low overall yield of (CII) (2%), which included oxidation to the γ-lactone (C), epoxidation of the interring double bond, and acid hydrolysis of the 8,9-epoxide (CI) to the 7(8),9(11)-diene system of (CII). A variant of this scheme used the 20-ketone of 3-hydroxylanosta-7,9-diene (LXVIIIa) as a starting compound.

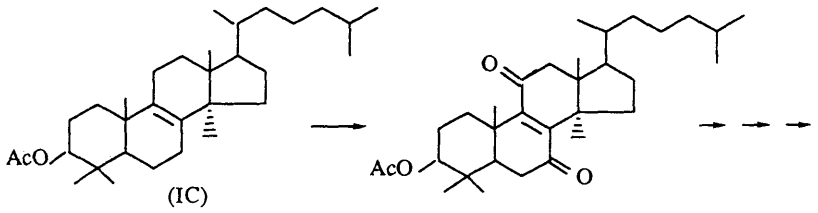
The aim of the second, fundamentally different approach[6,105] was to improve the yield of the required seychellogenin (CII). At the first stage of the synthesis, commercial lanosterol containing a certain amount of 24,25-dihydrolanosterol was hydrated, and pure dihydrolanosterol (IC) was thus obtained. After oxidation of the allylic methylene groups in the rings at C(7) and C(11) with chromium trioxide, the central double bond was reduced using zinc in acetic acid. Further reduction with lithium aluminium hydride followed by selective acetylation gave the 3,7-diacetoxy-11-hydroxylanostane (CIII), which was converted by photoreaction with lead tetraacetate in the presence of iodine to the cyclic ether (CIV). Cleavage of the latter with boron trifluoride etherate in anhydrous acetic acid, hydrolysis with KOH, and hydrogenation of the 9(11)-double bond gave the compound (CVI) with the required *trans* linkage of the *B*/*C* rings. An important subsequent feature was selective acetylation, so that the hydroxyl group at C(18) would remain free. After this problem was solved and (CVII) was obtained, a photoreaction was carried out under the conditions described above to give the cyclic ether (CVIII), oxidation of which with ruthenium tetroxide, hydrolysis, and further selective acetylation gave compound (CX). After dehydration and oxidative introduction of the diene system using mercuric acetate, the acetate of seychellogenin (CII) was obtained in satisfactory yield. The authors of the above synthesis of seychellogenin believe that the 20-ketone having the structure (CXII) would be an excellent precursor in the



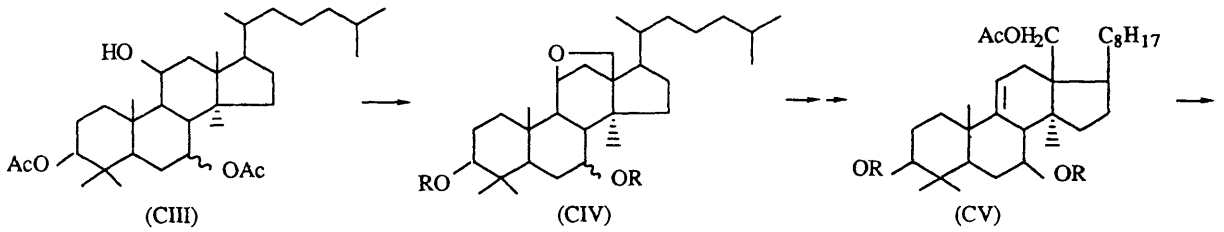
synthesis of other holothurigenins. It is simple to obtain by a combination of the two synthetic methods[104,105] with degradation of the side chain of lanosterol.



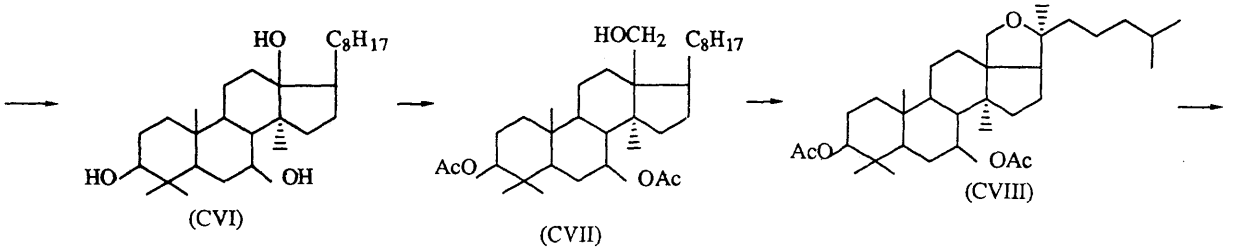
(CXII), R = Ac



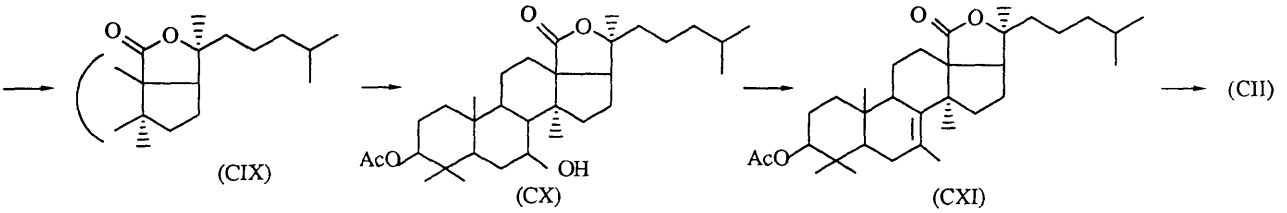
(IC)



(CIII) (CIV) (CV)



(CVI) (CVII) (CVIII)



(CIX) (CX) (CXI)

The molecule of (CXII) can be converted to the 17α-hydroxy derivative as well as to a compound with a natural 9(11)-double bond after cleavage of the cyclic ether. Although most of the intermediates in these syntheses were converted to hemisuccinates in order to impart greater solubility to these molecules in water, not one of the derivatives exhibited the same degree of activity (toxicity) as the natrual glycosides.[7] Habermehl and Kirsch[5] proposed in future to modify the molecule of natural seychellogenin in this manner in order to study the structure–function relationship.

Thus, it may be concluded from an analysis of the literature that nature has an abundance of various polyfunctional lanosterol derivatives that possess therapeutic properties that are useful for human medicine. Lanosterol itself is an inexpensive, available product that is isolated from the wool "suint" together with cholesterol. This makes it an attractive source in the preparation of synthetic triterpenoids and steroids having hydrophobic alkyl groups in the molecule which play an important part in the interaction with receptors. Therefore considerable opportunities are being opened up in the chemistry of lanosterol for research both into novel reactions and in the application of established methods in steroid chemistry for deriving biologically active polyfunctional structures.

References

1. L Ruzicka, R Denss, O Ieger *Helv. Chim. Acta,* 1945, **28** 759
2. P P Boiteau, R Ratsimamanga *Triterpenoides en Physiologie Vegetable et Animale,* Gauthier-Villars, Paris, 1964
3. P Pant, R P Rastogi *Phytochemistry,* 1979, **18** 1095
4. I G Reshetova *Antibiotiki,* 1979, **18** 1095
5. C G Habermehl, I N Kirsch *Toxicon,* 1983, **3** 179
6. V A Stonik, G V Elyakov *Bioorg. Marine Chem.,* 1988, **2** 60
7. Y Sonoda, Y Sato *Chem. Pharm. Bull.,* 1983, **31** 1698
8. A V Kamernitskii, I G Reshetova, S V Chernov *Khim.-farm. Zh.,* 1987, **10** 1239
9. Z Paryzek, R Wydra *Can. J. Chem.,* 1985, **63** 1280
10. N Entwistle, A D Pratt *Tetrahedron,* 1968, **24** 3949
11. N Entwistle, A D Pratt *Tetrahedron,* 1969, **25** 1449
12. N Entwistle, A D Pratt *J. Chem. Soc.,* 1973, 1235
13. N Entwistle, A D Pratt *Phytochemistry,* 1976, **15** 1782
14. T G Halsall, G C Sayer *J. Chem. Soc.,* 1959, 2031
15. F G Hirtzbach, G Ourisson *C. R. Seances Acad. Sci., Ser. C,* 1971, **273** 1448
16. D M Piatak, K A Reimann *Tetrahedron Lett.,* 1972, 4525
17. K Kahlos, R Hiltunen, M V Schants *Planta Medica,* 1984, 197
18. A K Batta, S Rangaswami *J. Chem. Soc., Perkin Trans 1,* 1975, 451
19. K Kahlos *Acta Pharm. Fennica,* 1986, **95** 113
20. J F Grova *Phytochemistry,* 1984, **23** 1721
21. M B Gewall, M Haltori, Y Tezuka, et al. *Phytochemistry,* 1990, **29** 1625
22. M Ikeda, et al. *Chem. Abs.,* 1979, **90** 204294
23. A M Lobo, P M De Abreu, et al. *Tetrahedron Lett.,* 1985, **26** 2589
24. Y Lee Seung, M Rhee Hee *Chem. Pharm. Bull.,* 1990, **38** 1359
25. T Nishitoba, K Oda, et al. *Agric. Biol. Chem.,* 1988, **52** 367
26. T Nishitoba, H Sato, K Oda, et al. *Agric. Biol. Chem.,* 1988, **52** 211
27. J Dillon, K Nakanishi *J. Am. Chem. Soc.,* 1975, **97** 5417
28. T G Halsall, R Hodges, G C Sayer *J. Chem. Soc.,* 1959, 2036
29. L Canonica, E Fedili, A Fiecchi *Gazz. Chim. Ital.,* 1959, 818
30. C G Anderson, W W Epstein, G V Lear *Phytochemistry,* 1972, **11** 2847
31. I H Kaise, K Munakata *Tetrahedron Lett.,* 1972, 3789
32. H K Adam, T A Bryce, I M Campbell, et al. *Tetrahedron Lett.,* 1967, 1461
33. L Tiasen, H Meifen *Chem. Abs.,* 1984, **101** 3913
34. X A Dominguez, R Franco, et al. *Chem. Abs.,* 1984, **100** 39495y
35. T Nishitoba, S Goto, H Sato, et al. *Phytochemistry,* 1989, **28** 193
36. M Hirotani, I Itsaka, C Ino, et al. *Phytochemistry,* 1987, **26** 2797
37. A Morigava, K Kitabatake, Y Fujimoto, et al. *Chem. Pharm. Bull.,* 1986, **34** 3025
38. I J Lin, M S Shiad, S F Yhr *J. Nat. Prod.-Lloydia,* 1988, **51** 918
39. J O Toth, B Luu, J P Beck, et al. *J. Chem. Res. (S),* 1983, 299; *Chem. Abs.,* 1984, **100** 117512t
40. M Hirotani, C Ino, T Furuya, et al. *Chem. Pharm. Bull.,* 1986, **34** 2282
41. T Kikuchi, S Matsuda, S Kadota, et al. *Chem. Pharm. Bull.,* 1985, **33** 2624
42. T Kikuchi, S Kanoni, Y Murai, et al. *Chem. Pharm. Bull.,* 1986, **34** 4018
43. T Kikuchi, S Kanoni, S Kadota, et al. *Chem. Pharm. Bull.,* 1986, **34** 3695
44. Y Komoda, H Nakamura, et al. *Chem. Pharm. Bull.,* 1985, **33** 4829
45. T Nishitoba, H Sato, D Sakamura *Phytochemistry,* 1987, **26** 1777
46. R C Cambie, R N Duve, J C Parnell *Chem. Abs.,* 1972, **77** 126887
47. B Bila, A Kilonda, S Toppet et al. *Tetrahedron,* 1989, **45** 5907
48. A G Gonzalez, M Cortes, L E Suares *Anal. Quim.,* 1973, **69** 817
49. F T Bond, D S Fullerton, et al. *J. Am. Chem. Soc.,* 1966, **88** 3832
50. S Matsunaga, I Okada, S Uyeo *J. Chem. Soc., Chem. Commun.,* 1965, 525
51. T P Kutney, N D Westcott *Tetrahedron Lett.,* 1971, 3463
52. A Kanematsu, S Natori *Chem. Pharm. Bull.,* 1972, **20** 1993
53. M De Bernardi, G Fronza, M P Gianotti, et al. *Tetrahedron Lett.,* 1983, **24** 1635
54. A M Lobo, P De Abreu, S Prabhakar, et al. *Tetrahedron Lett.,* 1983, **24** 2205
55. K K Purushohaman, A Sarada, A Saraswathy *Can. J. Chem.,* 1987, **65** 150
56. A G Gonzalez, J Bermejo, M J Mediavilla, et al. *Heterocycles,* 1990, **31** 841
57. A V Kamernitskii, I G Reshetova *Khim. Prir. Soedin.,* 1977, **2** 156
58. R M Tursunova, V A Maselnnikov, N K Abubakirov *Khim. Prir. Soedin.,* 1977, **2** 147
59. E Glotter, I Kirson, D Lavie *Bioorg. Chem.,* 1978, 57
60. I Kirson, E Glotter *J Nat. Prod.,* 1981, **44** 633
61. M Hirotani, Ch Ino, T Furuya, et al. *Phytochemistry,* 1984, **23** 1129
62. Y Takaishi, Y Murakami, T Ohashi, et al. *Phytochemistry,* 1987, **26** 2341
63. B W Halstead *2. Poisonous and Venomous Marine Animals of the World,* US Printing Office, Washington, 1965, Vol. 1, p. 570
64. I Kitagawa, T Sugawara, I Yosioka *Tetrahedron Lett.,* 1974, **47** 4111
65. K F Nigrelli, T D Sullivan, K T Ladne *Zoologica,* 1955, **40** 49; *J. Am. Chem. Soc.,* 1969, **91** 4918
66. T Miyamoto, K Togawa, R Higuchi, et al. *Liebigs Ann. Chem.,* 1990, 39
67. T Miyamoto, K Togawa, R Higuchi, et al. *Liebigs Ann. Chem.,* 1990, 453
68. Y Sonoda, Y Sato, Y Sekigawa *Chem. Pharm. Bull.,* 1988, **36** 966
69. R B Boar, D A Lewis, J F McGhie *J. Chem. Soc., Perkin. Trans. 1,* 1972, 2231
70. M Morisaki, T R Lightbourn, N Ikekawa *Chem. Pharm. Bull.,* 1973, **21** 457
71. W J Rodewald, J J Jagodzinski *Pol. J. Chem.,* 1981, **55** 1751
72. W J Rodewald, J J Jagodzinski *Pol. J. Chem.,* 1979, **53** 1203
73. W J Rodewald, J J Jagodzinski *Pol. J. Chem.,* 1978, **52** 2473
74. W J Rodewald, J J Jagodzinski *Pol. J. Chem.,* 1979, **53** 2529
75. A Horeau *Tetrahedron Lett.,* 1961, 506
76. D E Barenkow, J H Cardellina II *Tetrahedron Lett.,* 1989, **30** 3629

77. Y Sato, Y Sonoda *Chem. Pharm. Bull.*, 1981, **29** 356
78. F Fetizon, F J Kakis, V Ignatadou et al. *J. Org. Chem.*, 1974, **39** 1959
79. Y Sonoda, Y Sato *Chem. Pharm. Bull.*, 1983, **31** 907
80. M Yamashita, M Naora, T Murae, et al. *Bull. Chem. Soc. Jpn.*, 1987, **60** 1383
81. K Namikawa, T Murae, T Takahashi *Chem. Lett.*, 1981, **6** 733
82. B M Trost *Chem. Rev.*, 1978, **78** 363
83. Japanese P. 61 172 895; *Chem. Abs.*, 1987, **106** 84908v
84. F Nictra, F Ronchetti, G Russo *J. Labelled Compd. Radiopharm.*, 1978, **14** 541
85. Y Sato, Y Sonoda *Chem. Pharm. Bull.*, 1984, **32** 1912
86. J O Toth, B Luu, G Ourisson *Tetrahedron Lett.*, 1983, **24** 1081
87. M Fetizon, F T Kakis, Ragoussis *J. Org. Chem.*, 1973, **38** 4308
88. F J Kakis, D Brase, A Oshima *J. Org. Chem.*, 1971, **36** 4117
89. S Iwasaki *Helv. Chim. Acta*, 1976, **59** 2753
90. I G Reshetova, R K Tkhaper, A V Kamernitskii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 687
91. R K Tkhaper, Dissertation for Doctorate in Organic Chemistry, Moscow, 1991
92. W Kreiser, W Ulrich *Liebigs Ann. Chem.*, 1976, 1199
93. A Amann, G Ourisson, B Luu *Synthesis*, 1987, 696
94. P Bisseck, G Charles *Tetrahedron Lett.*, 1983, 4223
95. A V Kamernitskii, I G Reshetova, E Yu Chernoburova *Khim. Prir. Soedin.*, 1988, **13** 3
96. Wu-Yi Wang, W Reusch *Tetrahedron*, 1988, **44** 1007
97. J P Poyser, F R Hirtzbach, G Ourisson *Tetrahedron*, 1974, **30** 977
98. J R Schauder, A Krief *Tetrahedron Lett.*, 1982, 4389
99. M Herin, P Delbar, J Remion, et al. *Tetrahedron Lett.*, 1979, 3107
100. E N Dianova, E I Zabotina *Usp. Khim.*, 1991, **60**(3) 317 [English translation in *Russ. Chem. Rev.*, 1991(3)]
101. R K Tkhaper, I G Reshetova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 969
102. S V Lindeman, M S Alexanyan, Yu T Struchkov, R K Thaper *Acta Crystallogr., Sect. C*, 1991, **47** 91
103. R K Tkhaper, I G Reshetova, A V Kamernitskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2654
104. G G Habermehl, K H Seib *Naturwissenschaften*, 1978, **65** 155
105. G G Habermehl, J H Kirsch, K J Rebstein *Heterocycles*, 1982, **17** 183

Received 24th December 1991

Translated from *Uspekhi Khimii* **61** 1601–1622 (1992) U.D.C. 535.34:543.424:536.7:546.776'311.786'311

Structural features and spectroscopic and energy characteristics of alkali metal molybdates and tungstates

V V Fomichev, M E Poloznikova, O I Kondratov
Institute of Fine Chemical Technology, Moscow

ABSTRACT. The results of X-ray structural, i.r. and Raman spectroscopic, and thermodynamic studies of alkali metal molybdates and tungstates $A_2M_nO_{3n+1}$ (A = Li, Na, K, Rb, Cs; M = Mo, W) are reviewed and analysed. The dependence of the vibrational spectra, activation energies, and crystal lattice energies on features of the structures of these compounds is discussed.

The bibliography comprises 51 references.

Contents

I.	Introduction	877
II.	Crystal chemistry of the alkali metal molybdates and tungstages	877
III.	Vibrational spectra	879
IV.	Stability of the crystals	886

I. Introduction

In recent decades there has been increased interest in the study of molybdates and tungstates of various compositions. The range of compounds whose structures have been determined using precision techniques has expanded considerably. It has been found that molybdates and tungstates can form a large number of fundamentally different structures, the number of structure types running to dozens. Molybdenum and tungsten have the ability to form various oxygen coordination polyhedra which have a tendency to condensation at appropriate cation ratios.

The general crystal-chemical principles of molybdates and tungstates are set out in two monographs[1,2] but there is not a great deal of discussion of the alkali metal compounds.

There are many publications devoted to studies of molybdates and tungstates by vibrational spectroscopic methods (i.r. and spontaneous Raman).[3–5] However no serious attempts have so far been made to collect together the available data and to review them together with X-ray structural data.

The present work aims to fill this gap. We have interpreted the vibrational spectra of the alkali metal molybdates and tungstates on the basis of an analysis of their crystal structures and proposed explanations for the variation in the spectroscopic and thermodynamic characteristics along this series of compounds. However information on the thermodynamics of molybdates and tungstates is disconnected and very meagre. Some values (atomisation energies and crystal lattice energies) have been calculated by the authors using known experimental data. Such information, and to such an extent, is not present in any of the available publications.

The compounds under discussion have structures with discrete tetrahedral or octahedral oxygen coordination polyhedra and also various types of linking of these to form chain or block structures. However alkali metal cations introduce very small perturbations into the energetics of molybdenum-oxygen or tungsten-oxygen ensembles compared to the cations of other elements. There is no mixing of the vibrations of the cationic sublattices with the vibrations of the molybdenum-oxygen or tungsten-oxygen systems. Lithium compounds form an exception. The frequencies of lithium cation vibrations appear in the deformation region of the oxygen polyhedra but they can be fairly safely distinguished in experiments using specimens in which the lithium is isotopically substituted ($^6Li-^7Li$).

Thus structural features of the molybdenum-oxygen and tungsten-oxygen systems and the type of interatomic interactions in them are controlling factors affecting the energy characteristics (vibration frequencies, thermodnamic values) of the molybdates and tungstates under discussion. The correlations obtained for them can be used successfully to interpret the results of studies of molybdates and tungstates of elements which form stronger cation–oxygen bonds with appreciable covalent contributions.

II. Crystal chemistry of the alkali metal molybdates and tungstates

Alkali metal molybdates and tungstates can be divided into four structural series depending on the types of molybdenum-oxygen and tungsten-oxygen polyhedra and the way in which they are joined together:[1]

structures with isolated tetrahedral MO_4 anions;

structures with chain-type anions composed of MO_4 tetrahedra (or MO_5 pyramids) and MO_6 octahedra;

polygon-network structures based on MO_6 octahedra sharing corners;

block structures formed by MO_6 octahedra sharing edges.

The first series comprises compounds with the general formula A_2MO_4 (A = Li, Na, K, Rb, Cs; M = Mo, W) in which the $MO_3:A_2O$ ratio is equal to one. They have structures formed by isolated MO_4 tetrahedra. The type of coordination polyhedron of the alkali metal depends on its ionic radius and varies along the series from lithium to caesium as the coordination number (CN) of the cation A increases from 4 to 10 (Table 1).

For example, in the structures of Li_2MoO_4 and Li_2WO_4 [6,7] the lithium has close tetrahedral coordination (hexagonal phenacite Be_2SiO_4 structure type[7]). On moving to Na_2MoO_4 and Na_2WO_4 [8,9] a spinel structure with octahedral coordination of the sodium cations by oxygen is found. As the size of the alkali metal cation increases further its CN rises to 8 in K_2MoO_4 and K_2WO_4, and also in

Rb_2MoO_4 and Rb_2WO_4 [10,11] while caesium, the largest cation in this series, has two types of coordination polyhedra, with CN's of 6 and 10, in Cs_2MoO_4 and Cs_2WO_4.[12]

Table 1. Changes in structural features in the alkali metal molybdates and tungstate series.

Compound	Structural series	Space group	Z	CN_A	r_{A-O}	CN_M	r_{M-O}*	Refs.
Li_2MoO_4	structure with tetrahedral MO_4^{2-} complexes	$R\bar{3}$	6	4				[7]
Li_2WO_4	ditto	$R\bar{3}$	6	4	1.96(8)	4	1.79(8)	[6]
Na_2MoO_4	»	$Fd3m$	8	6				[8]
Na_2WO_4	»	$Fd3m$	8	6	2.378(8)	4	1.819(8)	[9]
K_2MoO_4	»	$C2/m$	4	8	2.74(1)–3.21(1)	4	1.76(1)	[10, 11]
K_2WO_4	»	$C2/m$	4	8				[10, 11]
Rb_2MoO_4	»	$C2/m$	–	–				[10, 11]
Rb_2WO_4	»	$C2/m$	–	–				[10, 12]
Cs_2MoO_4	»	$Pnam$	4	4,10				[12]
Cs_2WO_4	»	$Pnam$	4	4,10				[12]
$Li_2W_2O_7$	structure with octahedral complexes	$P\bar{1}$	2	4	1.90(5)–2.11(4)	6	1.74(2)–2.30(1)	[14]
$Na_2Mo_2O_7$	chain structure with tetrahedra and octahedra	$Cmca$	8	6	1.2–1.75	4 6	1.71; 1.75; 1.69; 1.90; 2.26	[15]
$Na_2W_2O_7$	ditto	$Cmca$	8	6	2.35(2)–2.56(1)	4 6	1.76; 1.807(9) 1.725; 1.921; 2.252	[16]
$K_2Mo_2O_7$	»	$P\bar{1}$	2	9	2.59–3.64	4 6	1.75–1.80 1.75; 1.76; 1.63; 2.10; 2.17; 2.27	[17]
$K_2Mo_3O_{10}$	chain structures with trigonal bipyramids and octahedra	$C2/c$	4	10	2.64–3.47	5 6	1.64–2.08 1.69; 1.99; 2.11	[18]
$Rb_2Mo_3O_{10}$	ditto	$C2/c$	4	10				[19]
$Cs_2Mo_3O_{10}$	»	$C2/c$	4	10				[19]
$K_2W_3O_{10}$	polygon-network	$P2/c$	6	9,13	2.58(4)–3.55(4)	6	1.68(5)–2.21(3)	[20]
$Li_2Mo_4O_{13}$	block structure	$P\bar{1}$	3	6	1.91(3)–2.58(3)	6	1.68(1)–2.47(1)	[21]
$Na_2W_4O_{13}$	polygon-network	$P\bar{1}$	1	5	2.16–2.65	6	1.71–2.28	[22]
$K_2Mo_4O_{13}$	chain structure with octahedra	$P\bar{1}$	2	8	2.67(3)–3.37(4)	6	1.67(3)–2.39(3)	[25]
$K_2W_4O_{13}$	polygon-network structure with octahedra	$P\bar{3}$	3	14,18	2.72(3)–3.75(4)	6	1.75(3)–2.12(4)	[23, 24]
$Rb_2Mo_4O_{13}$	ditto	$P\bar{1}$	2	8				[25]
$Rb_2Mo_5O_{16}$	block structures	$C2/c$	4	10				[26]
$Cs_2Mo_5O_{16}$	ditto	$C2/c$	4	10	2.96–3.41	6	1.70–2.51	[27]
$Rb_2Mo_7O_{22}$	»	$C2/c$	4	10				[26]
$Cs_2Mo_7O_{22}$	»	$C2/c$	4	10	2.94–3.53	6	1.70–2.51	[26]

*For the set of compounds with chain structures formed from tetrahedra and octahedra all the r_{M-O}(oct) values are listed in the order: r_{M-O}(terminal), r_{M-O}(bridging, *trans*), r_{M-O}(bridging, *cis*).

Since molybdenum and tungsten in higher oxidation states have fairly similar ionic radii[5] molybdates and tungstates with the same alkali metal cation are expected to be isomorphous. However, this assumption is valid only for the low-temperature modifications of A_2MO_4. As the $MO_3:A_2O$ ratio is increased diferences appear in the structure of isopolymolybdates and isopolytungstates. Nevertheless in both instances systems of condensed MO_n (n = 4, 5, 6) polyhedra are formed.

The structure of $Li_2W_2O_7$, which forms triclinic crystals,[6] is composed of LiO_4 tetrahedra and distorted WO_6 octahedra linked by shared edges to form $(W_2O_7)^{2-}$ anions, which in turn form infinite chains. Moving to the larger sodium cation in $Na_2Mo_2O_7$ [7] and $Na_2W_2O_7$ [8] leads to changes in the coordination of both the alkali metal and the molybdenum or tungsten. Here the $(M_2O_7)^{2-}$ anions, which form infinite chains, are composed of MO_4 tetrahedra and MO_6 octahedra with shared corners. This combination of different coordination polyhedra is typical of the stereochemistry of molybdenum and, to a significant extent, tungsten. The sodium has octahedra coordination in $Na_2Mo_2O_7$ but occupies two sets of positions, in oxygen octahedra and pentagonal pyramids, in the structure $Na_2W_2O_7$.

A further increase in the size of the alkali metal cation is accompanied by an increase in the CN to 9. The structure of $K_2Mo_2O_7$,[9] like that of $Na_2Mo_2O_7$, is composed of chains of molybdenum-oxygen tetrahedra and octahedra but their mutual arrangement is different. A pair of octahedra has a shared edge and is linked by means of two tetrahedra, via shared corners, to the next pair. Each tetrahedron and octahedron has two free vertices.

Increasing the $MO_3:A_2O$ ratio to three leads, in the structure of $K_2Mo_3O_{10}$,[10,11] to the production of a new type of chain which is formed from square-pyramidal MoO_5 polyhedra and MoO_6 octahedra. The chain unit comprises an octahedron and two pyramids but each octahedron is linked via corners to four pyramids.

Thus there is a general tendency to a change in the chain structure on going from $Na_2Mo_2O_7$ to $K_2Mo_2O_7$ and $K_2Mo_3O_{10}$. In $Na_2Mo_2O_7$ the octahedra share corners and are also linked in pairs by tetrahedra. In $K_2Mo_2O_7$ two neighbouring octahedra share edges and each pair is joined to the next pair via the corners of two tetrahedra; the relative number of tetrahedrally coordinated molybdenum atoms is greater than in $Na_2Mo_2O_7$. In the structure of $K_2Mo_3O_{10}$ all the octahedra are linked by pairs of tetrahedra with a change in the latter to distorted tetragonal pyramids due to the formation of a fifth, longer Mo–O bond with the tetrahedra drawn appreciably closer together.

A comparison of the MoO_6 octahedra in these structures reveals a number of trends in the Mo–O bond lengths:

(i) there is a tendency to form two long, two short, and two medium-length bonds between the central atom and oxygen;

(ii) in the *trans* position to a short bond there is a long bond and this is usually longer (weaker), the shorter (stronger) is the short bond;

(iii) the mean Mo–O distances are fairly similar (~1.94 Å) in compounds with different compositions.

These rules are also valid for the WO_6 octahedra in the structure of $Na_2W_2O_7$.[8]

In all cases a decrease in the Mo_{tetr}–O bond lengths is accompanied by lengthening of the associated O–Mo bonds, the tetrahedron becoming quasi-free (the bonds in the octahedron nearest to it are weakened while the bonds in the tetrahedron itself are strengthened).

Although the molybdenum-oxygen distances differ considerably the lengths of the O...O edges of the octahedra lie within a fairly narrow range, 2.75 ± 0.1 Å. The preference of the oxygen atoms to be spaced at equilibrium distances from each other influences the magnitude and form of the angular distortions. The electron density is increased at one, two, or three *cis*-located Mo–O bonds but decreased at the others. This phenomenon can be likened to a *trans* effect.

The polymolybdates $K_2Mo_3O_{10}$, $Rb_2Mo_3O_{10}$, and $Cs_2Mo_3O_{10}$ are isostructural.[11] The structure of $K_2W_3O_{10}$ [12] differs considerably from that of the molybdates of similar composition. Among the compounds under discussion it provides the simplest example of a polygon-network structure with planar nets made up of ensembles of WO_6 octahedra linked to form infinite chains and channels running through the whole structure. The potassium cations occupy positions in the channels with coordination numbers of 9 and 13.

When the $MO_3:A_2O$ ratio is increased to 4 or more the molybdenum or tungsten atoms change to exclusively octahedral coordination. Thus on going from simple molybdates to di-, tri-, and tetra-molybdates the coordination of molybdenum by oxygen changes from tetrahedral with octahedral, square pyramidal with octahedral, and finally pure octahedral.

An oxygen atom deficiency in the tetramolybdates necessitates appreciable joining together with the edges and/or corners of the octahedra. For example, $Li_2Mo_4O_{13}$ has a three-dimensional block structure.[13] The structure of $Na_2W_4O_{13}$ [14] is composed of groups of four WO_6 octahedra sharing edges and linked to form an infinite chain, also via shared edges, whereas the tunnel structure of $K_2W_4O_{13}$ [15,16] contains WO_6 octahedra linked by shared contents to form six-membered rings. The reason for this is that the larger potassium ion requires a larger number of neighbours and the rigid unit chain of octahedra present in $Na_2W_4O_{13}$ cannot be distorted to such an extent.

The triclinic potassium and rubidium tetramolybdates are isomorphous.[17] Caesium tetramolybdate probably has a similar structure.[17] In the structure of $K_2Mo_4O_{13}$ groups of four MoO_6 octahedra with almost coplanar central atoms have shared edges and are joined to similar groupings, by shared edges, to form infinite chains. The latter do not have shared oxygen atoms but are held together by potassium ions in eight-coordinate positions.

With this mutual arrangement of the MoO_6 octahedra the molybdenum atoms are drawn closer together, leading to their mutual repulsion from the centres of the octahedra. This in turn causes differences between the molybdenum–oxygen interatomic distances which is typical of many structures of compounds containing molybdenum in a high oxidation state.

The three types of chain structure known at present for di-, tri-, and tetra-molybdates remain stable in the presence of alkali metal cations of a certain size. The lower limit of the cation size is determined by the arrangement of the chains but the upper limit depends on the way in which the polyhedra are joined together to form a chain and also their potentiality for ensuring coordination of large cations. For example, the helical chain structure of the trimolybdate may remain stable in the presence of potassium, rubidium, or caesium due to it ability to rotate and to extend somewhat whereas the dimolybdate chain structure is not in a position to be extended and is therefore not found with cations larger than sodium.

The tetramolybdate chain structure is the most compact of those discussed and even with its greater rigidity it proved possible to retain it for potassium and rubidium cations. The structure of caesium tetramolybdate is however different from those of $K_2Mo_4O_{13}$ and $Rb_2Mo_4O_{13}$.[17]

The occurrence of polymolybdates with the largest $MoO_3:A_2O$ ratio for rubidium and caesium is evidently due to the ability of these large cations to be combined effectively with the largest number of molybdenum-oxygen fragments.

III. Vibrational spectra

The study of the vibrational spectra of alkali metal molybdates and tungstates has received great attention. However most of the research has been concerned with the compounds in the A_2MO_4 (A = Li, Na, K, Rb, Cs; M = Mo, W) series which have comparatively simple structures. Their i.r. spectra in the region down to 70 cm^{-1} [3,4] and Raman spectra of polycrystalline specimens[28–31] have been obtained.

A group-theoretical analysis of the distribution of the vibrations of MO_4^{2-} anions, which form the basis of the crystal structure of these compounds, among the irreducible representations of the point group T_d gives

$$\Gamma_{vib} = A_1(\text{Raman}) + E(\text{Raman}) + 2T_2(\text{IR, Raman}).$$

Hence the Raman spectrum of "free" tetrahedral MO_4^{2-} anions will contain one line due to the totally symmetric stretch $\nu_1(A_1)$, one line due to the triply degenerate vibration $\nu_3(T_2)$, and two lines due to the deformations $\nu_2(E)$ and $\nu_4(T_2)$. Only the two triply degenerate vibrations $\nu_3(T_2)$ and $\nu_4(T_2)$ will be i.r.-active.

The values of the vibrational wavenumbers of "free" MoO_4^{2-} and WO_4^{2-} ions have been obtained from measurements of the spectra of aqueous solutions[29] in polarised light and of ions isolated in an inert-gas matrix,[31–34] in conjunction with a theoretical analysis of the wavenumbers and modes of the normal vibrations.[35]

Table 2. Wavenumbers (cm^{-1}) of the vibrations of the free tetrahedral ions.[35]

Ion	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(T_2)$	$\nu_4(T_2)$
MoO_4^{2-}	896	381	833	318
WO_4^{2-}	931	373	833	320

The effect of the alkali metal cations on the vibrations of MoO_4^{2-} and WO_4^{2-}, as functions of their concentration, was considered. The presence of lithium and sodium cations in the solution increases the vibrational wavenumbers of the anions, the effect being more marked in the case of lithium. The introduction of potassium, rubidium, and caesium cations into the system leads to a reduction in the vibrational wavenumbers due to enhancement of the effective polarisability of the water molecules surrounding the anions. The perturbation recorded was more appreciable for the tungstate ion. Extrapolation of the experimental data to infinite dilution gives values of the symmetric vibration ν_1 of 931 cm^{-1} for WO_4^{2-} and 896 cm^{-1} for MoO_4^{2-}.

The data given in Table 2 provide a basis for analysing the vibrations of crystalline specimens. Such vibrations are described not only by the wavenumbers of the internal vibrations of the oxo-anions but also by the wavenumbers of the external vibrations — the librations of the anions and the translational vibrations of the anions and cations.

The changes in the wavenumbers in the vibrational spectra of Na_2MoO_4 and Na_2WO_4 on moving from liquid to crystalline specimens have been analysed.[36] The Raman lines at 928 and 892 cm^{-1} were assigned (by analogy with the spectra of the solutions) to the symmetric stretches $\nu_1(A_1)$. Lines at 813 and 808 cm^{-1} were assigned to $\nu_3(T_2)$. The fact that, if the anion symmetry is T_d, only the T_2 mode can appear in the i.r. spectra of crystalline Na_2MoO_4 and Na_2WO_4 enables the two remaining wavenumbers to be safely assigned to the deformations $\nu_2(E)$ and $\nu_4(T_2)$.

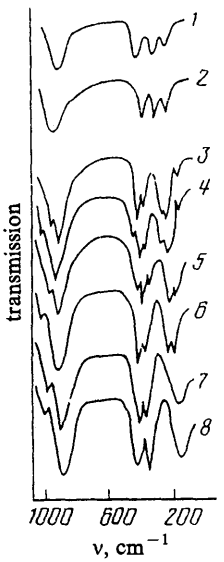


Figure 1. Ir spectra of alkali metal monomolybdates and monotungstates:[25] *1*, Na_2MoO_4; *2*, Na_2WO_4; *3*, K_2MoO_4; *4*, K_2WO_4; *5*, Rb_2MoO_4; *6*, Rb_2WO_4; *7*, Cs_2MoO_4; *8*, Cs_2WO_4.

It was found that $\nu_2(E) > \nu_4(T_2)$ for both the free ions and the anions in a crystal field, so that there is inversion of these wavenumbers in the spectra of Na_2MoO_4 and Na_2WO_4 compared to those in the spectra of the tetrahedral anions ClO_4^-, SO_4^{2-}, PO_4^{3-}, and CrO_4^{2-}, for which $\nu_4(T_2) > \nu_2(E)$. Similarly $\nu_1(A_1) > \nu_3(T_2)$ which is also in the reverse order compared to the wavenumbers for the other tetrahedral ions. The Raman lines at 116 and 93 cm^{-1} in the spectra of crystalline Na_2MoO_4 and Na_2WO_4 relate to external lattice vibrations. Similar results were obtained from a study of the i.r. and Raman spectra[4] of anhydrous mono-molybdates and -tungstates of the whole series of alkali metals, with the exception of lithium in the region down to 70 cm^{-1} (Table 3, Figs. 1 and 2). The spectra were interpreted using the results of a group-theoretical analysis of the vibrations of Na_2MoO_4 crystals which have a spinel structure composd of MoO_4 tetrahedra and NaO_6 octahedra.[8] The bands in the spectra of the other alkali metal compounds were assigned by analogy with Na_2MoO_4. All the vibrations are active in both the Raman and i.r. spectra. This, and also the considerable difference between the wavenumbers observed in these spectra, is due to interaction between the vibrations of crystallographically equivalent tetrahedral anions and their distortion in the crystal field.

For all the compounds under discussion the vibrations of the tetrahedral oxo-anions were found to occur in the regions shown in Table 2.

In the molybdates and tungstates the vibrations of the alkali metal cations with octahedral coordination occur below 230 cm^{-1}. The two i.r. bands at 230 and 170 cm^{-1} and the Raman line at 120 cm^{-1} in the spectrum of Na_2MoO_4 are assigned to T_{1u} and T_{2g} type vibrations. The wavenumbers of the vibrations of the cations decrease in the order Na > K > Rb > Cs and show little change on going from molybdates to tungstates. The proposed assignment is fully consistent with the results of a calculation of the vibrational wavenumbers and modes of K_2WO_4 and K_2MoO_4.[37]

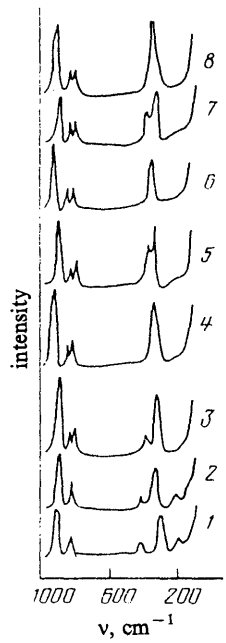


Figure 2. Raman spectra of alkali metal monomolybdates and monotungstates:[25] *1*, Na_2WO_4; *2*, Na_2MoO_4; *3*, K_2MoO_4; *4*, K_2WO_4; *5*, Rb_2MoO_4; *6*, Rb_2WO_4; *7*, Cs_2MoO_4; *8*, Cs_2WO_4.

Analysis of the vibrations modes and the displacements of the atoms shows that the Raman line at 926 cm^{-1} and the i.r. band at 925 cm^{-1} in the spectra of K_2WO_4 are due to vibrations of the WO_4 tetrahedron with the predominant change in the shortest W—O bond (1.76 Å); the Raman line at 829 cm^{-1} and the i.r. band at 830 cm^{-1} are due to the longest bond (1.81 Å). The wavenumbers in the 357—298 cm^{-1} region are assigned to deformations of the tetrahedron. The bands at 164, 145, 132, and 100 cm^{-1} in the spectrum of K_2WO_4 can be assigned to the predominant vibrations of the potassium cations involving the oxygen neighbours and the tungsten atoms.

Table 3. Vibrational wavenumbers (i.r. and Raman) (cm^{-1}) of A_2MO_4 and their assignment

Na_2MoO_4	Na_2WO_4	K_2MoO_4	K_2WO_4	Rb_2MoO_4	Rb_2MoO_4	Cs_2MoO_4	Cs_2WO_4	Assignment	Type of vibration	Symmetry type*
897	932	890	926	893	924	888	922	$\nu_{1,T}$	ν(M–O)	A_{1g}
		889	925	892	923	889	923			
		852	853	855	847	840	840			
840	840	835	830	830	828	826	826	$\nu_{3,T}$	ν(M–O)	T_{1u}
810	810	824	829	834	824	820	820			T_{2g}
387	379	357	357	335		328	338	$\nu_{4,T}$	δ(O–M–O)	T_{2g}
317	309									T_{1u}
307	313	318	331	315	329	311	322	$\nu_{2,T}$	δ(O–M–O)	E_g
			338	345	333		338			
		333	319	325	317	338	315	$\nu_{2,T} + \nu_{4,T}$		
		311	298	305	300	321	301			
		168	164							
230	228	147	145	132	138	110	110—95	$\nu_{3,o}$	ν(A–O)	T_{1u}
		138	132	115	115	95				
178	168	100	100					$\nu_{4,o}$	δ(O–A–O)	T_{1u}
120	98							$\nu_{5,o}$	δ(O–A–O)	T_{2g}

* The assignment to symmetry types is given only for Na_2MoO_4 and Na_2WO_4.

Table 4. I.r. wavenumbers (cm^{-1}) and their assignment for $A_2M_nO_{3n+1}$ (A = Na, K, Rb, Cs; M = Mo, W).[5]

$N_2W_2O_7$	$K_2Mo_2O_7$	$K_2W_2O_7$	$Rb_2Mo_2O_7$	$Cs_2Mo_2O_7$	$K_2W_3O_{10}$	$Rb_2Mo_3O_{10}$	$Cs_2Mo_3O_{10}$	$Na_2Mo_4O_{13}$	$K_2W_4O_{13}$	$K_2W_4O_{13}$	$Rb_2Mo_4O_{13}$	$Cs_2Mo_4O_{13}$	Assignment
							992	970	960		955	955	
957	930					940	941	960	945		945	945	$\nu_{3,o}$; $\nu_{1,T}$
949			925	930			932	940	935	955	932	932	
911	905	908	912	919	920	910	910	925	919		915	910	
			890	908	870		900	910	901		900	900	
882	870	840	882	888	840	890	890	895	890	870	890	890	$\nu_{3,T}$
865			877	870	820		870	870	868		860	858	
			860	855			856						
			840	820			830	835					
820			809		798		820			790			
770			765	782									$\nu_{1,o}$; $\nu_{2,o}$
		740		755	760		750	745	755		752	752	
	720		721			722	725			730		730	
	705	670			650	705	710	650	700		700	700	
		620							622	640	628	625	
640				580		560	570		580		575	570	
						535			552		550	550	
458	480				465				518		515	515	
		441	453	452	450	480	480		470	470	470	470	ν_4O; $\nu_{4,T}$
			420		437		432	438	431	440	431	431	
420	402			402	410			405	405	420	405	408	
		390	380	395	390	385	390		390		391	391	
372	375	370	372				380	382	372		372	372	
361	362			362	370	361	365		360		360	359	
			355	351	350	355	355			352			
		346						348					
342			335	335	330	330	332	335					
	321		330	320		325			328	330	328	330	$\nu_{5,o}$; $\nu_{6,o}$; $\nu_{2,T}$
308		322	310					320					
		307	305		300		305					305	
		285	300				285	295	292	290	295	295	
280		275			270	265	260	272	270		270	265	
	242		242	255				255					
			230			230	230	220	222			227	
	220		220								220		
				215		210	210				212	210	
			205			205	205						

Lithium molybdates and tunsgate Li_2MO_4, whose crystal structures contain almost undistorted MO_4^{2-} tetrahedra, have simple i.r. spectra the interpretation of which causes no difficulties.[38]

The analysis of the vibrational spectra of alkali metal polymolybdates and polytungstates is an incomparably more serious problem due to the complex structure of the anions which are composed to condensed molybdenum or tungsten coordination polyhedra. This makes it impossible to interpret the vibrational spectra using the "free" ion approximation.

Nevertheless such attempts were made in some of the earlier papers. From studies of the i.r. spectra of $Na_2Mo_2O_7$, $Na_2W_2O_7$, and $Na_2W_4O_{13}$ the existence of $(O_3M-O-MO_3)^{2-}$ ions was proposed[39,40] by analogy with ions like $P_2O_7^{4-}$, $S_2O_7^{2-}$, $Cr_2O_7^{2-}$. It was found that in the vibrational spectra of molybdates and tungstates, and also vanadates, and in contrast to the spectra of phosphates, sulphates, and chromates, the wavenumbers of the M–O symmetric stretches are always higher than those of the antisymmetric vibrations. Tarte[40] showed that the wavenumbers of the M–O stretches increase as the number of oxygen atoms coordinated to the molybdenum or tungsten decreases. Further, the higher the degree of condensation of the molybdenum–oxygen or tungsten–oxygen groups, the higher are the wavenumbers of the stretches of the polyhedra.[40]

The vibrational spectra of alkali metal polymolybdates and polytungstates have been analysed.[5] The i.r. spectra of the compounds $A_2M_nO_{3n+1}$ (A = Na, K, Rb, Cs; M = Mo, W) in the 4000–200 cm^{-1} region were studied (Table 4). An interpretation of the observed spectra was proposed on the assumption that in the structures of these compounds distorted MO_6 octahedra and MO_4 tetrahedra are linked by shared corners. It was shown by spectroscopy that there is a similarity between the structures of potassium, rubidium, and caesium tetramolybdates on one hand, and rubidium and caesium tritungstates on the other.

The vibrational wavenumbers of polymolybdates isotopically substituted with lithium ($^6Li-^7Li$) and molybdenum ($^{92}Mo-^{100}Mo$),[37,41,42] supplemented with our own previously unpublished data for tungstates, are given in Table 5.

In analysing the spectra of complex systems containing octahedral, as well as tetrahedral, groupings it must be borne in mind that for an isolated, regular MO_6 octahedron with O_h symmetry six normal vibrations are possible:

$$\Gamma_{vib} = A_{1g}(\text{Raman}) + E_g(\text{Raman}) + 2T_{1u}(\text{IR}) + T_{2g}(\text{Raman}) + T_{2u}(\text{n.a.}),$$

of which only ν_3 and ν_4 with symmetry T_{1u} will be i.r.-active. On the basis of these ideas, and using known structural data for $Na_2Mo_2O_7$, $Na_2W_2O_7$, and $K_2Mo_3O_{10}$,[15,16,18] Caillet and Saumagnt[39]

Table 5. Wavenumbers (cm^{-1}) of the vibrations in the i.r. and Raman spectra of some polymolybdates and polytungstates (including specimens with isotopic substitution of the cations).

$Li_2W_2O_7$*				$Na_2Mo_2O_7$ (Ref.42)				$K_2Mo_3O_{10}$ (Ref.41)				$Rb_2W_3O_{10}$		$Cs_2W_3O_{10}$		$Na_2W_4O_{13}$	
IR		Raman		IR		Raman		IR		Raman							
^6Li	^7Li	^6Li	^7Li	^{92}Mo	^{100}Mo	^{92}Mo	^{100}Mo	^{92}Mo	^{100}Mo	^{92}Mo	^{100}Mo	IR	Raman	IR	Raman	IR	Raman
1015	1015			952	942					968	963	975		950			953
		955	955			939	935			958	953	944		942		950	
									955								
								958	942			932		938			
945	945								936								
				929	922					942	942		932		935		
		936	936								937						
		925	925			920	918			934	931						920
907	907			915	913					922	916		921				
					904					915	908		914		904		
				892	890					909	902						
855	855			874	882			904	904							882	
		852	852			875	869		893								
						836	828			897	890	872		867			
835	835				822			872	868			855		853			
		816	816			818	815			853	850	830		826		830	
				800	780			762	765			771		764			790
		765	765			774	765			769	755		747		759	775	
								733	728			742		732			774
755	755					741	739			724	722				731		
								715	710								
									672			686		667			674
665	665									671	668		681		653		
										634	630	637		625		620	
				600	590			620	620								
										610	610		613		612		

Table 5 (continued).

$Li_2W_2O_7$*				$Na_2Mo_2O_7$ (Ref.42)				$K_2Mo_3O_{10}$ (Ref.41)				$Rb_2W_3O_{10}$		$Cs_2W_3O_{10}$		$Na_2W_4O_{13}$	
IR		Raman		IR		Raman		IR		Raman							
^6Li	^7Li	^6Li	^7Li	^{92}Mo	^{100}Mo	^{92}Mo	^{100}Mo	^{92}Mo	^{100}Mo	^{92}Mo	^{100}Mo	IR	Raman	IR	Raman	IR	Raman
								575				585		580		578	
								572	562								
		551	551							568	568						
											550						
540	540							539	533								539
						526	525			510	505						
									503								
496	480			487	481					480	479						
472	470			470	465			479	477								
458	458					464	460			449	449					460	
448	442						454	439	447			453		455		450	
								421	430				436				445
419	419			417					405			407		408		418	
						411	411			392	388		405				369
389	383							390	389			395		395			360
		370	370					376	370			365		365		355	
						369	368			374	369						344
350	342			364	361			359	356							342	
321	321					340	336			340	338		339		354		336
					339			327	324			337		340			319
		305	305	315	314			299	290				301		299	312	
						296	294			278	276	283		309			310
286	284			276	270			267	267			274		294			280
				262	264					260	258	259		252			274
		237	237			245	245			240	239	250				265	
237	235					228	227			233	230		247		252		265
				227	228			232	228			224		220		252	
206	206					215	215			223	222		219		223	228	
		199	205	195	195			209	206				196		201		222
		183	185			199	199			205	202			190			208
181	179			184	184			185								198	
				182						167	164				166	182	
169	169			168	168			165	164			160		160			167
		162	162	153	152												
159	159		158		159												
		144	149	148	148							150		138		148	
						140	138			145	141						147
				138	138							130		118		130	
128	128				129												
				125	120												
						120	120			127	123						
				112	112			115	115			106					
				102	103					114	114						
						90	87			109	88						
88	88			86	78												
						84	84			84	82						
				79	75												
					71												
					66												
62	62				63							62		68			
						45	44			59	57						

*Our data.

[Ref. 4? (Ed. of Translation)] assigned the highest wavenumbers to the $\nu_3(T_{1u})$ vibrations of the MO_6 octahedra. Confirmation of the correctness of this assignment was evident in the splitting of the corresponding band in the i.r. spectra of many polymolybdates and polytungstates into three components due to removal of the degeneracy. The next highest wavenumber was assigned to $\nu_1(A_1)$ of the MO_4 tetrahedron. The $\nu_3(T_2)$ vibration of the same tetrahedron appears in the i.r. spectra as a strong triplet with its centre at $\sim$890 cm^{-1}. The i.r. bands in the 350–200 cm^{-1} region were assigned to deformations of the tetrahedron $[\nu_2(E)]$ and $[\nu_3(T_{1u})]$. The absence of simple criteria led to difficulties in interpreting the spectra in the 560–350 cm^{-1} region where bands due to the vibrations $\nu_4(T_{1u})$ or $\nu_5(T_{2g})$ of the octahedron and $\nu_4(T_2)$ of the tetrahedron are expected.

The proposed assignment is rather provisional and open to serious doubts in a number of aspects. For example, the wavenumbers of the stretches of the tetrahedral MO_4 groups will, because of the smaller interatomic distances and higher bond energies, be higher than those of the stretches of the MO_6 octahedra.

The structures of the other polymolybdates and polytungstates were established later and therefore a hypothetical assignment of their vibrational wavenumbers was made from a comparison with the spectra of the whole series of compounds, and also of $Na_2Mo_2O_7$ and $Na_2W_2O_7$ as described previously. In the 400–200 cm^{-1} region there are a number of i.r. bands with increased wavenumbers which were difficult to describe by considering only structural fragments formed from tetrahedra and octahedra. No analysis of the vibrations of the cationic sublattice was made in Ref. 35.

The i.r. spectra of $Na_2Mo_2O_7$ and $Na_2W_2O_7$, studied by Dupuis and Veltange,[39] were also found to be very similar. Antisymmetric stretches of the M–O–M bridges were assigned to the bands in the 600 cm^{-1} region for $Mo_2O_7^{2-}$ (a very strong band) and the 625–575 cm^{-1} region for $W_2O_7^{2-}$ (a doublet of strong bands). It is likely[39] that the symmetric vibrations of the bridges occur at 465 cm^{-1} for $Mo_2O_7^{2-}$ and 455 cm^{-1} for $W_2O_7^{2-}$. The antisymmetric stretch of MO_3 groups appears as a doublet in the 825–780 cm^{-1} region for $Na_2Mo_2O_7$ and the 825–775 cm^{-1} region for $Na_2W_2O_7$. Deformations were recorded at 360, 333, and 315 cm^{-1} for $Mo_2O_7^{2-}$ and 418 and 360 cm^{-1} for $W_2O_7^{2-}$. Thus it was shown that the i.r. spectra of sodium dimolybdate and ditungstate can be interpreted and satisfactorily in terms of the vibrations of a model $M_2O_7^{2-}$ anion with symmetry C_{2v} and containing two symmetrical MO_3 groups linked by an M–O–M bridge, as in pyrophosphates, pyrosulphates, and dichromates. The wavenumbers of the stretches of the M–O–M bridges decrease as the atomic weight of M increases.

The Raman spectra of polycrystalline $K_2W_3O_{10}$ and $K_2W_4O_{13}$, and also polytungstates with a higher tungsten content, have been published and discussed.[43] In the opinion of the authors the vibrations of terminal W–O bonds appear in the Raman spectra of these compounds as a pair of lines at 962 and 902 cm^{-1}.

The external vibrations of the alkali metal tungstates and molybdates have not been studied in detail. However precision studies of the i.r. and Raman spectra of a number of lanthanide molybdates, where the greatest attention was paid to the external vibrations,[44] confirm the assignment, proposed from an analysis of the spectra of compounds with the scheelite structure,[45] of the wavenumbers 140–110 cm^{-1} to translational, and 260–200 cm^{-1} to librational, vibrations of the molybdate ions. It seems that these values are general, remaining valid for the alkali metal molybdates (and with small adjustments tungstates also) provided, of course, that the structure of the compound contains tetrahedral anions.

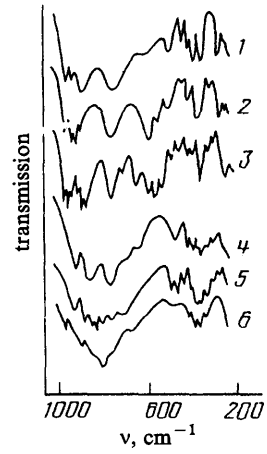


Figure 3. I.r. spectra of potassium polymolybdates and polytungstates: *1*, $K_2Mo_2O_7$; *2*, $K_2Mo_3O_{10}$; *3*, $K_2Mo_4O_{13}$; *4*, $K_2W_2O_7$; *5*, $K_2W_3O_{10}$; *6*, $K_2W_4O_{13}$.

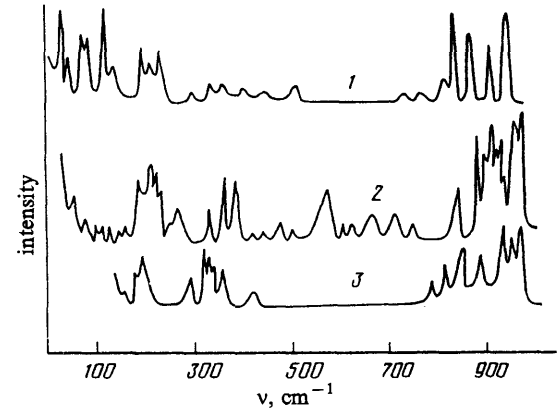


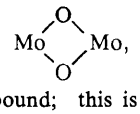
Figure 4. Raman spectra of alkali metal polymolybdates: *1*, $Na_2Mo_2O_7$; *2*, $K_2Mo_3O_{10}$; *3*, $K_2Mo_2O_7$.

The appearance in print of Refs. 15, 18, and 19 with a description of the structures of a large number of molybdates stimulated studies of their vibrational spectra.

A number of recent papers[37,41,42] have been concerned with a detailed study of the vibrational spectra of potassium and sodium molybdates including a factor-group analysis of the vibrations of the crystals and a theoretical calculation of the normal vibrational modes and wavenumbers using the valence-force field approximation, with the aim of demonstrating the relationship between the type of spectrum and the structure. The compounds K_2MoO_4, $K_2Mo_2O_7$,[37] $K_2Mo_3O_{10}$,[41] and $Na_2Mo_2O_7$ [42] were chosen as models for the calculation because of the diversity of their crystal structures [including structures with isolated tetrahedral anions (K_2MoO_4), chain structures with tetrahedra and octahedra ($Na_2Mo_2O_7$, $K_2Mo_2O_7$), and chain structures with trigonal bipyramids and octahedra ($K_2Mo_3O_{10}$)] and hence the presence of

different types of Mo—O—Mo bridging bonds, to the vibrations of which particular attention was paid. The range of Mo—O bond lengths in the compounds studied was 1.64—2.27 Å, so enabling the effect of the interaction at "long" Mo—O bonds on the vibrational spectrum to be investigated.

In Refs. 37, 41, and 42 experimental data are given on the i.r. and Raman spectra in the 4000—50 cm^{-1} region (Figs. 3 and 4) of specimens isotopically substituted with molybdenum ($^{92}Mo-^{100}Mo$) and an assignment of the vibrations of the different sublattices in the crystal is made. These data were supplemented by the results of studies of some alkali metal tungstates by the authors of the present review.

The lengthening of the Mo—O bonds in $K_2Mo_2O_7$ crystals to 2.27 Å leads to a reduction of the wavenumbers of the vibrations involving these bonds to 600—480 cm^{-1}.[37] In this region the coordinates of the change in the O—Mo—O angles also make a substantial contribution to the vibrational modes. An analysis of the normal vibrations of $K_2Mo_3O_{10}$ [41] shows that the vibrations in the system with the highest wavenumbers (970—900 cm^{-1}) are accounted for by the coordinates of the change in length of the very short terminal Mo—O bonds and the vibrations of the Mo—O—Mo bridging bonds occur over a broad spectral range (860—480 cm^{-1}). A single vibration is not found for the closed grouping  , which is present in the crystal structure of this compound; this is evidently due to the considerable different between the bond angles at the bridging oxygen atoms.

The vibrations of the tetrahedral MoO_4^{2-} grouping in $Na_2Mo_2O_7$ [45] occur over a broader spectral range (910—770 cm^{-1}) than is the case for the isolated tetrahedra in the A_2MoO_4 structures or for the free MoO_4^{2-} ion.[4] The coordinates of the bonds in the octahedral grouping make the predominant contribution to the vibrations in the 940—460 cm^{-1} region which is considerably broader than the wavenumber range for stretches of isolated MoO_6 octahedra.[5] The reasons for these discrepancies are both the presence in the structure of long Mo—O bonds (up to 2.26 Å) and the formation of Mo—O—Mo bridging bonds between a tetrahedron and an octahedron and between two octahedra. The broadening of the range for deformation of the molybdenum-oxygen polyhedra to 420—240 cm^{-1} is also due to condensation of the coordination polyhedra.

The analysis of the vibrations for the series of alkali metal molybdates enabled the assignment of the wavenmbers in their i.r. and Raman spectra to be improved and also the effect of the bridging bonds on the crystal lattice dynamics to be found. A comparison of the geometrical and spectroscopic characteristics of the bridging groups (Table 6) shows that an increase in the Mo—O interatomic distances is accompanied by a decrease in the wavenumbers of the vibrations of these groups and that an increase in the bond angles at the oxygen atoms leads to an increase in the wavenumbers of their antisymmetric vibrations and a decrease in those of the symmetric vibrations. The latter occupy the wavenumber region between the stretches and deformations of the coordination polyhedra and this complicates the interpretation of the spectra. The values of the force constants of the Mo—O bonds which we obtained in these calculated show a correlation with the interatomic distances.

We obtained similar results for $Li_2W_2O_7$ and $Na_2W_4O_{13}$. In these compounds we are faced with a more complex structure for the set of condensed polyhedra. In addition to W—O—W bridging bonds formed by pairs of tungsten coordination octahedra, the structures of these compounds contain oxygen nodes shared between three tungsten octahedra.

Table 6. Characteristics of the M—O—M bonds.

Compound	Bond angle at oxygen atom, °	Interatomic distance M–O, Å	Force constant 10^{-6} K, cm^{-2}	Wavenumbers of vibrations, cm^{-1}		
				$\nu_{antisym}$	ν_{sym}	$\Delta\nu$*
K_2MoO_4**	–	1.74	9.45	852, 835,824	890, 889	
	–	1.78	8.8			
K_2WO_4**	–	1.82	9,7	835, 813	828	
$K_2Mo_3O_{10}$	101	2.08	2.7	620—610	540—510	93
		2.11	2.7			
$K_2Mo_2O_7$	101	1.83	6.1	720—570	570—560	150
		2.17	3.2			
$K_2Mo_3O_{10}$	114	1.88	7.5	870	630	240
		1.99	4.5			
$Na_2Mo_2O_7$	125	1.78	7.8	822—815	487—460	345
		2 26	2.8			
$K_2Mo_2O_7$	138	1,77	9.3	930	480	450
		2,27	2.8			
$Na_2Mo_2O_7$	141	1.90	6.4	952—942	600—525	390
		1.90	6.4			
$Li_2W_2O_7$	107	1.78	9,3	816	665	151
		2.29	3,0			
$Na_2W_4O_{13}$	112	1,88	7,0	790—774	674	108
		2.04	4,7			
$Li_2W_2O_7$	114	1.90	8.1	1015—852	700—698	234
		2.03	5.7			
$Li_2W_2O_7$		1.92	7.8			
	101, 106, 148	2.02	5.5	1015—852	700—698	234
		2.18	4.0			
$Na_2W_4O_{13}$***		1.92	6.0			
	96, 101, 157	2.09	4.4	920—882	578	323
		2.28	2.9			

*$\Delta\nu = \nu_{antisym} - \nu_{sym}$ was determined from the mean wavenumbers of the vibrations of the bridging oxygen atoms.

**The data given are for the terminal M—O bonds in the MO_4 tetrahedra.

***Oxygen atom in the field of three tungsten atoms (node). For $Li_2W_2O_7$ the vibrations of the bridging and nodal oxygen atoms are strongly mixed.

[*The units used for the force constant are not clear (Ed. of Translation)].

For lithium ditungstate the wavenumbers of the antisymmetric vibrations of the bridging and nodal oxygen atoms are mixed and lie in the fairly broad range 1015—852 cm^{-1}. In sodium tetratungstate

these vibrations are separated in mode and wavenumber. The wavenumber range 920–882 cm^{-1} is asigned to the vibrations of the nodal oxygen atoms and the range 790–774 cm^{-1} to vibrations of the bridging bonds. As in the molybdates, the symmetric vibrations of these structural fragments occur in the region of the spectrum adjacent to the high-wavenumber limit of the deformations of the tungsten-oxygen polyhedra.

The lithium isotope effect is well developed in the i.r. spectra of $Li_2W_2O_7$, $\Delta\nu$ reaching 16 cm^{-1}. The relatively high wavenumbers of the vibrations of the cations in the lithium sublattice (up to 500 cm^1) are consistent with tetrahedral coordination by oxygen and short lithium–oxygen interatomic distances.

In all the polymolybdates and polytungstates the antisymmetric vibrations of the M–O–M bridging atoms usually have higher wavenumbers than the vibrations of the terminal oxygen atoms, given that the interatomic distances are comparable.

IV. Stability of the crystals

Various thermodynamic quantities are used for comparing the stabilities of crystalline compounds: the enthalpies of formation of crystalline compounds from the elements under standard conditions $\Delta H^\circ_{f298.15}$ or $\Delta H^\circ_{ok\,298.15}$ [of representing formation of crystal (Ed. of Translation)], the melting point T_f, the crystal lattice energy U, or the energy of atomisation E_a. Urusov[46] showed that the most definitive characteristic of binding energy in a crystal is the energy of atomisation E_a which is released as a result of the formation of the crystal from an infinitely rarefied gas of individual atoms. However, the crystal lattice energy, which is used fairly frequently, is the energy released on formation of the crystal from individual gaseous ions at infinite distances from each other. For all compounds the energy of atomisation E_a is measured from the absolute zero level of the energy of interaction of a rarefied gas composed of atoms and it can therefore be used quite rigorously for comparison with various properties in a series of compounds of the same type. The greater the absolute value of the energy of the atomisation, the more stable is the structure.

The experimental determination of the lattice energy at 0 K[47] is based on use of the equation:

$$U_0 = \Delta H^0_{298} - \sum_M \Delta H^0_{298}(M) - \sum_X \Delta H^0_{298}(X) - \sum_M I + \sum_X F - \int_0^{298} C_p(MX)dT + \sum_{M,X} \int_0^{298} C_p(M,X)dT$$

where ΔH°_{298} is the enthalpy of formation of a crystalline compound from the elements under standard conditions

$$\sum_M \Delta H^0_{298}(M), \quad \text{and} \quad \sum_X \Delta H^0_{298}(X) —$$

are the sums of the enthalpies of formation of gaseous atoms of the metal (M) and metalloid (X) respectively from the elements under standard conditions, $\sum_M I$ — is the sum of the ionisation enegies of all the cations, $\sum_X F$ — the sum of the electron affinities of all the anions, and C_p the heat capacity at constant pressure.

The last two integrals allow for the enthalpy change on going from the standard temperature to 0 K; the first represents the enthalpy change of the crystal and the second that of a gas of individual ions.

The experimental value of the energy of atomisation is determined using the following cycle:

$$E^0_a = \Delta H^0_{298} - \sum_M \Delta H^0_{298}(M) - \sum_X \Delta H^0_{298}(X) — \int_0^{298} C_p(M,X)dT + \sum_{M,X} \int_0^{298} C_p(M,X)dT.$$

Hence

$$U_0 - E_a = \sum_M I + \sum_X F.$$

We have calculated the crystal lattice energies and the energies of atomisation for the compounds A_2MoO_4 (A = Li, Na, K, Rb, Cs) (Table 7). Use was made of the enthalpies of formation of the crystalline compounds from the elements under standard conditions,[48] and enthalpies of formation of the gaseous atoms from the elements and the ionisation energies of the alkali metals[49] and the ionisation energy of molybdenum;[47] the affinity of oxygen for two electrons was taken to be −142 kcal.[50] An original method for calculating $-\Delta H^\circ_{298}$ using the thermal and energy characteristics of the compounds has been proposed.[51] The values of $-\Delta H^\circ_{298}$ so obtained are somewhat different from the experimental reference data[48] but the discrepancies are no more than 5%.

The calculated crystal lattice energies of A_2MoO_4 decrease as the atomic number of the alkali metal increases, indicating a decrease in the stabilities of the respective structures. The values of the energies of atomisation very similarly. This rule breaks down only for Cs_2MoO_4 (which has E_a = 793.6 kcal mol^{-1} whereas for Rb_2MoO_4 E_a = 790.9 kcal mol^{-1}). Thus Li_2MoO_4 has the most stable, and Rb_2MoO_4 the least stable, of these structures. The energy of atomisation of Li_2MoO_4 exceeds the corresponding values for the other members of the series by ~40 kcal mol^{-1}.

The particular stability of Li_2MoO_4 is evidently due to its structural peculiarities: the lithium has a tetrahedral environment of close packed oxygen atoms,[7] i.e. its CN is 4 whereas the CN of the other alkali metals is 6 in the structure of the Na_2MoO_4, 8 for potassium and rubidium, and 6 and 10 for caesium. These conclusions agree with results obtained by studying the perturbing effect of the alkali metal cation on the vibrations of the MoO_4^{2-} anion,[4] the effect being greatest for Li^+.

It is commonly assumed that there is a correlation between the variation in T_f and E_a.[47] However in the alkali metal molybdate series the variation in T_f, $\Delta H^\circ_{f298.15}$, and $\Delta G^\circ_{298.15}$ is not uniform. Rb_2MoO_4 has the highest T_f (1228 K) and Na_2MoO_4 the lowest (960 K) (see Table 7).

It was found[47] that $U - E_a$ is greater, the greater the deviation of the character of the A–O bond from the ionic type. However in the present A_2MoO_4 series the difference $U - E_a$ decreases as the ionisation energy of the alkali metal decreases. Thus on going from caesium to lithium the estimation of the stability of the molybdates using the ionic model introduces an ever increasing error in accordance with a greater deviation of the A–O bond from the ionic type as the ionisation energy of A increases.

For the alkali metal tungstates, owing to the paucity of reference data the energy of atomisation and crystal lattice energy can be calculated only for the first three members of the series: Li_2WO_4, Na_2WO_4, and K_2WO_4 (see Table 7). In the series A_2WO_4 (A = Li, Na, K) E_a and U very in the same way and, as with the molybdates, the lithium compound has the highest stability: the increase in the energy of atomisation from the potassium to the sodium compound

Table 7. Thermodynamic data for $A_2M_nO_{3n+1}$ (A = Li, Na, K, Rb, Cs; M = Mo, W).

Compound	T_fK (Ref.47)	$-\Delta H^0_{f298.15}$, (Ref.47)	$-\Delta G^0_{f298.15}$, (Ref.47)	E_a^*	U	$U-E_a$	E_a(add)=$E_a(A_2O)$+ $+nE_a(MO_3)$	E_a-E_a(add)
		kcal mol^{-1}						
Li_2MoO_4	975,65	353.53±0.18	336,318±0,91	834,9	6862,07	6027,1	792.4	42,5
$Li_2Mo_2O_7$	836	543.75±0,26	498,098±1.5	1350.8	13014,3	11663.5	1306,2	44,6
$Li_2Mo_3O_{10}$		723.92±0.24	659.977±1,8	1866.6	19166.5	17299.9	1820.0	46.6
$Li_2Mo_4O_{13}$	852	900,74±0,36	818,208±2,4	2379,1	25315.4	22936,3	2333,8	45 3
Na_2MoO_4	960	351.1±0.1	323,888	797,8	6813.2	6015.4		
$Na_2Mo_2O_7$	888	536.7±0.3	492.032	1319,1	12970,9	11651.8		
K_2MoO_4	1193	358,14±0,24	330.182±1.5	796,0	6774,6	5978,6	702.6	93,4
$K_2Mo_2O_7$	763	547,7±0,3	501.154±2.1	1321,2	12936,2	11615,0	1216.4	104,8
$K_2Mo_3O_{10}$	843	727.0±0.8	662,163±2,5	1836,2	19087,6	17251.4	1730.2	106.0
$K_2Mo_4O_{13}$	834	912,8±1,0	829.374±3.1	2357.6	25245.4	22887.8	2244.0	113,6
Rb_2MoO_4	1228	356.99±0.14	329.326±1.5	790.9	6762,0	5971.1		
Cs_2MoO_4	1208	362.0±0.1	336.314	793,6	6751.6	5958,0		
$Cs_2Mo_2O_7$	743	550.32±0.18	506.236±2.4	1317,6	12911.9	11594,5		
Li_2WO_4	1013	383.3	355.651	901.7	6196.2	5294.5		
Na_2WO_4	969	369.9	342.519	863.6	6146.4	5282,8		
$Na_2W_2O_7$	1013	574,9	529,925	1451.3	11637.9	10186,6		
K_2WO_4	1196	377,7	349.157	862,6	6108,6	5246,0		

* Our determination.

is only 1 kcal mol^{-1} but lithium tungstates has a value which is much higher (by 38.1 kcal mol^{-1}). As with the molybdates, the appreciable stabilisation of Li_2WO_4 compared to the other members of the series can be attributed to tetrahedral close packing of the oxygen atoms around the lithium cations.[6] In the light of this the slightly higher value of the energy of atomisation of Cs_2Mo[4] compared to Rb_2MoO_4 is understandable as being due to the placing of some of the caesium cations in positions with a smaller CN.

Turning to Na_2WO_4 and K_2WO_4 the CN's of the alkali metals increases to 6 and 8 respectively and less compact structures are formed. As with the alkali metal molybates, a comparison of the melting points of the tungstates does not lead to the correct conclusion regarding the relative stability of the compounds. K_2WO_4 which is the least stable compounds in the series $Li_2WO_4-Na_2WO_4-K_2WO_4$ has the highest T_f (1196 K). It is clear from Table 7 that the difference $U - E_a$ varies in the same way for A_2WO_4 as for A_2MoO_4. Hence the use of the crystal lattice energy to estimate the stability is the least reliable in the case of the lithium compounds.

Furthermore the standard enthalpies and Gibbs free energies of formation of the compounds do not match the variation of the energy of atomisation and the melting points in the A_2MO_4 (A = Li, Na, K, Rb, Cs; M = Mo, W) series.

To compare the stabilities of the crystals in the series $A_2MO_4-A_2M_2O_7-A_2M_3O_{10}-A_2M_4O_{13}$ is quite difficult because the calculation scheme presupposes the summation of the contributions of individual atoms and for comparison the values of the energy of atomisation quoted are required. One of the possible methods is to compare the E_a values obtained with the sum of the E_a values for the respective constitutent oxides. In the potassium molybdate series the differences obtained increase on moving from potassium molybdate to the dimolybdate, the trimolybdate, and then the tetramolybdate (Fig. 5). However the greatest increase in E_a is for $K_2Mo_2O_7$. This is likely to be the most stable of these compounds. The condensation of the coordination polyhedra in the structure of $K_2Mo_2O_7$ results in there being very short M–O bonds which have relatively high dynamic coefficients for bridging bonds.

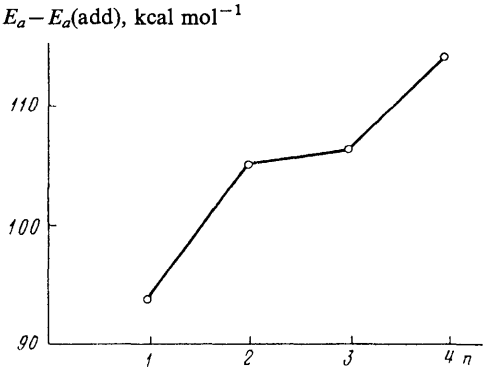


Figure 5. Variation of the activation energy ΔE_a for the potassium molybdates $K_2Mo_nO_{3n+1}$ (n = 1–4) with their composition.

The data for alkali metal molybdates and tungstates presented here and their analysis show that vibrational spectroscopy is a sensitive method enabling very small changes in the structures of the compounds to be recorded. However, because the vibrations of complex condensed systems are not characteristic, it is not always possible to interpret the results obtained unambiguously. Systematic changes in the crystal structure with the size of the alkali metal cation and the cation content in the system show correlations with the thermodynamic properties. Nevertheless the latter, being integrated quantities, are not responsive to the detailed features of the structure of the substance.

References

1. M A Porai-Koshits, L O Atovmyan *Kristallokhimiya i Stereokhimiya Koordinationnykh Soedinenii Molibdena* (The Crystal Chemistry and Stereochemistry of Molybdenum Coordination Compounds), Nauka, Moscow, 1974, 231 pp
2. V K Trunov, V A Efremov, Yu A Velikodnyi *Kristallokhimiya i Svoistva Dvoinykh Molibdatov i Vol'framatov* (The Crystal Chemistry and Properties of Double Molybdates and Tungstates), Nauka, Leningrad, 1986, 173 pp
3. P Caillet *Bull. Soc. Chim. Fr.*, 1965, 1271
4. P Caillet, P Saumagnt *J. Mol. Struct.*, 1969, **4** 191
5. P Caillet, P Saumagnt *J. Mol. Struct.*, 1969, **4** 351
6. W H Zacharasen *Acta Crystallogr.*, 1961, **14** 229
7. W L Bragg *Proc. R. Soc., London, A*, 1927, **113** 642
8. I Lindqvist *Acta Chem. Scand.*, 1950, **4** 1066
9. K Okada, H Morikawa, F Marumo, S Iwai *Acta Crystallogr., Sect. B*, 1974, **30** 1872
10. B K Gatehouse, P Leverett *J. Soc. Soc. A*, 1969, (5) 849
11. A S Koster, F X N M Kools, R D Rieck *Acta Crystallogr., Sect. B*, 1969, **25** 1704
12. F X N M Kools, A S Koster, R D Rieck *Acta Crystallogr.*, 1970, **26** 1974
13. R D Shannon *Acta Crystallogr., Sect. A*, 1976, **32** 751
14. K Okada, H Morikawa, S Iwai *Acta Crystallogr., Sect. B*, 1975, **31** 1451
15. M Seleborg *Acta Chem. Scand.*, 1967, **21** 499
16. K Okada, H Morikawa, F Marumo, S Iwai *Acta Crystallogr., Sect. B*, 1975, **31** 1200
17. S A Margaril, R F Klevtsova *Kristallografiya*, 1971, **16** 742
18. M Seleborg *Acta Chem. Scand.*, 1966, **20** 2195
19. B M Gatehouse, P Leverett *J. Chem. Soc. A*, 1968, (6) 1398
20. K Okada, H Morikava, F Marumo, S Iwai *Acta Crystallogr., Sect. B*, 1976, **32** 1522
21. B M Gatehouse, B K Miskin *J. Solid State Chem.*, 1974, **9** 247
22. V Krishmanoorthy *J. Chem. Soc., Dalton Trans.*, 1974, (20) 2170
23. M Seleborg *J. Chem. Soc., Chem. Commun.*, 1967, (21) 1126
24. K Okada, F Marumo, S Iwai *Acta Crystallogr., Sect. B*, 1978, **34** 3193
25. B M Gatehouse, P Leverett *J. Chem. Soc. A*, 1971, (13) 2107
26. B M Gatehouse, B K Miskin *Acta Crystallogr., Sect. B*, 1975, **31** 1293
27. R Salmon, P Caillet *Bull. Soc. Chim. Fr.*, 1969, 1569
28. H J Becher, *Z. Anorg. Allg. Chem.*, 1981, **474** 63
29. K J Dean, G R Wilkinson *J. Mol. Struct.*, 1982, **79** 293
30. B K Breitinger, L Emnaert, W Kreb *J. Mol. Struct.*, 1980, **61** 195
31. M Spoliti, L Bencivenni, M Mattese, C S Nunziante *J. Mol. Struct.*, 1980, **60** 259
32. M Spoliti, C S Nunziante, L Bencivenni, L D'Allessio *High Temp. Sci.*, 1980, **12** 215
33. L Bencivenni, K A Ginderich *J. Chem. Phys.*, 1982, **76**(I) 53
34. J R Beattie, J S Ogden, D D Price *J. Chem. Soc., Dalton Trans.*, 1982, (3) 505
35. L J Basile, J R Ferraro, P Labonville, M C Wall *Coord. Chem. Rev.*, 1973, **11** 21
36. R H Busey, O L Keller *J. Chem. Phys.*, 1964, **41**(1) 215
37. M E Poloznikova, O I Kondratov, V V Fomichev *Zh. Neorg. Khim.*, 1988, **33**(3) 617 [English translation in *Russ. J. Inorg. Chem.*, 1988(3)]
38. G M Clark, W P Dogle *Spectrochim. Acta*, 1966, **22** 1441
39. T Dupuis, M Veltange *Mikrochim. Acta*, 1963, 232
40. P Tarte *Spectrochim. Acta*, 1962, **18** 467
41. M E Poloznikova, O I Kondratov, V V Fomichev *Zh. Neorg. Khim.*, 1988, **33**(8) 2001 [English translation in *Russ. J. Inorg. Chem.*, 1988(8)]
42. M E Poloznikova, O I Kondratov, V V Fomichev *Zh. Neorg. Khim.*, 1988, **33**(10) 2526 [English translation in *Russ. J. Inorg. Chem.*, 1988(10)]
43. H J Becher *J. Less Common. Met.*, 1980, **76** 169
44. S Sheik Saleem, G Aruldhas *Spectrochim. Acta, Part A*, 1983, **39** 630
45. P Tarte, M Liegeois-Duyckaerts *Spectrochim. Acta, Part A*, 1972, **28** 2029
46. V S Urusov *Energeticheskaya Kristallokhimiya* (Crystal Chemistry and Energetics), Nauka, Moscow, 1975, 335 pp
47. V S Urusov, G F Ivanova, I L Khodakovskii *Geokhimiya*, 1967, (10) 1050
48. V P Glushko (Ed.) *Termicheskie Konstanty Veshchestv* (Thermal Constants of Substances), No. X (Li, Na, K, Rb, Cs, Fr), VINITI, Moscow, 1981, Part 1, 299 pp
49. L V Gurvich, G V Karachevtsev, V N Kondrat'ev, et al. *Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu* (Dissociation Energies of Chemical Bonds. Ionisation Energies and Electron Affinity), Nauka, Moscow, 1974, 351 pp
50. V S Urusov, V V Shcherbina *Geokhimiya*, 1966, (10) 1160
51. B K Kasenov *Zh. Neorg. Khim.*, 1991, **36**(6) 1565 [English translation in *Russ. J. Inorg. Chem.*, 1991(6)]

Received 23rd April 1992

Translated from *Uspekhi Khimii* **61** 1623–1655 (1992) U.D.C. 541.138:620.197.3

Cooperative models of dissolution of metal crystals

G V Khaldeev, V V Kamelin
A M Gorki State University, Perm

ABSTRACT. The results of new approaches to the problem of dissolution of metal crystals in electrolytes are summarised and analysed. The analysis is based on consideration of a metal/electrolyte interface as a system of two coupled, structurally organised, condensed phases in which cooperative excitation processes take place. Excitation (suppression) of dissolution is discussed in terms of local initiation (inhibition) of surface linearly extended defects of the crystal structure. The ideas proposed are supported by experimental results.

The bibliography contains 63 references.

Contents

I.	Introduction	889
II.	Kinematic theories of dissolution	890
III.	Dissolution in the form of a monatomic step	891
IV.	Multilayer dissolution steps	895
V.	Soliton dissolution models	897
VI.	Inhibition of motion of dissolution steps	900
VII.	Conclusions	905

I. Introduction

The study of the mechanism of dissolution of metals is a task with many practical applications (protection from corrosion, cementation, electrochemical technologies, etc.). In the last few years new models of dissolution of metals have been proposed[1–3] and in these models the dominant role is assigned to surface defects. The kinetics of dissolution of a metal depends on its crystallographic characteristics governed by the type of face. Different dissolution mechanisms are proposed for flat atomically smooth singular F faces and for rough S and K faces that have surface defects.

According to the Ising and/or cluster representations, the adsorption centres on the surface of a metal form structure elements which are short in one dimension ($\leqslant 10a$, where a is the lattice parameter). The structure motif in adsorbed films of inhibiting surfactants depends on predominance, on the surface of a dissolving crystal, of faces with a specific orientation (hkl). There is a considerable interest in the dissolution of rough S faces with linearly extended surface defects such as steps (ledges). In accordance with the terrace-step-kink (TSK) or terrace-ledge-kink (TLK) model, the terraces are closely packed, whereas extended defects (steps or ledges) carry highly active centres known as kinks, which represent projections of the step edge (Fig. 1).

The possibility of appearance of kinks on steps as a result of thermal fluctuations was first demonstrated by J Frenkel (1945). Heating of modified metal surfaces in vacuum gives rise to monatomic steps with a surface roughness (r). Formation of kinks increases greatly r. An estimate of the roughness of a step due to the formation of kinks (r_K) is important in estimates of corrosion and, if allowance is made only for the first coordination sphere (nearest neighbours), it depends nonlinearly on the metal–metal binding energy (E_{M-M}):

$$r_K=[\sinh(E_{M-M}/2k_BT)]^{-1}$$

where k_B is the Boltzmann constant and T is the absolute temperature.

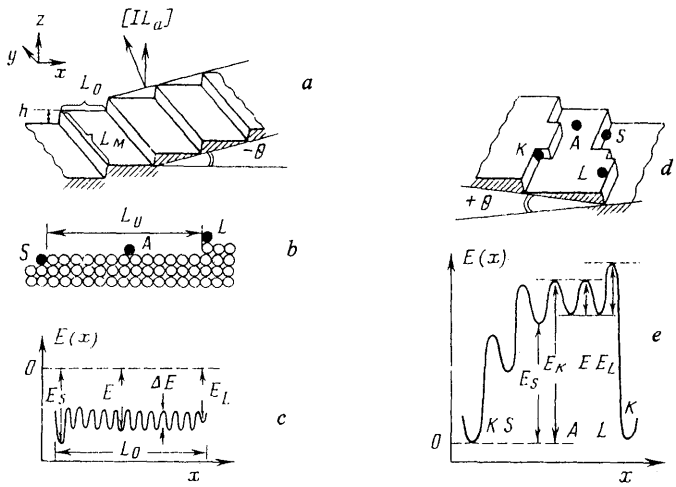


Figure 1. Energy diagram of adsorption of particles on S (a–c) and K (d, e) faces of a crystal. The diagrams show the binding energies of an adparticle on a terrace A (E), at the ledge of a step L (E_L), on the face of a step S (E_S), and in a kink K (E_K); the rest of the notation is explained in the text.

When a metal is in contact with an electrolyte, nonlinear wave processes occur on the surface of the metal crystal and they generate roughness of a dissolution step. Even if the description of dissolution is limited to a planar (two-dimensional) model, computer modelling of the displacement of dissolution steps $<IL_a>$ (L_a is a lattice step and I is the number of steps) on a cubic face of a Kossel crystal[4] shows—if allowance only for the interaction with the nearest neighbours is taken into account—that the process of dissolution does not reduce to the events of ionisation on a metal at specific active centres. The dissolution and growth of crystals is

modelled on the basis of ideas put forward by Gilmer.[5] It had become obvious that when the roughness is strong (i.e. when the Jackson–Temkin factor $E_{M-M}/2k_BT$ is small), the opposite to dissolution, i.e. crystallisation, involves cooperative attachment of chains of atoms and not consecutive growth of a new phase at an active centre.

From the thermodynamic point of view the appearance of roughness during the process of dissolution is the result of the 'fight of a crystal to ensure survival'. This should lower and then stabilise the rate of corrosion. However, when a metal/electrolyte system is acted upon by an external perturbation (for example, when an anodic potential is applied, a crystal is deformed in a solution, activating ions are introduced into an electrolyte, or when a metal is hydrogenated), linearly extended defects (waves) moving on the surface and characterised by a higher chemical activity may produce the opposite effect, i.e. they may prevent deceleration of the corrosion process with time.

It follows from the diagram demonstrating changes in the free energy of an adsorbed atom in the TLK model (Fig. 1) that an adsorbed surfactant particle experiencing a periodic field of the potential E on a terrace (position A) reaches states with higher coordination (K, S, L). The ease and strength of adsorption at a kink (position K) in the case of a low concentration of a surfactant in a solution ($C_{surf} = 10^{-4}-10^{-3}$ M) makes it possible to account for numerous observations of effective nonmonolayer ($\theta_{surf} < 1$ monolayer) inhibiting adsorption.

Stepped surfaces (Fig. 1*a*) are described by the Miller indices of the terraces and steps; for example, in the case of the b.c.c. and f.c.c. crystals we have $[n(110)-(011)]$, $[n(110)-(001)]$, $[n(111)-(001)]$, etc. Some ('magic') vicinal stepped surfaces are stable because of reconstruction of the steps. The width (L_0) of a stabilised step is close to an integral multiple of a superstructure period.[6] In the course of dissolution of a polycrystalline solid its surface is bounded by stabilised grain faces with specific values of (hkl), which are the planes of b.c.c. crystals with the $[n(110)-(001)]$ steps. Less closely packed $[n(110)-(0\bar{1}\bar{1})]$ or $[n(110)-(011)]$ vicinal faces are more stable and carry less strongly bound adatoms. The rate of dissolution of a metal then decreases with time.

However, in spite of the physical attractiveness of the TLK model (ionisation of a metal is regarded as a system of consecutive transitions of metal ions M from the lattice into a solution: $M_L^{n+} \rightarrow M_S^{n+}$), it fails to describe satisfactorily the process of dissolution at high and/or very low corrosion rates. The first problem is the disagreement between the characteristic times of adsorption of the solution particles forming a surface intermediate layer and the characteristic times of elementary events of the ionisation of a metal. The second problem is related to high densities ($i_a \geqslant 10^4$ A/m^2) of anodic currents in the electrochemical process at defects on the K faces; such high local rates cannot be retained for a long ($>10 \times 10^3$ s) time. If the dissolution rate depends only on the local concentration of the electrolyte, then in the absence of diffusion limitations we can expect only spherical corrosion pits. The third problem is the delocalisation of atoms in the first layers of the crystals, which are in contact with a liquid phase, at sufficiently high anodic overvoltages ($\eta_a > 0.2$ V). A special structurally disordered state appears in such layers.

It is therefore necessary to consider alternative mechanisms of dissolution of a metal which allow for the cooperative ionisation events when the first surface layers of the atoms of the metal crystal go over to an excited state. Such resonant excitation creates a quasi-liquid (quasi-crystalline) state in a surface layer of a metal crystal and it is characterised by a short-range order typical of a two-dimensional ($2-D$) adsorption layer in an electrolyte. Concentration and deformation waves appear on the surface of a dissolving crystal as a result of collective excitations in the contact layers of the metal/electrolyte system. Resonant tunnelling of light chalcophilic particles near extended surface defects no longer occurs because of enhancement of the localisation of adsorbed solution particles. Therefore, the action of a corrosion inhibitor (when C_{surf} = const) is manifested more effectively on a stepped surface than on one which is atomically smooth.

This review summarises the results of theoretical investigations of dissolution of transition metals in electrolytes, which is treated by a new approach to the surface layers. A phase transition occurs in such contact layers by excitation of linear one-dimensional ($1-D$) surface defects.

II. Kinematic theories of dissolution

The first theoretical concepts allowing for cooperative effects during dissolution of crystals, known as kinematic theories, were proposed by Lighthill and Whitham[7] and by Frank,[8] and then extended by Hirth, Rouse, and Pound.[9] An analogue of such work in electrochemistry is the unusual approach of Hertz,[10] who considered collective effects of motion of electrolytes without recourse to the concepts of a 'charge' or 'electrochemical potential' and used only the equations for a nonlinear oscillator.

A microscopic approach to dissolution on singular and diffuse (nonsingular) faces of metal crystals shows that a morphological manifestation of a sequence of elementary events involved in the transfer of atoms from a crystal to a liquid phase involves formation of dissolution steps of different height h. The process of dissolution begins as a local form at a subsurface structure defect of a passive metal and rapidly changes to generation of dissolution steps (Fig. 2). Tunnelling electron microscopy has shown that local forms (0.4–0.6 mm) are observed on a passive surface of a crystal of stainless steel even as a result of brief (< 100 s) contact with a 3% aqueous solution of NaCl. The velocity of dissolution steps (V_S) increases on reduction of the density of these steps $\beta_0 = L_0^{-1}$ (which is the number of steps per unit length). In the case of a diffuse surface the height h and the flux of dissolution steps $J_S = f(\beta_0)$ depend strongly on the surface indices (hkl), on the degree of supersaturation of the solution $\Delta\gamma^*$, on the applied electrode potential E, and on the kinetics of diffusion processes at the phase boundary. An important experimental observation is that local dissolution nuclei, usually formed at a subsurface structure defect, grow quite independently and that dissolution steps propagate along the surface without 'noticing' one another.

Even the early kinematic theories of dissolution of ionic crystals deal with systems of $1-D$ (steps) and $2-D$ (terraces) regions with a low step concentration β_0, when the boundary effects can be ignored. Enhancement of dissolution of ionic crystals at steps is attributed to breakdown of the electrical neutrality at a phase boundary and to the long-range effects of steps in the process of their decoration with impurities from the solution. The steps on nonsingular faces of metal crystals have a considerable influence on surface reconstruction in the course of adsorption of the solution particles. A theoretical description of the reconstruction process is based on the theory of phase transitions. This process always occurs on the surface of a metal considered as the main defect of a solid.[11] Adsorption of the solution particles changes the kinetics and

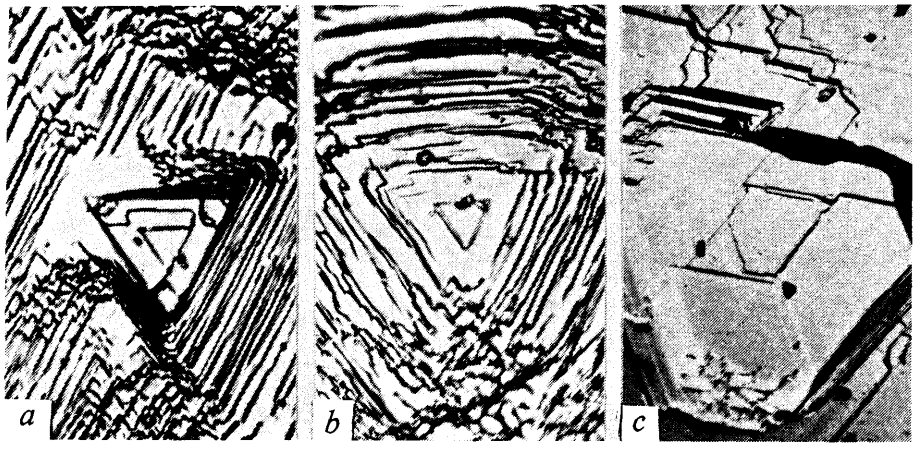


Figure 2. Evolution of dissolution steps beginning from a single subsurface defect in a system formed by (111)Ni and 1 M HNO_3 solution, obtained using an anodic current of density i_a = 50 A/m^2; 298 K; magnification 960. Time t (s): *a*, 20; *b*, 40; *c*, 60.

sometimes even the phase diagram because of reconstruction. The rate of dissolution i of a crystal in an electrolyte is largely determined by supersaturation with metal ions $\Delta\gamma^*_{M^{n+}}$ and with a surfactant $\Delta\gamma^*_{surf}$ at the phase boundary, and by the diffusion of M^{n+} in the bulk of the solution.

III. Dissolution in the form of a monatomic step

An ideally atomically smooth singular low-index F face should form a monatomic step during dissolution and the step should move from the extreme positions on a crystal. Experiments[12] have shown that such monatomic steps appear when the electrode potential is 'cycled' and a surface is prepared carefully under near-equilibrium conditions from a high-purity single crystal.

The shape of monatomic steps, which represent Frenkel–Kontorova surface dislocations, can be described at a given moment t by a wave function

$$\varphi(x, t) = \pi - 4\arctan\{\exp[-(x_i - V_i t)/kD_V]\} \quad (1)$$

where kD_V is the half-width (size) of the Frenkel–Kontorova dislocations; D_V is the diffusion coefficient (viscous); V_i is the velocity of an i-th atom of size a moving from one cell to another; $x_i = ika$ is the diplacement. The mathematical solution given by Eqn. (1) represents a domain wall with a kink; it is obtained by solving the nonlinear differential equation of the sine–Gordon type

$$\varphi_{tt} - \varphi_{xx} + \sin\varphi = 0, \quad (2)$$

where $\varphi = \Phi(X)$ and $X = x_i - V_i t$. The master equation for $\Phi(X)$ is

$$\tfrac{1}{2}\left(V_i^2 - 1\right)\Phi_x^2 + 2\sin^2 \tfrac{1}{2}\Phi = A,$$

where A is a constant of integration related to the wave amplitude.

It follows from an investigation of Eqn. (2) that the appearance of a dissolution step and its subsequent behaviour (including the stability of a step wave against external perturbations by an electrolyte) depends on the initial velocity and the initial amplitude of the wave.[13] Dissolution steps stable in the presence of such perturbations form in at least two cases. The first is represented by $A < 0$ and $V_i^2 - 1 < 0$, when helical waves obeying the following relationships are observed

$$\Phi_x = \pm\left[\frac{2}{1 - V_i^2}\left(|A| + 2\sin^2 \tfrac{1}{2}\Phi\right)\right]^{1/2}, \quad (3a)$$

where Φ_x may increase or decrease. In the second case we have $A > 2$ and $V_i^2 - 1 > 0$, when helical waves obeying the following relationship appear:

$$\Phi_x = \pm\left[\frac{2}{V_i^2 - 1}\left(|A| + 2\sin^2 \tfrac{1}{2}\Phi\right)\right]^{1/2}. \quad (3b)$$

The source of the Frenkel–Kontorova dislocations may be the edges of a crystal, where the characteristics of the displacement processes reach their critical values, or the numerous subsurface defects. When the solution particles are adsorbed, the local positions of a strong disturbance of the translational invariance of a crystal stimulate the motion of a step wave.

In the case of a monatomic dissolution step (a Frenkel–Kontorova dislocation) on a metal crystal the velocity of its propagation in a surface layer is governed primarily by the density ρ of the metal and by the surface tension of stress γ_S:

$$V_S = \left(2\pi\gamma_S/\rho b\right)^{1/2} \sin\left(\frac{\pi a}{b}\right) \Big/ \left(\frac{\pi a}{b}\right). \quad (4)$$

If the distance between the atoms is $b \gg a$ (where a is the lattice parameter), then bearing in mind that $\sin x \approx x - x^3/3!$, we find that Eqn. (4) can be reduced to

$$V_S = (2\pi\gamma_3/\rho b)^{1/2}\left(1 - \frac{\pi^2 a^2}{6b^2}\right). \quad (5)$$

Eqn. (5) is used to describe dissolution of f.c.c. and h.c.p. crystals in view of the anisotropic dependence of the corrosion rate on (hkl).

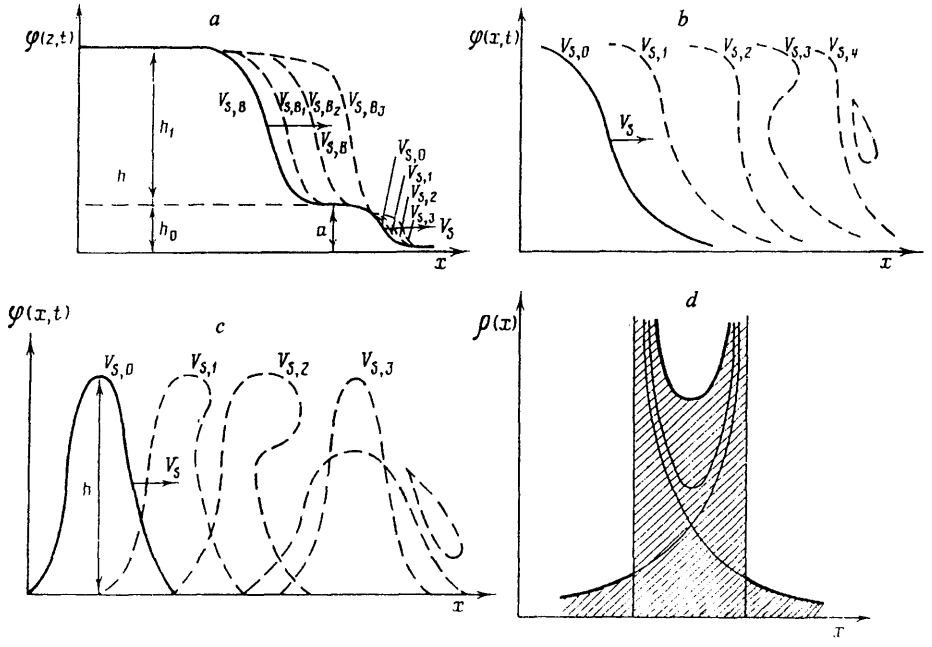


Figure 3. Changes in the surface profile of a dissolving crystal in the case of a shock wave (*a*), a kink (*b*), and a solitary wave (*c*), and characteristic features of the density of a crystal in the course of evolution of a kink (*d*).

Such an integral characteristic as the density $\rho = f(S_{hkl})$, where S_{hkl} is the reticular density of a crystal face, may be modified anisotropically on adsorption of the solution particles (reconstruction of the surface layer). The distance between the first and second (Δa_{12}) layers along the normal to the surface is less than the corresponding distance in the bulk. The changes in Δa_{12} appear under the action of unidirectional mechanical surface tension forces and the stimulus for the reconstruction is provided by the energy gained by the electron states as a result of a small deformation of the surface structure. The appearance of a monoatomic step is usually analysed in terms of the surface stresses γ_S, directional strains $\vec{\varepsilon}$, displacements x_i, and the elastic energy $E_{L,a}$ of a step of atomic length. The energy of appearance of a Frenkel–Kontorova dislocation E_{FK} originates mainly from perturbations of the electron and phonon subsystems, and it has two components: an elastic energy E_{La}, associated with directional strains $\vec{\varepsilon}$ in the course of phase modification of the surface layer, and a linear energy E_K, localised at distances $< k$ (Burgers vector) and estimated in terms of the free energy of an outer face of the step.

A strong reduction in γ_S as a result of adsorption of nucleophilic surfactants (such as halogen ions, OH^-, H^-, etc.) on a hydrophilic surface of a *d*-metal reduces V_S and slows down correspondingly the dissolution rate. An adsorbed surfactant quenches vibrations (reduces the vibration amplitude Φ) in the surface layer of atoms and in the final analysis destroys the resultant surface Frenkel–Kontorova dislocation.

These ideas are based on a Kossel–Stranski model of a defect-free crystal on the surface of which a particle may be in various energy states (Fig. 1*d*). A description of a model of monatomic parts of the first surface layer can be given in two variants: as a shock wave (kink) and as a solitary wave ('rolled-up carpet'). In the former case (*i*) a nonlinear diffusion equation of the Burgers type is considered:

$$\varphi_t + \varphi\varphi_x = D_V\varphi_{xx}, \qquad (6)$$

where D_V is the viscosity of a concentration wave $C(z, t) = C(t)\exp(ikz)$, in which the dependence of the particle concentration C on time t along the coordinate z, directed into a solution, obeys the second Fick law $dC/dt = D_V(\partial^2 C/\partial z^2)$ in the electrode layer (Fig. 3*a*). The amplitude of a concentration wave in a solution is h_1 and the velocity of its motion $V_{S,B}$ is higher than the velocity of a kink V_S in the first surface layers of a crystal of thickness a ($V_{S,B} \gg V_s$, $h_1 \gg a$). The profile of a kink (Fig. 3*b*) corresponding to Eqn. (1) changes in the course of dissolution. In the case of the curves representing the dependence of $\varphi(x, t)$ on x there are regions with a negative slope $[d\varphi(x, t)/dx < 0$, represented by the curve $V_{S,3}]$. From this moment we can expect resonant excitation of a surface layer of a metal and a phase transition $M_L^{n+} \rightarrow M_S^{n+}$, corresponding to the position $V_{S,4}$. The amplitude does not change in the course of the subsequent nondissipative development of the process.

In the phase space on a rolled-up surface, when the projection ($0z$, $0x$) is nonmonotonic — $dx/dt > 0$ above the $dx/dt < 0$ below — the path of a particle in the course of the $M_L^{n+} \rightarrow M_S^{n+}$ transition is such that the motion is slow on the upper and lower planes, but it is catastrophic at the fold.

We shall now analyse the process. It is known[14] that a mathematical description of a quantum-mechanical potential differs from the expression for the potential energy by a multiplicative constant. Any system tends to assume a position which minimises its energy and, if there are several minima, these minima can be identified with different phase states. The minima of the relevant

potential reflect the phase states. The catastrophe theory[15] shows that if a function depends on parameters, then there are such zones or such states that—depending on the set of parameters—a smallest deviation results in a transition from one phase state to another.

We shall consider a potential of the type

$$E(x) = E_0 - a_0 \frac{e^2}{\Omega^{1/3}} x + b\frac{e^2}{\Omega^{2/3}} x + c\frac{e^2}{\Omega} x^3 + d\frac{e^2}{\Omega^{4/3}} x^4,$$

where Ω is the atomic volume; $a_0 = 6 - 12/\sqrt{2} + 8/\sqrt{3} - \ldots$ is the Madelung parameter which depends on the geometry of the metal crystal lattice; b, c, and d are constants that determine the properties of the metal.

We shall find the surface of the minimal potential

$$a_0 \frac{e^2}{\Omega^{1/3}} + 2b\frac{e^2}{\Omega^{2/3}} x + 3c\frac{e^2}{\Omega} x^2 + 4d\frac{e}{\Omega^{4/3}} x^3 = 0$$

and reduce it to the form

$$x^3 + rx^2 + sx + t = 0,$$

where

$$r = \frac{3c}{4d}\Omega^{1/3}, \quad s = \frac{2b}{4d}\Omega^{2/3}, \quad t = \frac{a_0}{4d}\Omega.$$

The boundary of a catastrophic phase transition lies on a surface described by the equation

$$\left(\frac{P_L^3}{3}\right)^3 + \left(\frac{Q_L}{2}\right)^2 = 0, \tag{7}$$

where

$$P_L = \frac{3s - r^2}{3}, \quad Q_L = \frac{3r^3}{27} - \frac{rs}{3} + t.$$

The resultant fold-type singularity is a V-shaped curve with a kink in the space of the parameters. Inside the region bounded by this curve the system is stable. At the boundary of the region the above function has three roots, two of which are identical. Consequently, in the case of the inner part of the region there are three real but different roots. A slight 'tremor' may displace a point from the boundary into the region in question, giving rise to a multisheet surface of a metal and a phase transition at the metal/electrolyte boundary between the condensed media. An analysis of Eqn. (7) shows that the occurrence of a catastrophe does not depend on E_0, e, or Ω: it is related only to the constants a_0, b, c, and d.

What is the process that gives rise to a concentration wave? In a general model of dissolution this is very important, since a nondissipative process of propagation of a dissolution step in a surface layer of a crystal may become a resonant effect on interaction with a concentration wave that appears in the adjoining electrolyte. The functional relationship between $V_{S,B}$ and V_S is manifested by a monotonic increase in V_S on increase in $V_{S,B}$. If $h_0 \gg a$ (where a is the lattice parameter) and the front of a concentration wave overtakes the front of a kink in the metal investigated, a solitary wave (soliton) appears (Fig. 3*c*) and its evolution in a nondissipative scenario involves either conservation of its amplitude or a reduction in the amplitude accompanied by a simultaneous broadening of the face of the wave. In time such a solitary wave may degenerate into a 'rolled-up carpet',

Dissolution differs from crystallisation of a metal because the motion of the M^{n+} ions is in the former case to a condensed medium with an undersaturation of M^{n+}, whereas in the latter case the motion of M^{n+} occurs from a supersaturated state. In the course of dissolution the M^{n+} particles may not 'notice' one another. However, the ionisation occurs at inequivalent positions on the crystal surface and, therefore, after a time t the fast particles (from defects) will overtake the slowly moving ones.[15] The velocity field V_S becomes triple-valued: three fluxes of particles may cross the same point in space (Fig. 3*b*) and their velocities at each point are different. If initially the density of the medium at a point x_0 is $\rho_0(x_0)$, it changes with time giving rise to a density singularity: at a distance x from the point on the fold the density is of the order of $(I\Omega)^{-1/2}$ (Fig. 3*d*). After a sufficiently long time t at the points with an infinitely high density of the medium we can expect formation of particle clusters, i.e. the $M_L^{n+} \rightarrow M_S^{n+}$ transition takes place. This conclusion applies also to a multidimensional space. Therefore, a concentration wave is excited in a surface layer of the electrolyte adjoining a metal because of inequivalence of the active points on the surface of the metal. Such a wave is coupled resonantly to a surface layer of the metal and excites there a kink (Fig. 3*b*) or a solitary wave (Fig. 3*c*).

The concentration wave penetrates the electrolyte when the matching of the solid (crystal) to the electrolyte supersaturated with M^{n+} is coherent. A combination of the equations for the dissolution rate (representing the density of the flux of the M^{n+} particles) $i = i_0 \sin V_j t$ (i_0 is the exchange current density) with the second Fick law leads to an equation describing a concentration wave with an amplitude that decays with depth (along the coodinate z) in the solution[16]

$$C(z,t) = C_0 + \Phi \exp\left(-\sqrt{\frac{V_j}{2D_i}} z\right) \sin\left(V_j t - \sqrt{\frac{V_j}{2D_V}} z - \frac{\pi}{4}\right), \tag{8}$$

where Φ is the amplitude, which is proportional to i_0, and V_j is the velocity of the wave (its angular frequency).

It follows from Eqn. (8) that

$$\frac{\partial C(z,t)}{\partial z} = -\Phi\sqrt{\frac{V_j}{D_V}} \exp\left(-\sqrt{\frac{V_j}{2D_V}} z\right) \sin\left(V_j t - \sqrt{\frac{V_j}{2D_V}} z\right). \tag{9}$$

The amplitude Φ of the concentration wave in the electrolyte and the depth of its penetration z_0 into the electrolyte fall proportionally to $V_j^{1/2}$.

When a kink or a solitary wave propagates in a metal, the value of the viscosity coefficient D_V depends on the action of periodic forces in a regular lattice, when

$$D_V \simeq \nu_L^{-1} \simeq 1\ \mathrm{P}^{-1},$$

where ν_L is the viscosity of a crystal (sound attenuation coefficient), or in the absence of a periodic short-range of a crystal when

$$D_V \simeq D_F/K_C a^2 \simeq 10^{-8}\ \mathrm{P}^{-1},$$

D_F is the diffusion coefficient of phasons and K_C is the elastic (Young's) modulus of a crystal.[17] If D_F is small, the solution of Eqn. (6) differs from Eqn. (1) and corresponds to a shock wave (kink) of the type

$$\varphi(x, t) = kD_V[1 - \tanh^{1/2}(kz - D_V k^2 t)], \tag{10}$$

which obviously appears when filamentary single crystals of metals with perfect singular surfaces are dissolved (Fig. 3*b*). In the limit

$z \to \infty$, we have $(x,\ t) \to 0$, whereas for $z \to -\infty$, we have $(x,\ t) \to 2kD_V$. The approach of a shock wave to the edge of a crystal results in an abrupt fall in the concentration and excitation of a new concentration wave

$$C(t) = C(t_0)\exp[-\alpha(k)t],\ \alpha(k) = D_V k^2, \quad \text{(I)}$$

which moves in the opposite direction. Near the edge the properties of a crystal are unusual: the Gaussian curvature ($R_G = r_1 r_2$, where r_1 is the largest and r_2 is the smallest curvature) has a finite discontinuity of universal amplitude; the fall of the transverse curvature is described by an universal exponent.

In the second case (*ii*) an allowance is made for the fact that crystals very rarely have singular faces and that diffuse (nonsingular) faces have a ready-made step right from the beginning. The subsequent development in the kinematic theories of dissolution of diffuse K faces is due to Lighthill and Whitham[7,13] who based their ideas on the models of dissolution of the surfaces of a crystal which have terraces, steps and kinks on the steps (TLK model). The steady-state velocity of linear steps in accordance with the 'rolled-up carpet' mechanism, representing consecutive detachment of a semi-infinite chain of atoms in the upper layer from atoms in the lower layer, can be described by the following nonlinear relationship containing parameters which can be determined experimentally:

$$V_S = 2K\bar{x}_S \tanh(L_0/2\bar{x}_S)\, D_V\Omega(C_0 - C_0')/(h\delta), \quad (11)$$

where $\bar{x}_S$ is the mean free path in the diffusion of the M^{n+} ions on a step; $\delta = 4.5(D_V/\nu_c)^{1/3}(\nu_c\bar{x}_S/V_L)^{1/2}$ is the thickness of the Nernst diffusion layer (in aqueous solutions this thickness is $\delta \approx 10^{-5}$ monolayer); ν_c is the kinematic viscosity of the solution; V_L is the velocity at which the solution moves away from the steps; $K = f(\tan\theta) \equiv f(P)$ is a kinetic coefficient; C_0 is the equilibrium concentration of the M^{n+} ions in the solutions; C_0' is the concentration of the M^{n+} ions in the metal near the phase boundary. The passage of a dissolution step along the surface of a crystal at a velocity V_S is determined by the relationships between the constants in Eqn. (11). The kinetic coefficient, depending functionally on a slope θ of a given face relative to a singular face (Fig. 1), is governed by the process of incorporation of atoms at the steps[18]

$$K(P) \simeq a\nu_D(a/\bar{L}_K)\exp(-E_{M-M}/k_BT),$$

where $\bar{L}_K$ is the average distance between the kinks on the steps and $\nu_D \approx 10^{13}\ s^{-1}$ is the Debye frequency of vibrations of the surface atoms.

The velocity of translational motion of a step reaches its limiting value $V_{S,\infty}$ when the hyperbolic tangent with the argument $\bar{x}_S \approx L_0/6$ or $L_0/2\bar{x}_S \approx 3$ in the relationship (11) becomes equal to 1:

$$V_{S,\infty} \simeq D_V\Omega(C_0' - C_0)L_0/3\delta h. \quad (12)$$

An analysis of Eqn. (12) shows that if $C_0 \to C_0'$ or, more accurately when the activities of the M_S^{n+} ions in the solution in the surface of the investigated crystal and of the M_L^{n+} ions in the metal are equal, the velocity of a dissolution step falls to zero. The size of the active surface which appears as a result of the passage of dissolution steps is determined by their density $\beta_0 \equiv L^{-1}$ and their height h:

$$L_0 h \equiv h/\beta_0 \simeq (hk_BT/19\Omega E_M)\ln(C_0' - C_0). \quad (13)$$

The relationship (13) includes the free surface enegy E_M, which rises and thus reduces the active surface of a metal. The difference between the concentrations $C_0' - C_0$ determines the supersaturation $\Delta\gamma^*$ at the phase boundary. In other words, we have

$$V_S \sim \Delta\mu = \mu_K - \mu_L = k_BT\ln(C_0' - C_0) \simeq -k_BT\Delta\gamma^*,$$

i.e. the velocity of a dissolution step is proportional to the difference between the chemical potentials of the M^{n+} ions in the solution and of the metal lattice.

The growth (dissolution) rate of a crystal normal to a singular F face in electrolytes can be estimated from a relationship similar to Eqn. (11):

$$V_{S,\perp} = K\Omega C_0(\Delta\gamma * - \Delta\gamma_{cr}^*), \quad (14)$$

where $\Delta\gamma_{cr}^*$ is a critical supersaturation governed by the mechanism of growth (dissolution) of a step, which may be two-dimensional nucleation or a dislocation mechanism. The critical supersaturation $\Delta\gamma_{cr}^*$ is different near the surfaces of large and small crystals and it depends strongly on the index (*hkl*) of the surface.

The undersaturation near the surface of a small crystal results in its faster dissolution; in the case of a polycrystalline aggregate the smaller crystallites (grains) with the orientations of the faces characterised by smaller values of E_M disappear first.

Slowing down of the tangential motion of the dissolution steps may be the result not only of lowering of E_M, but also of crystallographic features of vicinal faces. It had been mentioned earlier[6] that specific 'magic' vicinal surfaces are stabilised by reconstruction. An investigation of the surface structure and of the energetics of the (100)Au and (111)Au vicinal faces by the model of multiparticle forces and molecular dynamics has shown that in the case of surfaces of the $(K11)$Au(100) type, where $K = 3-45$, the 'magic' orientations correspond to the (111) and (511) faces. These surfaces are characterised by local surface energy minima ($E_M = 1.06 \times 10^4$ and 1.04×10^4 meV/nm^2, respectively) of the dependences of the surface energy on $P \equiv \tan\theta$ [where the tilt angle is $\theta = 0-0.5$ rad, defined by $\theta = \tan^{-1}(h/L_0) = \tan^{-1}(h\Delta\mu/19\Omega E_M)$]. Stabilisation of other vicinal faces occurs as a result of formation of a set of these 'magic' orientations for surfaces tilted slightly from (100)Au. In the case of the surfaces $(H + 1,\ M - 1,\ H)$ close to (111)Au, the 'magic' vicinal faces are different: they correspond to minimisation of the energy for $H = 11, 22, \ldots$, when the step with L_0 is a multiple of the superstructure period.[19] Therefore, faceting of the surface by the motion of monatomic steps and formation of 'magic' orientations may reduce the rate of dissolution of the metal to zero. This unexpected result of recent experimental investigations has not yet been considered properly from the practical point of view.

It also follows from Eqn. (11) that an increase in the height h of the steps should slow down the velocity of their motion. A kinetic and morphological analysis of a metal/electrolyte contact between condensed phases, based on the experimental results, demonstrates the opposite: the value of V_S increases on increase in h. This conflict is implicit in the very 'rolled-up carpet' model, which has been applied successfully to monatomic spallation when $h \approx a$. If $h \gg a$, a solitary wave 'collapses' (see curve $V_{S,2}$ in Fig. 3*c*) and the velocity of this wave falls strongly.

Determination of the rate of growth of crystal faces in accordance with the $2-D$ nucleation mechanism,[20] shows that difficulties associated with the relationship between V_S and h can be overcome. The rate of normal growth of a crystal face due to the motion of a growth step is

$$V_{S,\perp} = hi_n S\Big/\left[1 + \left(S\Big/\beta b_n^{1/3}\right)(i_n/V_S)^{2/3}\right], \quad (15)$$

where $i_n = f(\Delta\gamma^*_{cr})$ is the nucleation rate; S is the area of the growing face; $\beta \approx 1$; b_n is the shape factor (in the case of dome-shaped nuclei, we have $b_n = \pi$). Eqn. (15) had been checked by computer modelling using the Monte Carlo methods and by experimental studies of electrochemical nucleation.

In Eqn. (11) the quantity $\bar{x}_S$ for one dimensional diffusion-like random motion is

$$\bar{x}_S \equiv \left\langle U_x^2 \right\rangle^{1/2} = \left(2D_V t\right)^{1/2},$$

whereas in the case of two-dimensional and three-dimensional motion, we have, respectively,

$$\bar{x}_S = 2(D_V t)^{1/2} \text{ and } \bar{x}_S = (6D_V t)^{1/2}.$$

In a surface nonisotropic layer of a crystal the rate V_S must be regarded as dependent on the action of directional forces $\vec{\varepsilon}$ (for example, a gradient of particle concentrations in the regions between the phases). We then have

$$\vec{\varepsilon} = -\frac{\partial}{\partial x} k_B T \ln \frac{C'_0}{C_0} = -\frac{k_B T}{C'_0} \frac{\partial C'_0}{\partial x}. \quad (16)$$

Eqn. (16) follows from generalisation of the Fermi–Dirac distribution to the case of a transition between two phases of any charged particle. In the case of directional (drift) velocity of motion of a dissolution step, we can write down[21]

$$V_S = (D_V / k_B T)\vec{\varepsilon}, \quad (17)$$

where ε is proportional to the displacement Δa and to the step height h, and is governed by directional tangential displacements of atoms in a surface layer $< U_x^2 >$:

$$\vec{\varepsilon} = \Delta a \left\langle U_x^2 \right\rangle h. \quad (18)$$

It follows from Eqns. (17) and (18) that the step velocity V_S is proportional to the step height h at low stresses in the surface layer which set the dissociation steps in motion:

$$V_S = D_V \left(\Delta a \left\langle U_x^2 \right\rangle h\right) / k_B T. \quad (19)$$

The differences in the kinetic situation in respect of the step height h appear not only because of the differences between the drift and diffusion of steps, but also largely as a result of nonuniform adsorption blocking of steps with smaller or larger height h by a surfactant.

IV. Multilayer dissolution steps

At high dissolution rates (anodic process) it is usual to find high steps ($h \geqslant 0.1$ μm) on the S faces; the value of h depends on (hkl) indices of the surface: the greater the deviation from singularity, the higher the step. High-index nonsingular faces of transition metals dissolved in electrolytes form the highest dissolution steps the heights of which are considerably higher than those of monatomic layers and they are quite readily distinguishable when examined in an electron microscope (with a resolution of 0.2–0.3 nm).

The height of a step h, multiplied by its length L_M, provides an estimate of an active surface which, combined with the density of steps β_0 given by Eqn. (13), can be used to obtain a preliminary value of the rate of dissolution of individual crystallites in a surface layer of a metal. For example, Fig. 4*a* illustrates dissolution in a galvanostatic anodic process ($i_a = 5 \times 10^2$ A/m^2, 295 K, $t = 120$ s) of a nickel single crystal with a nonsingular stepped surface close to (111)Ni when immersed in a 5% ethanol solution of HNO_3. The degree of deviation of the close-packed singular (111)Ni surface, deduced from $\gamma' = h\beta_0$, is $\gamma' = 0.4$, and we then have $\theta = \tan^{-1}(\gamma') = 15°$. Differences between the rates of dissolution of the individual crystallites of annealed polycrystalline samples of high-purity metals can also be seen quite clearly (Figs. 4*b* and 4*c*). The experimental data reported in Refs. 22 and 23 demonstrate that in the case of b.c.c. structures a higher rate of dissolution is exhibited by the {111} faces which are those with the 'loosest' packing.

It should be pointed out that already in the early kinematic theories[24] it has been assumed that a stepped surface of a metal has a discrete nature and the velocity of the steps depends on β_0. A change in the separation between the steps L_0 results in a discontinuity of the density of the steps; such an effect is observed readily in the case of polycrystalline samples near crystallite boundaries (Fig. 4*d*). Branching of the steps and a discontinuity of their density gives rise to shock waves [see Eqns. (1) and (10) and Fig. 3]. According to the kinematic theory of dissolution the velocity of a single monolayer microscopic step is higher than the velocity of a multilayer shock wave (Ref. 24), which depends directly on the diffuseness of a face

$$V_S = \left(V_0 - V_1\right) / \left(\gamma'_0 - \gamma'_1\right), \quad (20)$$

where the rate of sinking of the metal is $V = (dz / dt) = \beta_0 h V_S$ and the diffuseness if $\gamma' = h\beta_0$, and the subscripts in the above equation correspond to the times t_0 and t_1 ($t_1 > t_0$). Hence it follows that for a fixed density of steps $\beta_0 = \text{const}$ an increase in the height of a step h tends to increase the velocity of a multilayer step V_S. This conclusion is in agreement with an analysis made above [see Eqn. (19)]

Microscopic steps are crystallographic planes[18] with the orientation P which can be determined from

$$P \equiv \left(dz/dx\right) = h\gamma' + hJ_S\left(dx/dt\right), \quad (21)$$

where x is the direction of motion of the steps, z is the direction perpendicular to such motion, and $J_S = V_S h^{-1}$ is the flux of steps at a given point. It follows from Eqn. (21) that in the case (*i*) when the density of steps β_0 is fixed, the orientation of the surface remains the same during dissolution ($P = \text{const}$), whereas in the case (*ii*) for a specific crystallographic orientation, when $P = \text{const}$, the dissolution occurs where

$$(dx / dt) = dJ_S / d\gamma'. \quad (22)$$

In the case (*ii*) the condition of conservation of the steps should be observed. In the absence of external perturbations, Eqn. (22) for a metal/solution system transforms to

$$\frac{dV}{d\beta_0} \frac{\partial \beta_0}{\partial x} + \frac{\partial \beta_0}{\partial t} = 0$$

or

$$\frac{\partial \beta_0}{\partial t} + V_c \frac{\partial \beta_0}{\partial x} = 0,$$

where $V_s(\beta_0) = dV/d\beta_0$. If $\beta_0 = \text{const}$, we have

$$\Delta\beta_0 = \frac{\partial \beta_0}{\Delta x} \Delta x + \frac{\partial \beta_0}{\partial t} \Delta t = 0$$

or

$$\frac{\Delta x}{\Delta t} = -\left(\frac{\partial \beta_0}{\partial t}\right) \Big/ \left(\frac{\partial \beta_0}{\partial x}\right) = V_S.$$

The regions of constant tilt characterised by P = const (kinematic waves) have the same dissolution rates, which agrees with Eqn. (20).

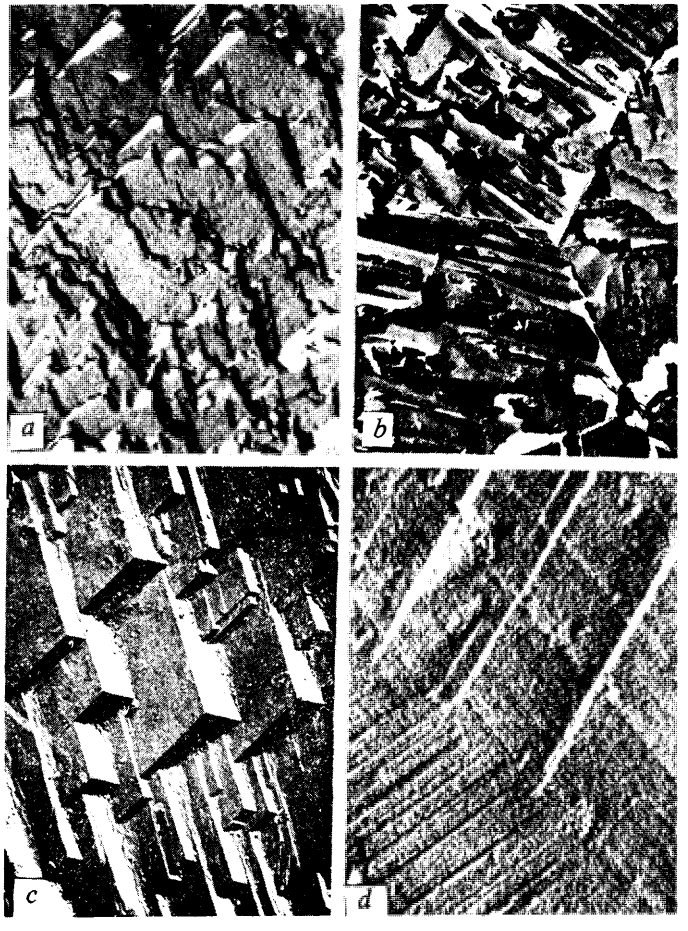


Figure 4. Dissolution steps on a [7(111)–(001)]Ni face (*a*), and on surfaces of high-purity (99.99%) polycrystalline samples of Ni (*b*) and Fe (*c*); magnification 12 000. Photomicrograph *d* shows a discontinuity of the density of dissolution steps on the surface of an Fe bicrystal.

If steps can travel not only along the x direction but also along the y axis on a face of a crystal (xy plane), an equilibrium shape of a crystal is described by[25]

$$z(x, y) = (\partial z / \partial x)x + (\partial z / \partial y)y - E_M(P), \quad (23)$$

where

$$x = (\partial E_M / \partial P)_x, \; y = (\partial E_M / \partial P)_y,$$
$$P = (\partial z / \partial x, \partial z / \partial y) = (P_x, P_y).$$

The term $E_M(P)$ is the free surface energy determined for a (hkl) face within the framework of the TSK model

$$E_M(P) = \gamma_S(\theta_L)|P| + \sigma_S(\theta)|P|^3 + \theta_L|P|^4,$$

where θ_L is the angle between the y axis in the direction of motion of the steps and σ_S is the specific surface energy.

In an analysis of the dissolution mechanism of metal crystals it is necessary not only to deal with the kinetic and morphological differences between the theory and experiment, but also to allow for the fact that the cooperative motion in the surface layer of a crystal (which differs considerably in the physical sense from the bulk) is practically dissipation-free. In a theory of solitons[26] a series of solutions of nonlinear diffusion equations has been proposed to describe a kink or a solitary wave (Figs. 3*b* and 3*c*). In practice it is possible to observe monatomic dissolution steps (Frenkel–Kontorova dislocations), by tunnelling electron microscopy, in an electrolyte and steps of significant height in the range 10^2 nm $\leqslant h \leqslant 10^4$ nm can be studied by optical spectroscopy and by the replica method (Figs. 2 and 4). It should be pointed out that a concentration wave which reaches the edge of a dissolution step may excite the passage of a kink in a plane perpendicular to the initial one. This process can account for the retention of an abrupt face on dissolution steps even after prolonged corrosion (Fig. 4).

We shall now go over from considering dissolution steps in the form of Frenkel–Kontorova dislocations [monatomic steps, see Eqn. (1)] to the dependences that describe the excitation of several surface layers of atoms. If the lattice step of a cubic Kossel–Stranski crystal (see Figs. 1*a* and 1*b*) is denoted by L_a, the potential describing the interaction of an immobile lower layer with the i-th atom in the upper layer is

$$U(x, t) = A[1 - \cos(2\pi x_i / L_a)], \quad (24)$$

where $x_i = ika$ is the displacement of the i-th atom and A is the amplitude.

The mean-square displacements of atoms in surface layers are anisotropic in respect of the dependence on the directions $<hkl>$ in a crystal and depending on its lattice (b.c.c., f.c.c., etc.). Subject to Eqn. (24), we obtain the following equation of motion:

$$m\ddot{x}_i = -2\pi A L_a^{-1} \sin(2\pi x_i / L_a) + \beta(x_{i+1} - 2x_i + x_{i-1}), \quad (25)$$

where making the substitutions $\Phi_K = 2\pi x_i / L_K$, $A = L_a^2 \overline{A}$, and $\beta = \overline{\beta} L_a^{-2}$ (β is the force constant) and going to the limit $L_a \to 0$ can yield one of the forms of the sine–Gordon equation

$$m\Phi_{tt} = \overline{L}_a \Phi_{xx} - (2\pi)^2 \overline{A} \sin \Phi, \quad (26)$$

where m is the mass of a soliton representing a dissolution step.

The solution of the soliton Eqn. (26) is a kink similar to a Frenkel–Kontorova dislocation

$$\varphi(x, t) = 4 \operatorname{arctg}\left[\exp 2\pi x \left(\overline{A}\overline{\beta}\right)^{1/2}\right], \quad (27)$$

which is formed at the expense of an energy

$$E_S = 4\pi^{-1}\left(\overline{A}\overline{L}_a\right)^{1/2}, \quad (28)$$

corresponds to 5–10 eV/atom and localised in a very small volume of a crystal (with a radius not exceeding 5a).

In general, the energy of a soliton is proportional to its mass (in accordance with the relationship similar to that used in the special

theory of relativity)

$$E_S = mV_0^2\left(1 - V_S^2/V_0^2\right)^{-1/2}, \quad (29)$$

where V_0 is the velocity of small-amplitude elastic waves (which is the velocity of sound in a metal). It follows from Eqn. (29) that if $E_S \leqslant 1$ eV, the velocity of a dissolution soliton, like that of a dislocation in a crystal, cannot exceed the velocity of sound in a given metal ($V_0 \leqslant 10^3 - 10^4$ m/s). In fact, numerous microscopic observations of the development of the morphology of the surfaces of metal crystals undergoing dissolution demonstrate that the velocities of dissolution steps are relatively low ($< 10^4$ m/s).

V. Soliton dissolution models

It follows from Eqn. (28) that a dissolution step forms a kink if the directional motion of atoms takes place in a surface layer of a crystal. Such motion is local and, as demonstrated by the above analysis, is in the nature of beats. The question is what are the mean-square displacements $(\overline{AL}_a)^{1/2}$ necessary for the appearance of a kink and what are the reasons for the displacements? The reasons can be adsorption of chalcophilic surfactant particles on the surface of a crystal or a charge (electron) density wave. The amplitude of waves moving tangentially relative to the surface (surface Rayleigh waves) decays exponentially with distance from the surface. These elastic waves in the bulk of a crystal represent superposition of waves with longitudinal and transverse components; in the case of surface waves it is not possible to separate the components.[27]

In the approximation of an ideal lattice the thermal vibrations of atoms in deeper layers can be estimated as follows. The distribution of the amplitudes of the vibrations is described by the Gaussian[28]

$$P_L(U) = \left(2\pi\langle U^2\rangle\right)^{-3/2} \exp\left[-U^2/2\langle U^2\rangle\right], \quad (30)$$

where $< U^2 >$ are small amplitudes of the distributions. In the $1-D$ case, we have

$$P_L(U) = \exp\left[-U_x^2/2\langle U_x^2\rangle\right]\left(2\pi\langle U_x^2\rangle\right)^{1/2}. \quad (31)$$

For cubic crystals, we obtain

$$\langle U_x^2\rangle = \langle U_y^2\rangle = \langle U_z^2\rangle = 1/3\langle U^2\rangle.$$

In the $2D$ case the square of the thermal amplitude of the vibrations is $< U_S^2 > = < U_x^2 > + < U_y^2 >$. The Debye temperature is $\theta_D = h_P \nu_D / k_B$ and, therefore,

$$\langle U^2\rangle = \frac{3h_P^2 T}{m_a k_B \theta_D^2}\left[\Phi\left(\frac{\theta_D}{T}\right) + \frac{\theta_D}{4T}\right], \quad (32)$$

where

$$\Phi(\xi) = \frac{1}{x}\int_0^x \frac{y\,dy}{e^y - 1}$$

is the Debye function, m_a is the mass of an atom, and h_P is the Planck constant. The Debye function can be represented graphically by a straight line when the coordinates are $\Phi(\theta_D/T)$ and θ_D/T; then, in the case of low amplitudes in the distributions, we have

$$\langle U^2\rangle = 439.2\left[\left(\frac{\Phi(\xi)}{x} + \frac{1}{4}\right)\Big/ m_a\theta_D\right], \quad (33)$$

where $\xi = \theta_D/T$. The Debye temperatures and the mean-square deviations are listed in Table 1 for a number of d metals and it follows from this table that the maximum values of θ_D and the minimum values of $< U_x^2 >$ are exhibited by the d metals with a half-filled d shell (Cr, Mo, W). These are the metals that form the most stable oxide structures and have a higher resistance to chemical action. The thermodynamic stability of the transition metals is related to the ease of the $s \rightarrow d$ electron transition; it rises steeply along the $3d < 4d < 5d$ series of metals (and this is accompanied by a rapid fall of θ_D at high values of $< U_x^2 >^{1/2}$).

Table 1. Parameters of d metals at 293 K.

Metal	Type of lattice	a, nm	θ_D, K	$\langle U_x^2\rangle^{1/2}$, nm
V	b.c.c.	0.3024	360	0.0082
Cr	b.c.c.	0.2884	485	0.0061
Fe	b.c.c.	0.2867	420	0.0068
Ni	f.c.c.	0.3524	425	0.0065
Cu	f.c.c.	0.3615	315	0.0084
Nb	b.c.c.	0.3300	275	0.0079
Mo	b.c.c.	0.3147	380	0.0057
Rh	f.c.c.	0.3803	340	0.0061
Pd	f.c.c.	0.3890	275	0.0074
Ag	f.c.c.	0.4086	215	0.0093
Ta	b.c.c.	0.3306	245	0.0064
W	b.c.c.	0.3165	310	0.0050
Pt	f.c.c.	0.3923	225	0.0066
Au	f.c.c.	0.4078	170	0.0087

The displacements of atoms in the surface layers of the metals have their own cooperative characteristics. Anisotropic mean-square displacements are inversely proportional to the frequency ($\nu_D = k_B T/h_P \approx 10^{13}$ s^{-1}) of vibrations of single atoms near their equilibrium positions:[29]

$$\langle \overline{AL}\rangle^{1/2} \equiv \langle U_{\vec{r}}^2\rangle = (h_p/2m_a)\int_0^{\lambda_m} \lambda^{-1/2}\rho_{\vec{r}}(\lambda)\coth(h_p\lambda^{1/2}/2k_BT)\,d\lambda, \quad (34)$$

where λ_m is the maximum value of the square of the frequency; $\rho_{\vec{r}}(\lambda)$ is the spectral density due to the vector $\vec{r}$. Displacements (quasi-stable pulsations) each reach several nanometers. Cooperative displacements of atoms due to the passage of a soliton in the form of a kink facilitate mass transfer of metal ions to a solvated state in the solution $M_L^{n+} \rightleftarrows M_S^{n+}$. The resultant local supersaturation in the electrode layer induces a delay before the appearance of the next soliton. Improvement in convection conditions [lower values of δ and ν_c, see Eqn. (11)] increases the frequency of appearance of a dissolution soliton.

A different soliton solution can be in the form of a solitary wave. We shall base it on the Boussinescq equation[30] for the $1-D$ case. We shall assume that there are N particles with a unit mass m_a and fixed final points; $x_{r,i}^{\rightarrow}$ is the displacement from an equilibrium

position of the i-th particle in the direction $\vec{r}$; then, the equation of motion can be written in the form

$$\ddot{x}_{\vec{r},i} = f\left(x_{\vec{r},i+1} - x_{\vec{r},i}\right) - f\left(x_{\vec{r},1} - x_{\vec{r},i-1}\right), \quad (35)$$

where

$$f(x_{\vec{r}}) = \gamma x_{\vec{r}} + \alpha < x^2_{\vec{r}} >,$$

i.e. the nonlinearity is quadratic and α and γ are the constants which can be determined experimentally. We shall introduce $L_a = \sqrt{2a}$ (lattice step) and define the variable representing the displacement $x = ika$ (here, $k = \sqrt{2}$) as the distance along the lattice; we shall also define the slope $P = dz/dx$ as $x_{\vec{r}} = L_a P$. Then, $\varphi = \partial P/\partial x$ is described by the Boussinescq equation

$$\varphi_{xx} - \varphi_{tt} + 6\left(\varphi^2\right)_{xx} + \varphi_{xxxx} = 0. \quad (36)$$

We shall identify the cases in which a soliton solution is obtained. The existence of such a solution was pointed out by Hiroma.[31] We shall seek the solution in the form $\varphi(\zeta) = \varphi(x - V_i t)$. Substituting in Eqn. (36) and integrating twice from respect to ζ, we obtain

$$\varphi_{\zeta\zeta} = A_\zeta + B - \left(1 - V_i^2\right)\varphi - 6\varphi^2, \quad (37)$$

where A and B are integration constants. We shall assume that $A \equiv 0$. We shall show that in this case there is a soliton described by

$$d^2\varphi / d\zeta^2 = B - \left(1 - V_i^2\right)\varphi - 6\varphi^2. \quad (38)$$

We shall substitute $d\varphi/d\zeta = z$ in Eqn. (38), which gives

$$d^2\varphi / d\zeta^2 = (dz / d\zeta)(d\zeta / d\varphi) = (dz / d\varphi)z,$$

$$zdz = [B - (1 - V_i^2)\varphi - 6\varphi^2]d\varphi$$

or

$$z^2/2 = B\varphi - \frac{1}{2}\left[\left(1 - V_i^2\right)\varphi^2\right] - 2\varphi^3 + D,$$

where D is an integration constant. We shall introduce

$$B\varphi - \frac{1}{2}\left[\left(1 - V_i^2\right)2\varphi^2\right] - 2\varphi^3 + D = f(\varphi), \quad (39)$$

and then we shall integrate Eqn. (39) as the equation of conservation of motion of particles in a field with the potential $f(\varphi)$ bearing in mind that φ and $\zeta = x - V_i t$ are the spatial and temporal coordinates. A solitary wave on the surface of a crystal appears if the roots of the cubic polynomial obey the condition $\gamma = \beta \neq \alpha$, where $\gamma \leqslant \beta \leqslant \alpha$.

Since $\lim_{\zeta=\pm\infty} \varphi(\zeta) = \varphi_{\pm\infty} = \gamma$, it follows that by introducing $\alpha - \gamma = \Phi_z$ and integrating (Φ_z is the amplitude of a displacement normal to the surface of a dissolving crystal), we obtain the following solution in the form of a solitary wave:

$$\varphi(\zeta) = \varphi_\infty + \Phi_z \operatorname{sech}^2 \sqrt{\frac{\Phi_z}{2}}\left[x - \left(\Phi_\infty + \frac{\Phi_z}{3} t\right)\right]. \quad (40)$$

An analysis of Eqn. (40) demonstrates that, in contrast to a kink [see Eqns. (1), (10), and (27)], a solitary wave describes less satisfactorily the process of dissolution (Fig. 3). It is found that the solitary-wave mechanism of dissolution begins to predominate when the density of a metal ρ is low, the directional interparticle interaction forces $\vec{\varepsilon}$ are weak, and the values of Δa are large. Shorter characteristic times of adsorption of the particles in the solution are required in the case of a solitary wave. Suppression of the motion of a kink is usually due to adsorption of the solution particles and the formation of stable films on steps.[29–32]

Therefore, we have to distinguish the motion of small (monatomic steps, representing Frenkel–Kontorova surface dislocations) and large (high dissolution steps) solitons on the surface of a crystal. Depending on the anodic value of a voltage η_a [and, consequently, on the supersaturation near the surface $\Delta\gamma^* = f(\eta_a)$], there can be quite considerable differences in the morphology of the dissolving surface. The experimental observations of Heusler et al.[36] of the distribution of steps with different kink concentrations ($\beta_{0,k}$) on a close-packed (110)Fe and 'loose' (112)Fe faces, dissolved in 1 M $NaClO_4$ and 1 M $HClO_4$ solutions, had demonstrated that $\beta_{0,k}$ depended linearly on $\eta_a = \partial \ln \beta_{0,k}/\partial \eta_a = F/RT$ (F is the Faraday constant) and increased on enhancement of the potential E of the iron electrode. The average distances between the steps $\overline{L}_0$ (when η_a = const) decreased (but the density β_0 increased) on increase in pH; $d\tan\overline{L}/d\mathrm{pH} = -0.6$.

The velocity of large parallel dissolution (growth) steps is described by a relationship similar to Eqn. (11) if use is made of the theory of Burton, Cabrera, and Frank.[8,24] If the velocity of these steps V_S is proportional to the flux

$$V_S = L_0 J_S / S_{hkl}, \quad (41)$$

the flux becomes

$$J_S = \frac{2}{L_0}\Gamma_\infty D_V \left(\frac{\Delta\gamma^*}{\gamma_\infty}\right)\frac{\sqrt{2}}{\overline{x}_S}\tanh\left(\frac{L_0}{\sqrt{2}\overline{x}_S}\right), \quad (42)$$

where Γ_∞ is the maximum coverage of the surface by particles M_L^{n+} and

$$\tanh\left(\frac{L_0}{\sqrt{2}\overline{x}_S}\right) = [1 - \exp(-2L_0/\sqrt{2}\overline{x}_S)]/[1 + \exp(-2L_0/\sqrt{2}\overline{x}_S)].$$

If $\overline{x}_S = a$ (where a is the lattice parameter), the quantity $\sqrt{2}\overline{x}_S$ corresponds to a lattice step

$$(L_a = \sqrt{2}a = \sqrt{2}\overline{x}_S)$$

and the whole surface area of a crystal becomes active.

If (case i) the distance between the steps is considerably less than the mean free path of ions M^{n+} on a step, $L \ll \overline{x}_S$, then

$$\tanh(L_0/\sqrt{2}\overline{x}_S) \to L_0/\sqrt{2}\overline{x}_S$$

and the flux depends linearly on the supersaturation

$$J_S = \tau_{\mathrm{surf}} \nu_D \Delta\gamma^*,$$

where τ_{surf} is the lifetime of surfactant particles M_L^{n+} in a surface layer given by $\tau^{-1}(M_L^{n+}) \approx \nu_D \exp(-\Delta H_{\mathrm{des}}/k_B T)$ and ΔH_{des} is the heat of desorption of the M_L^{n+} particles in the course of the process $M_L^{n+} \to M_S^{n+}$.

If (case ii) $x_S \ll L_0$, then

$$\tanh(L_0/\sqrt{2}x_S) \to 1$$

and the flux is governed by the surface morphology:

$$J_S = [L_0/\sqrt{2}\overline{x}_S]^{-1} \tau_{\mathrm{surf}} \nu_D \Delta\gamma^*.$$

The M^{n+} ions in the metal lattice (M_L^{n+}) are not equivalent to the ions M_S^{n+} in the low-entropy electrode layer of the electrolyte. In the electrolyte they are solvated, whereas in the metal lattice they are

screened by the electron gas. The high supersaturation $\Delta\gamma^*$ in terms of the M^{n+} ions in the electrolyte layer in the quasi-liquid excited state of the surface layer of the metal allows us to construct a model of dissolution in the form of matched shock waves (bora wind) in the electrolyte of height h_1 and a kink h_0 in the metal (Fig. 3*a*). The velocity of such a fast large dissolution soliton, which appears under anodic potentials, is governed by its height h (the larger the value of h, the higher the soliton velocity):

$$V_{S,B} = [Gh(h_0 + h) / 2h_0]^{1/2}. \quad (43)$$

Here, G is the shear modulus and the heights are related by $h = h_1 + h_0$. If $h_0 \neq 0$ and $h_1 \gg h_0 \approx a$, $h \approx h_1$, then Eqn. (43) becomes

$$V_{S,B} = (Gh^2 / 2a)^{1/2}. \quad (44)$$

The rate of dissolution of a metal predicted by this model depends differently on the heights of the layers in the electrolyte and in the metal.

The models of cooperative dissolution events allow us to explain many new experimental observations that cannot be accounted for by the Burton–Cabrera–Frank (BCF) theory. The soliton mechanism of dissolution allows us to understand the primary event in corrosion of perfect ideally smooth (on the atomic scale) surfaces of single crystals. According to the BCF theory, dissolution of a defect-free ideal face of a metal is impossible, because there is no defect to stimulate the first elementary dissolution event. However, in spite of our better understanding of real crystals, which always have defects, the BCF theory is still valuable,[24] especially as the physical interpretation of the dissolution and growth processes assumed in this theory is very simple and attractive.

What are the reasons (stimuli) responsible for the appearance of a dissolution soliton? They include, above all, local fluctuations of the surface concentration (or density) when the solution particles are adsorbed and the surface coverage by a surfactant is less than one monolayer ($\theta_{surf} < 0.2$ monolayer) and also a metastable state of the surface layer characterised by an increase in the entropy factor and the appearance of fluctuations of strains in this layer. In the case of singular low-index faces a dissolution soliton may appear also because of the alternating, along the z axis, difference between the lattice parameter in the first atomic layers of a surface layer of a metal, which is damped nature $\Delta a_2 = \pm a \exp(-kz)$, where k is the damping (attention) coefficient. The lattice parameter a, occurring also in Eqn. (44) for the velocity of a large dissolution soliton, implies also the physical meaning of the dimensions (or mass) of an atom $\Omega \propto f(a\ m_a)$. At low binding energies E_{M-M}, when the dissolution of M involves solitary waves (Fig. 3*c*), the change in the parameter Δa_z is of fluctuating nature on transition from the state $V_{S,2}$ to the state $V_{S,3}$.

Discontinuous fluctuations of the density in the case of solitary waves (when a phase transition takes place) correspond to dissolution[37]

$$\varphi(x,t) = (10\Gamma\varphi'' / \varphi^{v})^{1/2}\tau^{-1}, \quad (45)$$

where $\tau = x/h_0$ is the time, $\Gamma = h\varphi'''(\vec{\varepsilon})/\varphi''(\vec{\varepsilon})$ is the Grüneisen constant, $h_0 = a(1 + \Delta a)$, and $\varphi(\vec{\varepsilon}) \equiv \varphi[a(1 + \Delta a)]$.

Therefore, the greater the value of Δa, the higher the strains $\vec{\varepsilon}$ in the surface layer and the most probable is the spallation of a $2-D$ plate of thickness $h_0 \approx a$ from the bulk of the metal crystal when this plate has the parameters of the interior of the crystal.

The points of emergence of dislocations on a highly heterogeneous surface of an imperfect crystal give rise to a 'loose' adsorption-active position, the preferential filling of which by the solution particles may induce the appearance of a dissolution soliton (spherical kink). As the process of the dissolution of a metal develops, a linear subsurface effect creates concentric waves and soliton kinks. The motion of the resultant kink during the dissolution of a crystal is then no longer related to the subsurface defect, but it is governed by the indices $<hkl>$ of the surface (by direction of motion of the dissolution steps).

A dissolution step (which in the simplest case is a Frenkel–Kontorova dislocation) can start to move under the influence of a very small ($\Delta a \approx 0.001$ nm) tangential displacement of each atom along the x, y, and/or normal (along z to the surface). When the degree of hydrogenation of a metal is low (the process of hydrogenation is practically always accompanied by the dissolution of a metal), the displacements as a result of modification of the surface by hydrogen may be particularly large ($\Delta a \approx 0.010$ nm). For example, when the surface coverage with hydrogen is $\theta_H = 0.3$ monolayers, the displacement of W atoms in the first surface layer on the (100)W face reaches $\Delta a_{12} \approx 0.003$ nm, whereas for the (011)Ni face it is $\Delta a_{12} = 0.011$ nm (Ref. 38). Surface atoms go over to a metastable state after the passage of a dissolution soliton and this facilitates rapid solvation of the resultant intermediate products, since it gives rise to a slowly moving fluctuation characterised by a lower density of the investigated metal and a higher concentration of the solution particles involved in the solvation process. However, the capillary forces by themselves are insufficient to initiate the first dissolution event and we have to allow for the electronic structure of the metal being dissolved and of the particles being adsorbed (this represents a state of non-Coulomb 'glue' in a double electrical layer located on the metal side).

The soliton mechanisms are fully acceptable (they agree with experiments) for the description of motion of linear defects in surface layers of crystals containing hydrogen[1,3] as well as condensed adsorbed layers of H_3O^+ where a proton can move.[39] In the case of epitaxial matching the double electrical layer between the condensed metal (M) and electrolyte phases when the continuity is preserved across the phase boundary, the cooperative model (Fig. 3*a*) describes practically all the corrosion processes. The soliton dissolution mechanism is capable of accounting for the differences between the rates of corrosion of semiconductor alloys of the III-V type, and of crystalline and amorphous structures with the same chemical composition. A close-packed amorphous structure (representing a disordered alloy of the d elements with one another or with nonmetals), where only the short-range order is preserved, is characterised by a low corrosion rate because of an irregular motion of a soliton along the surface. The dependences of the velocity of propagation of steps (dissolution solitons), with positive or negative deviations from the closest packing, on the index (hkl) of a face and on the direction of growth $<hkl>$ of a crystal was estimated theoretically in Ref. 40 and observed experimentally for hydrogenated low-index faces of nickel single crystals in sulphate solutions.[41]

In the stepped surface model the probability that a particle being adsorbed reaches a step moving 'upwards' is not equal to the probability for a step moving 'downwards' (Ref. 40). This unusual situation can be understood if we turn back to Fig. 1*c*. An adatom diffusing along the x axis along a close-packed terrace to its edges becomes more strongly bound in a 'niche' which is at a position S, than at the 'edge of a dip' L ($E_S > E_L$, $\Delta E = E_S - E_L$). In the

former case an atom is reflected by a potential barrier of a monatomic step (external projection), whereas in the latter it 'drops' into the potential well (E_L). Diffusion of an adatom along the y axis (parallel to a step) depends weakly on the step density β_0^{-1}.

The dependence of dissolution of 'loose' faces of an Ni crystal in 0.5 M H_2SO_4 solution on the direction of removal of layers of crystallographically identical faces[32] can be explained by differences in the adsorption activity of dissolution steps moving along different directions. There is some analogy between this model and positive and negative kinks on dislocations. In the BCF theory these kinetic differences are explained as follows. In the $2-D$ case the slope of the surface after the passage of dissolution steps is

$$P \equiv (dz / dx) = h\beta_0,$$

and the sinking of the surface of a dissolving crystal (velocity of displacement along the z axis of a plane normal to the surface of a crystal) is given by

$$-(dz/dt) = \frac{P}{\rho}\left(\frac{m_a}{2\pi k_B T}\right)^{1/2} = hJ_s.$$

Allowing for the functional relationship between the flux J_S and the density of steps β_0 plotted using the coordinates β_0 and J_S, we can describe two types of step motion: inhibited and uninhibited. In the latter case at low densities β_0 there is a proportionality between β_0 and J_S. For all β_0 the $\beta_0 = f(J_S)$ curve has a negativity curvature ($\partial^2 J_S/\partial\beta_2^0 < 0$) and the velocity of a single dissolution step is higher than the velocity of a kinetic wave: $V_S > V$. If $V_S = V$, there is a proportional relationship, but this time it is between β_0^2 and J_S and the curvature of the kinetic wave exhibits reversal of the sign ($\partial^2 J_S/\partial\beta_2^0 < 0$). It should be pointed out that the efficiency of the action of a surfactant depends on the direction of motion of waves: it is possible to suppress the wave process by a small amount of a surfactant that blocks the wave nucleation centres.

Initiation of the formation of dissolution steps and their propagation on the surface of a crystal occurs when a metal is subjected to tensile elastic loads that alter the values of γ_S. In this case the range of protectic (inhibiting) concentrations of a surfactant moves toward higher values.[42,43] There is special interest in the propagation of a soliton in surface layers of metals covered by oxides, which can be insulating or semiconducting. High-intensity fields in the oxides ($>1 \times 10^5$ V/cm) give rise to electrostriction phenomena and generation of solitons at the metal–oxide surface, where the electrostrictive strains are concentrated.

VI. Inhibition of motion of dissolution steps

The problem of drag or acceleration of steps during dissolution or growth of a crystal by inhibiting (stimulating) impurities is very important in the practical sense and its solution has attracted the interest of many electrochemists and physicists working on crystals. The mathematical solutions proposed for the growth of a crystal with a stepped surface are based on the following mechanism. Impurities are captured by a step moving during the growth of a crystal ($2-D$ process) and their motion disturbs the Boltzmann distribution. The concentrations of impurities in a surface layer formed by the passage of such a step are not the equilibrium values. The process of relaxation results in a redistribution of the impurities in the surface layer during the passage of the second step. Therefore, in the kinetic estimates an important characteristic is the density of steps β_0, the frequency W at which they occur, the height h, the frequency f of jumps of impurity atoms into the surface layer from the bulk of the metal, and the frequency f_L of jumps of impurities between bulk layers.

In the case of monatomic spallation (Frenkel–Kontorova dislocations) the solutions of these problems can be obtained using the theory of dislocations: blocking of the motion is due to the formation of chain-like segregations (clouds) along the line of a defect.[21] In the case of a linear $1-D$ system, a chain of atoms in which a defect inhibiting the chain vibrations is incorporated at distances characterised by a period L_D (the defect may be an adparticle of an inhibiting surfactant with a mass exceeding the mass of a crystal atom, $m_d > m_a$) and the solution of the equation of motion of the type given by Eqn. (35) reduces to the differential Korteweg–de Vries equation, which has the following soliton solutions[44]

$$\frac{\partial W_D}{\partial \tau} + \Phi_D W_D \frac{\partial W_D}{\partial \zeta} + V_{S,D}\frac{\partial^3 v_D}{\partial \zeta^3} = 0, \qquad (46)$$

where

$$\Phi_D = (\alpha_D/2\eta_D)\theta^3,\ V_{S,D} = \left(\delta_D\theta^4/2\eta_D\right)\frac{\partial v_D}{\partial \zeta} = W_D.$$

The constants Φ_D and $V_{S,D}$ determine the amplitude and velocity of a soliton with a defect. The parameter

$$\theta = (\eta / \eta_D)^{1/2} = (m_a K_D \beta_D^2 / m_D K \beta^2)^{1/2}$$

contains the constants β and K (velocity constant), as well as m_a (mass of an atom of M): the index D denotes that a particular property describes a defect;

$$\alpha = -3\beta\eta^{1/2},\ \delta = \eta / 12,\ \tau = \varepsilon^3\eta t,\ \xi = \varepsilon(x - t),$$

$$x = \eta^{1/2} n = m_a(2k\beta^2)^{1/2},\ \varepsilon = (m_a - m_D) / m_a$$

is the order parameter. Near a surfactant particle adsorbed and incorporated in the metal lattice we can expect the appearance of additional spherical solitons similar to kinks of subsurface dislocations. The length of an arc for spherical solitons is πr_0 (r_0 is the radius of a critical nucleus). The process of motion of a dissolution step across the resultant obstacles (spherical solitons) is retarded in the $2-D$ case when the condition $L_D \geqslant 2r_0$ is obeyed.

The velocity of a wave described by a Korteweg–de Vries equation of the type (46) is determined by the amplitude Φ_D and the higher the amplitude of the wave, the faster its motion. This is in good agreement with the experimental observations of the process of dissolution of nonsingular faces of crystals with a relatively low ($<99.6\%$) degree of purity. Irregular incorporation (departure from the period L_D) of many inhibiting particles with a large mass m_D destroys a dissolution soliton. Multidimensional ($2-D$ and $3-D$) variants of the Korteweg–de Vries equations demonstrate[26] the possibility of appearance of specially active localised states due to their interaction with solitons.

The lowering of the amplitude and reduction in the velocity of a dissolution step is due to its coarsening and broadening (Figs. 3*b* and 3*c*). Multilayer steps also become coarser as a result of adsorption of the solution particles. The criterion of this dynamic process is[45]

$$E_S^2 / (h\rho\Delta\mu\, k_B T) \simeq r_0 / L_0 \leqslant 1,$$

where $\Delta\mu = \mu_S - \mu_L$; $L_0 = \beta_0 D_{surf}$ is the correlation length; E_S

is the free energy of a step; as pointed out above, in the case of $2-D$ nucleation, we have $V_S \propto K\Delta\mu$ and the critical radius is $r_0 = E_S/h\rho\Delta\mu$.

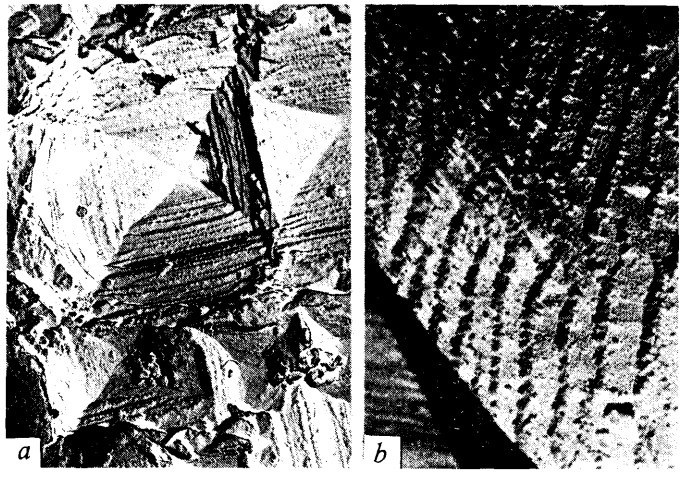


Figure 5. Blocking of the motion of dissolution steps by clusters of adparticles from a solution on [5(111)−(001)]Ni (*a*) and [9(110)−(001)]Cu (*b*) faces; magnification 9000.

The surface energy of a vicinal stepped F face (Fig. 1*a*) consists of two terms:[18]

$$E_V = E_0\cos\theta + (E_S/h)\sin\theta,$$

where E_0 is the surface energy of a terrace (close-packed singular face). When the angle is $\theta = 0, \pm\pi/2, \pi$, the values of E_V have sharp minima. Spreading of a multilayer step occurs when the surface energy E_S is much less than the surface energy of a terrace ($E_S/\gamma_S h \ll 1$), as shown in Fig. 5, but the opposite behaviour is observed and a clear step is conserved if $E_S/\gamma_S h \approx 1$ (see Fig. 4).

Numerous experimental data confirm that the velocity of large solitons depends on the distance between them L_0 (in general, it depends also on β_0: the higher the value of β_0, the lower the velocity V_S). A dependence of the wave velocity on amplitude h follows even from a $1-D$ analysis, which leads to the simple dependence

$$V_S = \left(\frac{hg}{2\pi} + \frac{2\pi\gamma_S}{h\rho}\right)^{1/2},$$

(g is the gravitational contant), from which it follows that lowering of h reduces rapidly the role of the first term and increases the importance of the capillary forces (second term). In the case when $h \approx b$ (the latter representing the distance between the atoms) the Thomson equation reduces to Eqn. (4).

A dissolution step of dislocation dimensions ($h \approx b \approx a$) may be decelerated by the adsorpton of point defects or the emission of vacancies in the course of its motion. The drift (directional) velocity of a step travelling a distance l along x under equilibrium conditions in the system formed by a dissolution step and a point defect can be estimated from [46]

$$V_S = \frac{4\pi D_V}{h}\left[\exp\left(\frac{\Delta a\langle U_S^2\rangle l\beta_0^{-1}}{k_B T}\right) - 1\right] \quad (47)$$

(where D_V is the diffusion coefficient of a point defect). For low values of Δa the velocity of the steps is

$$V_S \propto \frac{4\pi D_V \Delta a\langle U_S^2\rangle l\beta_0^{-1}}{hk_B T}, \quad (48)$$

and for large values, it is

$$V_S \propto \frac{4\pi D_V}{h}\exp\left(\frac{\Delta a\langle U_S^2\rangle l\beta_0^{-1}}{k_B T}\right). \quad (49)$$

The term $\langle U_S^2 > 1\beta_1^{-1}$ represents the area 'swept through' during the motion of a dissolution step. When Δa influences not only the adsorption of surfactant on a step, but also the actual mechanism of the distribution of a surfactant in a double electrical layer located in the electrolyte near the crystal surface, hyperbolic functions appear in the relationships for the velocity

$$V_S \propto \sinh\frac{\Delta a\langle U_S^2\rangle l h}{k_B T}. \quad (50)$$

In electrochemical terms the strength of the dissolution current i_a is given by an expression similar in form to Eqns. (11), (41), and (42), which is natural because the initial assumptions are based on the kinetic representations of the BCF theory. The steps may travel in the form of concentric circles, Archimedes spirals, or linearly extended formations. Without allowance for the kinks on the steps the above description is still quite accurate and has been confirmed by experiments. In the $2-D$ case the slope of concentric steps is described by[47]

$$(dy/dx) = (x + ky)/(kx - y). \quad (51)$$

Integration of Eqn. (51) yields a dependence of the type

$$r = r_0\exp(K\varphi), \quad (52)$$

where $\varphi = \arctan(y/x)$ and $r_0 = (x^2 + y^2)^{1/2}$. If $K = 0$, concentric points propagate from the origin of the coordinates. If $K > 0$, an Archimedes spiral is observed. Eqns. (51) and (52) describe a stable pattern. When dealing with the multidimensional case of the dynamics of changes in a concentric (spherical) kink, considered by I A Bogolyubski and B G Makhan'kov in 1976 (see Ref. 26), it is necessary to base the analysis on the Klein−Gordon equation

$$(\partial^2\varphi/\partial x^2) + (\partial^2\varphi/\partial y^2) - \varphi_{tt} = F(\varphi), \quad (53)$$

which in the one-dimensional case reduces to the sine−Gordon Eqn. (2) if $F(\varphi) = \sin\varphi$. In a situation when $F(\varphi) = \varphi^{IV}$. The initial conditions for a spherical kink expanding from the origin can be written in the form of a steady-state solution of Eqn. (53), which is $\varphi(r, 0) = \tanh(r - r_t)/\sqrt{2}$ and the running radius is $r_t \gg 1$. Numerical calculations on a computer[26] showed that such a kink first collapses (at $t > 0$) and then expands giving rise to what is known as a pulson. In experiments such a situation is encountered when an edge dislocation emerges on the surface of a crystal. The propagation conditions become easier when a screw dislocation emerges on the surface and then a pulson gives rise to a nonvanishing dissolution step.

The structure of equations of the (42) type describing dissolution dynamics becomes more complex in the electrochemical case. Then if a step propagates in the form of an Archimedes spiral,[16] the velocity (current density i) of dissolution is controlled by an electrochemical term multiplied by a hyperbolic function that describes the transport of charges in a double electrical layer at the phase boundary

$$i = i_0\{\exp(\alpha nF\eta_a/RT) - \exp[-(1-\alpha)^n F\eta_c/RT]\}\frac{L_0}{2\pi r_0}\tanh\left(\frac{2\pi r_0}{L_0}\right), \quad (54)$$

where $a \approx 0.5$ is the coefficient of transport by the anodic and cathodic reactions, η_c is the cathodic overvoltage, R is the gas constant, and n is the valence of the electrode reaction,

$$L_0 = (nFD_{M^{n+}}\bar{c}/i_0)^{1/2}\exp(-\alpha nF\eta_a/2RT),$$

$$\tanh\left(\frac{2\pi r_0}{L_0}\right) = [1-\exp(-4\pi r_0/L_0)]/[1+\exp(-4\pi r_0/L_0)].$$

Bockris and Dem'yanovich[48] used, as in the preceding case [Eqn. (54)], the ideas of Whitham[13] to derive a similar relationship for linearly extended steps

$$i = i_0\{\exp(\alpha nF\eta_a/RT) - \exp[-(1-\alpha)nF\eta_c/RT]\}\times$$
$$\times\left(\frac{4\beta_0 D_{M_K^{n+}}}{P}\right)\tanh\left(\frac{P}{4\beta_0 D_{M_K^{n+}}}\right)^{1/2}, \quad (55)$$

where

$$P \equiv L_0^{-1} = i_0\Big/\left(nFC_{S,M_{S,K}^{n+}}\exp\left[-(1-\alpha)nF\eta_K/RT\right]\right), C_{S,M_{S,K}^{n+}}$$

$C_{S,M_{S,K}^{n+}}$ is the equilibrium concentration of M^{n+} on a step, and $D_{M_K^{n+}}$ is the surface diffusion of M^{n+}. The steps disappear when the correlation length is large, so that

$$P \le \beta_0 D_{M_K^{n+}}, \left(4\beta_0 D_{M_K^{n+}}/P\right)^{1/2}\tanh\left(P/D_{M_K^{n+}}4\beta_0\right)^{1/2} = 1$$

and Eqn. (55) reduces to the usual equation of electrochemical kinetics.[16] In the other case when $P \gg \beta_0 D_{M_K^{n+}}$, Eqn. (55) becomes

$$i = i_0\{\exp(\alpha nF\eta_a/RT) - \exp[-(1-\alpha)nF\eta_c/RT]\}\frac{4\beta D_{M_K^{n+}}}{P}. \quad (56)$$

At low anodic overvoltages ($\eta_a < 0.1$ V) and when the radius of curvature of an Archimedes spiral satisfies the condition $r > L_0$, a segment of the spiral travels at a velocity

$$V_S = V_\infty(1 - r_t/r_0).$$

Linearly extended steps are not related to a point source of expansion. The substitution $P^{-1} = \beta_0 \equiv 2L_0$ allows us to obtain from Eqn. (55) a very simple expression for the velocity of such steps:

$$V_S = i_0(L_0C_0nF)^{-1} = i_0(0.5\beta_0C_0nF)^{-1}, \quad (57)$$

from which it follows that if i_0, an increase in the equilibrium concentration C_0 of M_S^{n+} in the solution and of the density of steps β_0 lowers V_S. This conclusion applies also in the case of propagation of steps during growth of a crystal. If the flux deduced from Eqn. (41) is

$$J_S = S_{hkl}V_S/L_0 \quad (58)$$

and the law describing growth obeys the Arrhenius dependence

$$J_S = KC_{surf}\nu_D\exp(-E_S/RT) \quad (59)$$

(C_{surf} is the concentration of a surfactant in the solution, E_S is the metal–surfactant binding energy on a step—see Fig. 1*e*), then the combination of Eqns. (58) and (59) yields

$$V_S = KS_{hkl}^{-1}L_0C_{surf}\nu_D\exp(-E_S/RT). \quad (60)$$

It is clear from Eqn. (6) that the velocity of steps (solitons) of dissolution may be influenced decisively by impurities in the form of inhibiting surfactants in the solution. The concentration of impurities on terraces $C_{A,surf}$ in front of a step and on a step $C_{S,surf}$ are different. The values of $C_{A,surf}$ and $C_{S,surf}$ are related functionally to the parameters of motion of steps by the expression $C_{A,surf} = C_{S,surf}[1 - \exp(-K\beta_0)]$. During the motion of a step the surfactant impurities are pushed away when the surface drops and go into solution (which is opposite to the burying of impurities in a growing crystal).

Inhibiting impurities may 'poison' the motion of steps when crystals with a low degree of purity are dissolved (see Fig. 5) and the blocking particles (the elements C, S, P) are supplied to the surface from the bulk of a crystal which is dissolving: the particles of carbon, sulphur, or phosphorus which cluster on the steps of the surface of a metal lower the dissolution rate. At low concentrations of such particles on the surface ($\theta_{C,S,P} < 0.2$ monolayers) we have the opposite effect of acceleration of the anodic process. For example, in the case of Ni–2.9% P alloys the density of the anodic current i_a increases in acid media, whereas in the case of Ni–12.3% P there is a reduction in i_a (Ref. 49). Examples of this kind are particularly numerous in the case of carbon steels when inert carbon from dissolving cementite Fe_3C decelerates the motion of the dissolution steps. However, the rate of dissolution of low-carbon steels may be higher than that of high-purity zone-melted iron (99.99%) because of the high level of elastic stresses in the matrix. The stresses are induced in α-iron by cementite precipitates.[50]

The velocity of a dissolution step (soliton) depends on the surface tension (stress) in a crystal γ_S. The velocity constant K in Eqn. (60) can be expressed in the form $K = (2\pi\gamma_S)^{1/2}$. A strong reduction in γ_S as a result of adsorption of a surfactant (for example, adsorption of nucleophilic particles such as Hal^-, OH^-, and H^-) on a hydrophilic surface of a *d* metal reduces strongly V_S. If the adsorption of a surfactant is described by the Langmuir isotherm

$$\theta_{surf} = \frac{\Gamma_i}{\Gamma_\infty} = \frac{C_{surf}}{\Lambda + C_{surf}}, \quad \Lambda = \frac{\Gamma_\infty\nu_D\exp(-\Delta H_{ads}/k_BT)}{(kT/2\pi m_D)^{1/2}},$$

the lowering of γ_S on adsorption of a surfactant (heat of adsorption ΔH_{ads}) from solutions with a concentration C_0 can be expressed using

$$d\gamma_S/dC_0 = (\Gamma_i k_B T)/C_{surf}$$

and the Shishkovskii equation, so that the final result is

$$\Delta\gamma = k_\beta T\Gamma_\infty\ln(1 - \Gamma_i/\Gamma_\infty) < 0.$$

The most effective surfactant (reducing γ_S) impurity is adsorbed hydrogen.

When a Langmuir adsorption equilibrium is established and also when γ_S begins to depend linearly on C_{surf}, the reduction in the surface tension $\Delta\gamma$ begins to influence decisively the propagation of a dissolution step, so that its velocity becomes

$$V_S = \theta_{surf}\Pi[E_{surf} - \Delta E_{surf}\exp(-Kt)], \quad (61)$$

where $\Pi = 1 - \exp(-\Delta\mu/k_BT)$ is the undersaturation of a solution in respect of the M_L^{n+} particles, $\Delta E_{surf} = E_{surf} - E_M$, E_M and E_{surf}

are the surface energies of clean and inhibited surfaces, respectively. The physical meaning of the dimensional velocity constant K follows from the above relationship. An adsorbed surfactant quenches oscillations and destroys a soliton and reduces (possibly to zero) the velocity of its propagation on a surface.

How can one block the motion of a dissolution step and thus increase the resistance of a crystal to the chemical action of an electrolyte? The first sufficiently rigorous thermodynamic solution of the problem of disappearance of a step on a singular F face was obtained by Onsager (1946). He used the Ising representations ($2-D$ model) of complete blocking by surfactant particles of one of two adjacent terraces separated by a step on which no surfactant adsorption takes place. In the interpretation of Dunning,[51] the thermodynamic solution is as follows. Let us assume that the potential energy per unit surface area is $E_{surf}/2a_0^2$ (a_0 is the Madelung parameter). A surfactant adsorbed on one of the terraces (θ_{surf} = 1 monolayer) is transferred to an unoccupied terrace and this is accompanied by simultaneous formation of surface vacancies on a deblocked terrace. The transition occurs as a result of diffusion on the surface of an ideal terrace and undoubtedly this is a correlated process which does not necessarily follow the shortest path. The total path or the displacement $<U^2(t)> = f\lambda^2 t$ is governed by the mean length of an elementary (from one adsorption centre to another) jump λ and by the frequency of such jumps f.

The formation of a vacancy increases the surface energy by $4E_{surf}/2a_0^2$, which is the energy of four dangling bonds. The surface energy density is then

$$E_M = E_{surf}/2a_0^2 + \theta_{surf} 4E_{surf}/2a_0^2 \quad (62)$$

and it is the same for adjacent terraces when the degrees of coverage of the steps by vacancies and surfactants become equal ($\theta_{surf} = \theta_V$). Such a situation occurs at T = 0 K. At higher temperatures it follows from the BCF theory that

$$E_S(T) = (E_{surf}/2a_0^2)\left\{2 - \frac{1}{2}\left[1 + (2/\pi)(1-k_1^2)^{1/2} K(k_1)\coth\eta\right]\right\}. \quad (63)$$

where

$$\eta = E_{surf}/2k_BT, k_1 = 2\sinh\eta/\cosh^2\eta$$

and

$$K(k_1) = \int_0^{\pi/2} \left(1 - k_1^2 \sin^2 \nu_i\right)^{-1/2} d\nu_i$$

is an elliptic integral.

The nonlinear relationship (63) includes the main energy parameters of blocking of a step, such as the binding energy of the nearest neighbours, the distance between the interacting particles, and the vibration frequencies of adparticles. The relationship (63) is used widely in computer modelling of modification of crystal surfaces due to external perturbations.

However, this model ignores the change in the energy of vibrations of adparticles. The dependence of $E_S(T)$ on the value of the Jackson–Temkin factor $\eta_1 \exp(-E_{surf}/2k_BT)$ is described by the Avrami–Kolmogorov equation $E(T) = (1 - \eta_1)^n$; a tangent to the curve representing the dependence at a point corresponding to a transition temperature T_c obeys the condition $\sinh H_c = 1$ and, consequently, $T_c \approx 0.57E_{surf}/k_V$. At the transition temperature the surface coverages become equal, $\theta_{surf} = \theta_V = 0.5$ monolayers, and the step separating the terraces disappears.

It was established quite early that the adsorption activity of steps and kinks is considerably higher than the activity of terraces (Fig. 3). An atom on a step (S) or in a kink (K) has at its disposal a large number of d holes the filling of which requires a lower energy: $E_K > E_S > E_L > E_s$ (E_A). The energies of chemisorption of chalcophilic particles (oxygen and hydrogen) on stepped surfaces of transition b.c.c. metals are calculated out by Jardin et al.[52] Differences between the energy characteristics of steps and terraces on surfaces of d.c.c. crystals were quite large: −3.78 and −5.90 eV for oxygen atoms, and −2.30 and −3.78 eV for adsorbed H atoms. In contrast to a metal/gas contact, when there is no need to allow for the short-range order in condensed thin layers adsorbed in different ways on terraces and steps, in the case of metal/electrolyte systems this order is of decisive importance. Purely topological treatments of dimensional effects on adsorption of solvated inhibiting surfactant particles have proved insufficient.

In models of this kind[53] the influence of impurities in a solution on the motion of dissolution steps is considered in two separate variants: blocking of 'loosely' packed steps, which occurs mainly due to adsorption at kinks, and also as a result of formation of discontinuous irregular adparticle islands on close-packed steps (Cabrera fence—see Fig. 5). According to Bliznakov,[54] blocking by a substance being dissolved on a nonideal surface of a crystal by surfactant fluxes may be achieved independently. Consequently, the overall rate of dissolution is a sum of the partial rates of dissolution of a metal $V = \sum_{ij} V_{ij}$. We then have

$$V_i = \Gamma_i(1-\theta_{surf})\exp(-E_a/k_BT), \quad (64a)$$

$$V_j = \Gamma_i\theta_{surf}\exp[-(E_a + \Delta H_{ads})/k_BT. \quad (64b)$$

The surface concentration Γ_i of adparticles is a function of the lifetime of surfactant particles on the surface of a metal $\tau_{surf}^{-1} = \nu_D \exp(-\Delta H_{des}/k_BT)$ and of the heat of desorption of surfactants from the surface ΔH_{des}. Combining Eqns. (64a) and (64b), and introducing the notation

$$E_a = 0.5E_{surf},\ V_{0,l} = \Gamma_i \exp(-E_{surf}/2k_BT),$$

$$E_S(T) = 1 - \exp(-E_{surf}/2k_BT),$$

where $V_{o,l}$ is the rate of dissolution of a crystal in a pure solution, we obtain the simple dependences:

$$V_S = V_{0,l}[1 - \theta_{surf} E_M(T)]. \quad (65)$$

If θ_{surf} = 1 monolayer and E_a = const, it follows from Eqn. (65) that

$$E_M(T) = (V_{0,l} - V_\infty) / V_{0,l}, \quad (66)$$

or if the rate of adsorption of a surfactant exceeds significantly the limiting rate $V_{surf} \gg V_\infty$, we find that

$$V_S = V_{surf}(1 - \theta_{surf}). \quad (67)$$

The blocking of the surface by screening can be allowed for by means of Eqn. (67), but we have to know the density of states β_0 and at least qualitatively the evolution of this density:

$$\beta_0 = f(t).$$

Even the early models have allowed for the energy aspects of adsorption-active linearly extended surface defects in dealing with the adsorption isotherms, so that the pre-exponential terms in Eqns. (64a) and (64b) are modified. In the case of sympathetic changes in the concentrations of a surfactant in the solution C_{surf} and on the surface of a metal Γ_i under conditions of a weak supersaturation

$\Delta\gamma^*$, the velocity of dissolution steps V_S decreases linearly on increase in $\Delta\gamma^*$ [see Eqn. (61)]. Experimental estimates of V_S for transition metals are in agreement with the Langmuir isotherm and are described by dependences of the type[55]

$$V_S = 2\theta_{surf}\Delta\gamma * \left(\frac{2(1-\theta_{surf})}{1+\Delta\gamma * \theta_{surf}}\right)^{1/2}\left[1-\left(\Delta\gamma * \theta_{surf}\frac{1-\theta_{surf}}{1+\Delta\gamma * \theta_{surf}}\right)^2\right]^{-1/2}. \quad (68)$$

At low supersaturations $\Delta\gamma^* = \Delta\mu/k_BT$ the evolution of a step in accordance with the screw dislocation mechanism is faster than at other defects [for example, at (111) stacking faults on f.c.c. crystals[56]]. According to Ref. 56, this is due to the relationships between the nucleation times t_n and the time t_S taken by a step to rotate around a point of emergence of a dislocation dipole on the surface. In the case of low values $\Delta\gamma^*$ we have $t_n > t_S$, whereas at high supersaturations we find that $t_n < t_S$.

An approach based on formal kinetics has been developed subsequently to allow for the formation of discrete $2-D$ and $3-D$ surfactant lattices on substrates with local dangling bonds. In the $1-D$ Ising case the process of blocking of step motion by adsorption of the solution particles is considered on the basis of square $\{IL_a\}$ lattice of a $2-D$ crystal (Fig. 1*a*). This is a very simplified model of the surface of a crystal with growth steps. Atoms in deeper layers $I \geqslant L_a$ lie on the steps and the density of dangling bonds for them is higher.

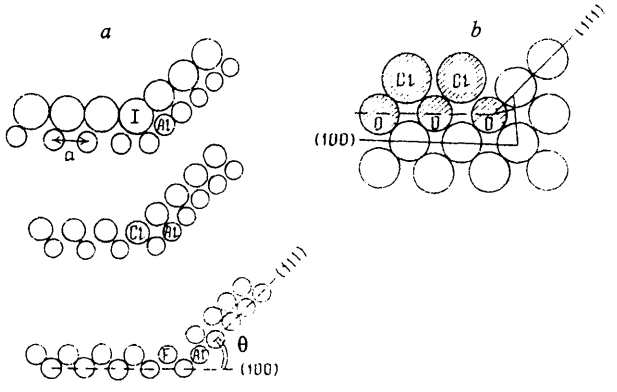


Figure 6. Schematic representations of the adsorption of Hal^- ions on clean (*a*) and oxygen-coated (*b*) stepped [*n*(001)−(111)]Al surfaces.[57]

In a practical analysis of inhibition of dissolution of a metal it is possible to use quite productively the principle of dimensional correspondence, particularly in studies of dissolution of individual faces of metal single crystals in aqueous solutions of the acids HF, HCl, HBr, and HI. For example Politizky and Fischer carried out a pioneering work[57] on the dissolution of stepped Al faces ({001} terraces + {111} close-packed steps) and found that the F^- ions were readily adsorbed in highly coordinated *s* states both on steps and terraces, whereas Cl^- and Br^- ions reached the *s* positions only on cubic {001} faces. Large I^- ions were unable to maintain the *s* states on {001} faces or on {111} octahedral faces (Fig. 6).

In modern interpretations,[58] subject to allowance for the relationship between the electrochemical characteristics of dissolution of Al in halide solutions and the changes in $\{hkl\}$ on a surface, it is usual to consider partial or total transfer of charge in the course of adsorption (Table 2) and formation of an intermediate particle in a two-stage electrochemical process:

$$Al + 2Hal^- \rightleftarrows AlHal_{2,ads} + 2c, \quad (69a)$$

$$AlHal_{2,ads} \rightleftarrows AlHal_2^+ + c, \quad (69b)$$

followed by a fast chemical stage

$$AlHal_2^+ + Hal^- \rightarrow AlHal_3.$$

The transported charge (represented by the Esin−Markov coefficient K_{EM}) depends on the topology of the particles adsorbed on the surface of a metal, starting from the reticular density S_{hkl} of the surface. A reduction in S_{hkl} and an increase in the dimensional mismatch $\Delta r_{hkl} = r_{hkl,Al} - r_{Hal}$ on transition from the (111)Al to the (011)Al surface makes possible a strong adsorption of the F^- ions at a multicentre *s* position. The values of the Gibs potential ΔG and of the normal potentials E_0 depend strongly on the nature of the Hal^- ion, and it is found that the F^- ions are characterised by anomalously high values of these quantities.

Table 2. Correlation between electrochemical parameters of dissolution in halide acids and crystallographic characteristics of aluminium.

Parameter		F^-	Cl^-	Br^-	I^-
Ionic radius, nm		0.136	0.181	0.195	0.216
Atomic radius, nm		0.072	0.099	0.114	0.133
$\Delta r_{hkl} = r_{hkl,Al} - r_{Hal}$, nm	(111)Al	−0.012	−0.039	−0.054	−0.073
	(001)Al	+0.071	+0.044	+0.029	+0.010
	(011)Al	+0.016	+0.089	+0.074	+0.055
ΔG_{AlHal_3}, eV		−12.76	−6.61	−5.24	−3.26
$E_{0,Al/Hal}$, V		4.25	2.20	1.74	1.08
$E_{0,Hal^-/Hal}$, V		2.85	1.36	1.07	0.54
$E_{0,Al/Hal^-}$, V		−1.40	−0.84	−0.67	−0.54

Halogen ions adsorbed in multicentre states on {001} and {011} of f.c.c. crystals 'feel' quite comfortable. The 'loosely' packed steps on the Al surface are blocked effectively by the I^- ions[59] and the change in the capacitance of a single-crystal Au electrode is then well correlated with the terrace length L_M and with β_0. There is experimental evidence that the electrochemical activity of steps is higher also in the case of other crystals of noble metals (Pt, Pd) with a stepped surface. 'Poisoning' of steps (and this applies even more strongly to kinks) results in an effective deceleration of the motion of steps in a corrosion process by the high concentrations of the

halogen ions, in accordance with the series $F^- > Cl^- > Br^- > I^-$ ($C_{Hal} > 10^{-1}$ monolayers). In the case of solutions containing Hal^- on an oxygen-coated stepped surface of Al the oxygen adatoms are gradually displaced by halogen atoms, as postulated by Fischer.[60]

Naturally, the blocking of steps on the surfaces of transition *d* metals and their passivation are performed effectively by oxygen atoms. This process occurs in several stages depending on the coverage θ_0. Direct experiments on well-investigated stepped faces are needed to obtain reliable electrochemical data: they should be carried out by the methods of low-energy electron diffraction (LEED) and an analysis of the electron energy loss spectra (EELS) when hydrogen and oxygen are adsorbed simultaneously.[11,61] Oxygen adsorbed on (001)Ni forms structures with a periodicity $p(2 \times 2)$ when the coverage is $\theta_0 = 0.25$ monolayers; at higher coverages of $\theta_0 = 0.5$ monolayers they transform into $c(2 \times 2)$ structures; in the case of the close-packed (111)Ni face we can expect $p(2 \times 2)$ structures for $\theta_0 = 0.25$ monolayers and $(\sqrt{3} \times \sqrt{3})R30°$ for $\theta_0 = 0.33$ monolayers. Low coverages of (110)Ni with oxygen ($\theta_0 < 0.1$ monolayers) do not modify this phase, which has the loosest structure; high values of θ_0 cause filling of long bridge positions and give rise to $a(2 \times 1)$ structures. The results of investigation by the EELS method of a system of this kind indicate that hydrogen is adsorbed in the molecular form only by kinks (Table 3). If oxygen fills kinks and steps, then hydrogen atoms can be adsorbed only on (001)Ni terraces. When $c(2 \times 2)$ structures appear on terraces at high values of θ_0, the nonsingular stepped (510)Ni surface is transformed into (410)Ni or (610)Ni.

Table 3. Density of adsorbed hydrogen layers on (510)Ni surfaces, determined by the EELS method.

State of adsorbent	Position	Energy loss, meV	
		hydrogen	deuterium
Atom	vacancies on terraces	58	43 60
Atom	short bridge, step	103 142	78 102
Atom	long bridge, step	95 154	71 115
Molecule	kink	28 83 147 398	21 69 116 286

It has been found subsequently[62] that deceleration of the motion of steps is largely due to easier formation of stacking faults on steps which penetrate terraces. Formation of such specially active adsorption positions enhances adsorption and gives rise to kinks on dissolution steps (Fig. 6). Chains of precipitates of inhibiting surfactants form along a step saturated with stacking faults, the motion of such a step slows down, and the result is a reduction in the rate of dissolution of a metal.

VII. Conclusions

We shall conclude our analysis of the cooperative models of dissolution of crystals by stressing the following features. The development of the cooperative models will depend in future on determination of the characteristic features of dissipation-free motion of a dissolution step along a basal plane of a crystal in contact with an electrolyte. These features are related to the conversion of a step from the normal to the superfluid state.[63] The problem has been solved for quantum crystals and the approach is fully applicable to a hydrogen sublattice in surface layers of *d* metals.

The models based on soliton solutions of the equations of motion of ensembles of particles, including elements of the catastrophe theory, provide a picture which is clearest from the physical point of view. Important aspects of the approaches described above are an allowance for change in the fine structure of double electrical layers of a metal and an adjoining electrolyte, for modification of the first layers in a crystal, for changes in the electron and photon subsystems of such a crystal, and for local processes of the solution particles. The cooperative models of dissolution are the most general and are capable of describing dissolution even of defect-free singular faces. This would have been impossible in the case of molecular-kinetic models

References

1. G V Khaldeyev *Proc. Intern. Symposium on Electrochemical and Inhibitor Corrosion Control*, Albena, 1989, Vol. 2
2. I V Katardijiev, G Carter, M J Nobes *Vacuum*, 1989, **39**(11/12) 1069
3. G V Khaldeev, V V Kamelin *Dokl. Akad. Nauk SSSR*, 1990, **310**(3) 653
4. A A Knizel', E B Treivus *Fizika Kristallizatsii* (Physics of Crystallisation), Kalinin Pedagogical Institute, 1989, p. 27
5. G H Gilmer *Science*, 1981, **135**(2) 317
6. A Bartolini, F Ercolessi, E Tosatti *Phys. Rev. Lett.*, 1989, **8**(8) 872
7. M J Lighthill, G B Whitham *Proc. R. Soc. London, A*, 1955, **229** 281
8. F C Frank *Growth and Perfection of Crystals*, McGraw-Hill, New York, 1958, p. 411
9. J P Hirth, G M Pound *Condensation and Evaporation: Nucleation and Growth Kinetics* (Translated into Russian), Metallurgiya, Moscow, 1966, 195 pp
10. H G Hertz *Electrochemistry: A Reformation of Basic Principles* (Translated into Russian), Mir, Moscow, 1983, 231 pp
11. G V Khaldeev, T A Syur *Usp. Khim.*, 1992, **61**(3) 1081 [English translation in *Russ. Chem. Rev.*, 1992(3)]
12. F T Wagner, P N Ross *J. Electroanal. Chem.*, 1988, **250**(2) 301
13. G B Whitham *Linear and Nonlinear Waves* (Translated into Russian), Mir, Moscow, 1977, 397 pp
14. R J Field, M Burger (Editors) *Oscillations and Travelling Waves in Chemical Systems* (Translated into Russian), Mir, Moscow, 1988, 720 pp
15. V I Arnold *Catastrophe Theory* (Translated into Russian), Nauka, Moscow, 1990, 127 pp
16. K J Vetter *Electrochemical Kinetics* (Translated into Russian from German), Khimiya, Moscow, 1967, 856 pp
17. S Ramaswany *Bull. Mater. Sci.*, 1988, **10**(1/2) 75
18. A A Chernov *Sovremennaya Kristallografiya* (Modern Crystallography), Vol. 3, Nauka, Moscow, 1980, pp 7–232
19. A Bartolini, F Ercolessi, E Tosatti *J. Vac. Sci. Technol.*, 1989, **19**(3) 190
20. W Obretenov, D Kashchieev, V Bostanov *J. Cryst. Growth*, 1989, **96**(4) 843

21. J P Hirth, J Lothe *Theory of Dislocations* (Translated into Russian), Atomizdat, Moscow, 1972, 599 pp
22. G V Khaldeev, V F Knyazeva, V V Kuznetsov *Zashch. Met.*, 1975, **11**(6)
23. G V Khaldeev, A B Volyntsev *Izv. Akad. Nauk SSSR, Met.*, 1984, (3) 134
24. K Sangwal *Etching of Crystals: Theory, Experiment and Application* (Translated into Russian), Mir, Moscow, 1990, 496 pp
25. T Yamamoto, Y Akutsu, N Akutsu *Proc. Inst. Stat. Math.*, 1989, **37**(1) 71
26. R K Dodd, J C Eilbeck, J D Gibbon, H C Morris *Solitons and Nonlinear Wave Equations* (Translated into Russian), Mir, Moscow, 1988, 694 pp
27. L D Landau, E M Lifshitz, A M Kosevich, L P Pitaevskii *Teoriya Uprugosti*, Nauka, Moscow, 1987, 246 pp
28. L C Feldman, J W Mayer *Fundamentals of Surface and Thin Film Analysis*, North-Holland, Amsterdam, 1986, 352 pp
29. I A Gospodarev, E S Syrkin *Poverkhnost'*, 1987, (4) 8
30. P L Bhatnagar *Non-Linear Waves in One-Dimensional Dispersive Systems* (Translated into Russian), Mir, Moscow, 1983
31. R Rajaraman *Solitons and Instantons: An Introduction to Solitons and Instantons in Quantum Field Theory* (Translated into Russian), Mir, Moscow, 1985
32. G V Khaldeev, V F Knyazeva *Dokl. Akad. Nauk SSSR*, 1984, **279**(4) 941
33. G V Khaldeev, L A Timofeeva, V V Kuznetsov *Poverkhnost'*, 1984, **3**(3)
34. G V Khaldeev, T F Borisova *Elektrokhimiya*, 1988, **24**(5) 618
35. G V Khaldeev, K A Timofeeva *Bull. Electrochem.*, 1990, **6**(5) 554
36. B Folloner, K E Heusler *J. Electroanal. Chem.*, 1984, **180**(1/2) 77
37. A I Mel'ker *Fiz. Tverd. Tela (Leningrad)*, 1988, **30**(11) 3407
38. J J Arrecis, Y J Chabal, S B Christman *Phys. Rev. B*, 1986, **33** 7906
39. A Gordon *Nuovo Cimento D*, 1990, **12**(2) 229
40. M Presioci, T-M Lu *Surf. Sci.*, 1984, **141**(1) 233
41. G V Khaldeyev, V F Knyazeva *Extended Abstracts of 37th Meeting of Intern. Soc. of Electrochemistry, Vilnius, 1986*, Vol. 1, p. 224
42. A B Shein, G V Khaldeev *Zashch. Met.*, 1983, **19**(5) 805
43. G V Khaldeev, A B Shein *Zashch. Met.*, 1983, **19** 952
44. K S Viswanathan, Ch Venugopal *Indian J. Pure Appl. Phys.*, 1989, **27**(2) 86
45. S Babilar, F Gallet, E Rolley *Phys. Ser.*, 1989, **T29** 265
46. P Sureshkumar, C Subramanian, P Ramasamy, M N Shetty *Scr. Metall.*, 1988, **22**(8)
47. G I Petrovskii *Lektsii po Teorii Obyknovennykh Differentsial'nykh Uravnenii* (Lectures on Theory of Ordinary Differential Equations), Nauka, Moscow, 1964, 272 pp
48. J O'M Bockris, B E Conway (Editors) *Modern Aspects of Electrochemistry* (Translated into Russian), Mir, Moscow, 1967
49. I Flis, D I Duguette *Corrosion (USA)*, 1985, **41**(12) 700
50. G V Khaldeev, V V Kamelin, A V Pevneva *Zashch. Met.*, 1984, **20**(2)
51. W J Dunning *Structure of Surfaces and Adsorption: Gas–Solid Interface* (Translated into Russian), Mir, Moscow, 1970, p. 230
52. J P Jardin, M C Desjongueres, D Spanjoand *Surf. Sci.*, 1985, **162**(1/3) 224
53. E V Treivus *Kinetika Rosta i Rastvoreniya Kristallov* (Kinetics of Growth and Dissolution of Crystals), Leningrad State University, 1979, p 248
54. G M Bliznakov *Kristallografiya*, 1959, **4**(2) 150
55. M Rubbo, D Aquiano *J. Cryst. Growth*, 1989, **94**(3) 619
56. J-M Jin, N-B Ming *J. Cryst. Growth*, 1989, **94**(2) 442
57. F Politizky, R Fischer *J. Am. Ceram. Soc.*, 1955, **38**(3) 102
58. A R Despic *J. Electroanal. Chem.*, 1985, **184**(2) 401
59. A Hamelin, I P Bellier *Surf. Sci.*, 1978, **78**(1) 159
60. Z Fischer *Corros. Sci.*, 1983, **23**(2) 183
61. A-S Martensson *Surf. Sci.*, 1989, **215**(1/2) 55
62. M N Shetty *Surf. Sci.*, 1984, **137**(1) 103
63. C E Korshunov *Zh. Eksp. Teor. Fiz.*, 1989, **95** 2163

Received 13th February 1992

Translated from *Uspekhi Khimii* **61** 1656–1686 (1992) U.D.C. 535.342:546.799.3:541.2:546.66.

The influence of relativistic effects and the crystal field on the properties of actinyl ions

G V Ionova, G A Gerasimova
Institute of Physical Chemistry, Russian Academy of Sciences

ABSTRACT. The electronic structure and properties of the most covalent compounds of the actinides, namely the actinyl ions AnO_2^{2+} (An = U, Np, Pu, Am, Cm, Bk, and Cf), have been analysed on the basis of X_α-SW calculations. The regularity of the change in the redox, crystal-chemical, spectral, magnetic, and other properties in a series of compounds containing the actinyl ions has been studied. The strictly regular, regular, or irregular (stepwise) nature of the dependence of different properties on the atomic number of the element is determined by the extent of the participation of the 5*f*- and 6*d*-electrons in chemical bond formation, that is by the crystal field effect and the influence of relativistic spin–orbit coupling.

The bibliography contains 174 references.

Contents

I. Introduction 907
II. Experimental studies 908
III. Electronic structure of the actinyl ions 912
IV. Summary 921

I. Introduction

In the last two decades, the regularity of the change in various physicochemical properties in the lanthanide and actinide series with change in the atomic number of the element has been studied, and a large number of models have been developed to explain them.[1] Some of these have survived, while others have been found untenable. The reason for this variety of models is the difficulty of obtaining an adequate description of the compounds of the *f*-elements using purely ionic or purely covalent models.[2] Thus the ionic model describes the properties of the compounds of the trivalent lanthanides effectively, and those of the trivalent actinides less effectively, but provides a poor description of the tetravalent actinides, and cannot be used at all to describe the electronic structure of compounds of An in high oxidation states (An^V, An^{VI}, and An^{VII}).

For compounds with a high bond polarity, there is a definite periodicity in the change in their physicochemical properties (P) with change in the atomic number of the element.[3] This is a general feature, and extends to the ionic compounds of both the *f*- and *d*-series and the super-heavy transactinide elements. The properties P of the lanthanides (Ln), actinides (An), or transition *d*-elements (M) with f^q- or d^q-electron configurations change periodically in accordance with the periodic change in the quantum numbers L of the normal terms. Thus in each series there are characteristic double–double effects $d^0-d^5-d^{10}$, $f^0-f^7-f^{14}$, $g^0-g^9-g^{18}$, $h^0-h^{11}-h^{22}$, and in each half of the series pairs of triads $d^0-d^1-d^2$, $d^3-d^4-d^5$, tetrads $f^0-f^1-f^2-f^3$, $f^4-f^5-f^6-f^7$, pentads $g^0-g^1-g^2-g^3-g^4-g^5$, and hexads $h^0-h^1-h^2-h^3-h^4-h^5-h^6$.[3] This periodicity is obviously revealed in the properties of the free atoms. The greater the difference between the atom in a molecule and the free atom, the greater the deviation from periodicity.

The present review deals with the most covalent systems formed by the actinides, namely the so-called actinyl cations AnO_2^{z+} (z = 1, 2), beginning with the uranyl ion UO_2^{2+}, whose stability is comparable to that of the vanadyl ion VO^{2+}. The actinyl ions are present as structural units in many compounds of the pentavalent and hexavalent actinides.

The regularity of the change in the crystal-chemical, redox, thermodynamic, spectral, magnetic, and other properties in the series of actinyl ions is determined by the extent of the participation of the 5*f*- and 6*d*-electrons in chemical bond formation, that is by the deviation from the purely ionic model. The study of these regularities represents a fundamental problem in the physical chemistry of the actinides, namely the problem of the "localisation–delocalisation of the 5*f*–6*d*-electrons", which to some extent can be solved by quantum-chemical calculations of the molecular orbitals (MO) of the ions AnO_2^{2+} or AnO_2^{+}, where An = U, Np, Pu, Am, Cm, Bk, and Cf.

A fundamental feature of the change in energy is the increase in the localisation of the 5*f*-electrons with increase in the atomic number of the actinide Z_{An}, which leads to a decrease in the overlap between the 5*f*-AO of the actinide and the 2*s*, 2*p*-AO of the ligands. Increase in the localisation of the 5*f*-electrons leads to an increase in the energy of excitation of the 5*f*-electrons into electron configurations involving 6*d*- and 7*s*-AO. As a result of these effects, increase in Z_{An} leads to a decrease in the stability of the actinyl and actinoyl ions in an isovalent series. This regularity is observed not only for the cations AnO_2^{2+} and AnO_2^{+} but also for other oxygen-containing molecules and ions, in particular the octahedral oxoanions AnO_6^{z-}.[2]

In the present review we try to analyse various aspects of the problem of the localisation–delocalisation of electrons in the most covalent actinide compounds, namely the actinyl ions, on the basis of the relativistic version of the X_α scattered-wave method, to obtain answers to the following questions:

—which fragments of the energy levels can be most definitely distinguished in AnO_2^{2+} and AnO_2^{+} cations, and to what extent are the electrons localised in these fragments;

—to what extent can these fragments be regarded as components for the series of actinyl and actinoyl ions;

—what changes take place in these fragments under the influence of the equatorial ligands X in AnO_2X_y;

—is it possible to distinguish a predominant electron configuration of an actinide in an ion and to go from it to a structural formula with a definite number of the multiple bonds—single, double, or triple?

The answers to these questions will make it possible to solve the fundamental problem in the chemistry of the actinides: in which cases and for what reasons can we expect a strictly regular, regular, or stepwise change in the properties of the actinyl ions along the series?

II. Experimental studies

1. An—O bond parameters obtained from structural studies and vibrational spectroscopy

A vast amount of experimental material has now been accumulated on compounds containing the actinyl and actinoyl ions of uranium, neptunium, plutonium, and americium.[4–31] The material for the uranyl ion has been reviewed.[32] For the problems formulated above, we shall analyse only the regularity of the change in the physicochemical properties of these ions with increase in Z_{An} observed in experimental studies.

For various reasons, the experimental studies which can be carried out for compounds of the elements from uranium to americium with corresponding compositions make up only a small part of the chemistry of actinyl compounds. Most of the studies relate to the uranyl ion. The properties established experimentally for this ion and its compounds are often extended to the neptunyl ion, and are sometimes extrapolated to the other ions, assuming a linear relationship between P and Z_{An}. As shown below, however, for most properties this relationship is irregular.

We shall end the description of various experimental properties of the actinyl ion series with the formulation of the regularity characterising these properties and with its theoretical interpretation if this follows from the classical MO scheme or with the formulation of the theoretical problem of this interpretation if the change in properties with increase in Z_{An} does not correspond to the semi-empirical classical MO scheme and requires up-to-date calculations.

Because of the exceptional stability of the uranyl ion and the ready availability of uranium, X-ray diffraction studies have been carried out for several hundred compounds of this ion, together with a number of studies for other actinyl ions.[33–40]

All the compounds contain a linear symmetrical or slightly distorted actinyl group. The related compounds of uranium, neptunium, plutonium, and americium are isostructural.[41–46] A common feature of all the compounds is the existence of short An—O distances (R_{An-O}) in contrast to the distances to the other ligands in the equatorial plane (R_{An-X}).

Figures 1 and 2 give the dependence of R_{An-O} on Z_{An} for various compounds. These relationships may be regular [as for $RbAnO_2(NO_3)_3$], strictly regular [as for $NaAnO_2Ac_3$ and $AnO_2(ClO_4)_2$], or irregular (as for $K_3AnO_2F_3$ and $Cs_2AnO_2Cl_4$). $R_{An-O}-Z_{An}$ relationships similar to those in Fig. 1*a* have been called arch-like (Ω-type), and relationships similar to those in Figs. 1*b*, 1*c*, 2*a*, and 2*b* have been called zigzag (*N*-type).[47] It is not always easy to distinguish these two types from the values of the internuclear distances. Thus in Figs. 1*b*, 1*c*, and 2*a* the continuous lines denote relationships of the Ω-type. For these series of compounds, the two types of relationship lie within the experimental error. From an examination of the series of relationships in Figs. 1 and 2 it can be reliably concluded that the internuclear distances R_{An-O} increase with increase in Z_{An} in related compounds of the elements for uranium to americium, and that these relationships are not linear, unlike the dependence of the ionic radii $R_{An^{6+}}$ on Z_{An}.

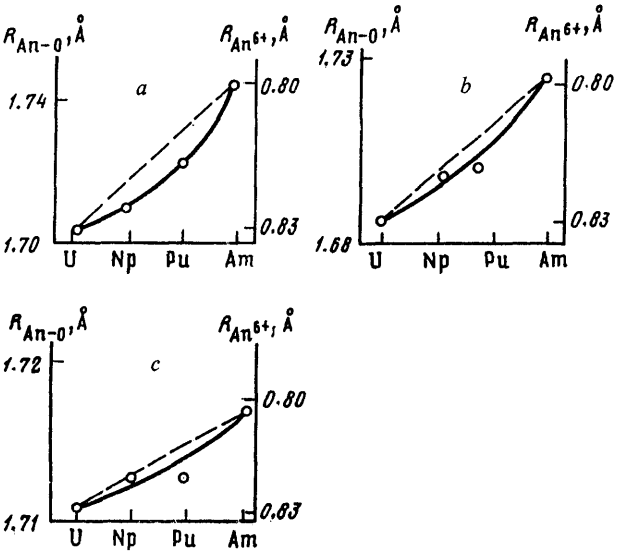


Figure 1. Dependence of the ionic radii of the sextuply-charged ions An^{6+} (broken line) and the internuclear distances R_{An-O} (continuous line) on Z_{An}:[48] *a*, *b*, strictly regular relationships for $NaAnO_2Ac_3$ [32] and $AnO_2(ClO_4)_2$;[35] *c*, regular relationship for $RbAnO_2(NO_3)_3$.[32]

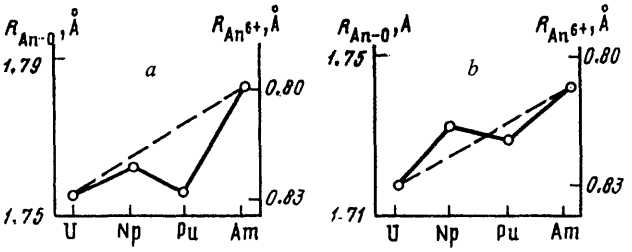


Figure 2. Dependence of the ionic radii of the sextuply-charged ions An^{6+} on Z_{An} (broken line) and the irregular dependence of R_{An-O} on Z_{An} for the compounds $K_3AnO_2F_3$ (*a*) [15] and $CsAnO_2Cl_4$ (*b*).[32]

Both types of relationship (Ω- and *N*-types) can be observed in other properties of the actinyl ions, and a qualitative explanation is not simple. Thus the ionic radii of the sextuply-charged actinide ions are 0.83, 0.82, 0.81, and 0.80 Å for uranium, neptunium, plutonium, and americium respectively.[48] If it is assumed that the ionic radius of the O^{2-} ion is 1.36 Å, the values of R_{An-O} in the actinyl ions of uranium, neptunium, plutonium, and americium should be 2.19, 2.18, 2.17, and 2.16 Å respectively. The experimental values of R_{An-O}, however, not only are 0.5 Å shorter but also change in the opposite order with increase in Z_{An}.

Thus an important problem in structural theory is to establish a direct relationship between the electronic structure of the actinyl ions and the non-additive, regular, or irregular increase in the internuclear distances R_{An-O}. The question of whether the *N*-type of relationship observed for the internuclear distances R_{An-O} is determined by the electronic structure of the free actinyl ions or by the influence of the equatorial ligands still remains open.

The changes in R_{An-O} are to some extent reflected in the values of the force constants of these bonds K_{An-O} in hexavalent actinyl compounds. The change in K_{An-O} for related compounds of uranium, neptunium, and americium shows a number of characteristic features.

1. The force constants of the An–O bonds decrease on going from the uranyl to the americyl ion. Our estimates of K_{An-O} for the curyl ion indicate a further decrease in the strength of the actinide–oxygen chemical bond. These results correspond to increasing localisation of the 5*f* electrons with increase in Z_{An} and increase in the number of antibonding electrons.

2. The change in K_{An-O} with change in Z_{An} is non-additive, and two types of deviation from additivity are observed: positive for $NaAnO_2Ac_3$ (70.8, 69.7, 67.5, 63.4 μdyn nm^{-1}) and $AnO_2(ClO_4)_2$ (77.5, 78.1, 77.1, 73.5 μdyn nm^{-1}) and negative for $Cs_2AnO_2Cl_4$ (68.0, 65.1, 63.6, 62.7 μdyn nm^{-1}).

3. Finally, it is possible to distinguish two types of $K_{An-O}-Z_{An}$ relationships, namely Ω- and *N*-types. Naturally, the separation of the curves into Ω- and *N*-types involves certain assumptions, as in the case of the internuclear distances.

For the perchlorate complexes, the force constant increases on going from the uranyl to the neptunyl ion. This is possibly due to errors in the measurement of the wavenumber of the antisymmetric stretches ν_{as} for U^{6+} or Np^{6+}. Morss[49] gives the same value ν_{as} = 935 cm^{-1} for the two ions, taken from an early paper.[50]

For the fluoride complexes of plutonium and neptunium, $K_{Pu-O} > K_{Np-O}$. A decrease in ν_{as} and K_{An-O} with increase in Z_{An} appears more logical if it is assumed that the influence of the equatorial ligands on the electronic structure of the cations is the same for all cations.

There are fewer published X-ray diffraction studies for compounds containing pentavalent actinoyl ions than for their hexavalent analogues.[51–56]

Studies of compounds containing AnO_2^{2+} and AnO_2^{+} ions reveal many common features in the stereochemistry of these complexes, namely in the values of the coordination numbers (CN) and the types of coordination polyhedra. Naturally, all the interatomic distances R_{An-O} in the actinoyl compounds are greater than those in the corresponding actinyl analogues. On the average, the difference in the bond lengths R_{An-O}, where An = Np and U, is 0.012 ± 0.006 nm.

A complete set of values of K_{An-O} and R_{An-O} for all the actinoyl ions is not available. The use of some published data[49,50] for $NpO_2(ClO_4)_2$ and $AmO_2(ClO_4)_2$ gave the following values of K_{An-O} for the AnO_2ClO_4 series (in μdyn nm^{-1}): 53.1, 56.5, 58.6, and 57.7 for An = U, Np, Pu, and Am respectively, and the use of other data[35] gave the values 50.1, 52.5, 52.9, and 50.7 μdyn nm^{-1} respectively. The $K_{An-O}-Z_{An}$ relationships observed are of the same Ω-type observed for the actinyl compounds with the same perchlorate anions.

Thus each of the above characteristics of the change in K_{An-O} with increase in Z_{An} represents a problem for quantum-chemical interpretation.

2. Optical spectra

The interpretation of the electronic–vibrational spectra[57–62] and the optical spectra by the method of molecular orbitals (MMO)[63–69] has led to important conclusions about the nature of the chemical bond in the actinyl series. In compounds containing "yl" groups, two types of electron transition have been detected in the visible range: uranyl-like charge-transfer transitions E_{CT} and *f*–*f* transitions. The first correspond to the excitation of an electron from a higher bonding MO of predominantly 5*f*-character. For the actinyl anions AnO_2^{2+}, the values of E_{CT} for An = U, Np, Pu, and Am are respectively 20679 ± 472, 13358 ± 338, 15396, and 10086 cm^{-1} [70–73] (Fig. 3).

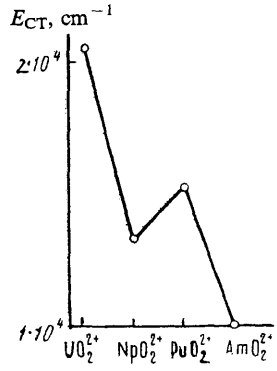


Figure 3. Dependence of the energy of the uranyl-like charge-transfer transition (E_{CT}) in actinyl ions on the atomic number of the acitnide.

Table 1. Energies of the *f*–*f* electron transitions for AnO_2^{2+} (cm^{-1}).[69]

Transition	NpO_2^{2+}	PuO_2^{2+}	AmO_2^{2+}
$\varphi_{5u}-\delta_{3u}$	-	-	-
$\varphi_{5u}-\varphi_{7u}$	6750	-	-
$\varphi_{5u}-\delta_{5u}$	8180	12024	13630
$\varphi_{5u}-3\pi_{1u}$	18180	19193	19300
$\varphi_{5u}-3\pi_{3u}$	21100	24040	-
$\delta_{3u}-\delta_{5u}, \varphi_{7u}$	-	10186	11710
$\delta_{3u}-3\pi_{1u}$	-	16060	16190
$\delta_{3u}-3\pi_{3u}$	-	21320	21420

For NpO_2^{2+}, a series of absorption bands has been detected with energies 13918, 16072, 16092, 7967, and 1951 cm^{-1} [70] or 13239, 15402, 15678, 16795, 19371 cm^{-1}.[71] For PuO_2^{2+} the values of E_{CT} are 15280, 15498, and 15658 cm^{-1}.[72]

In the sequence of E_{CT} values for the actinyl ions, a red shift is observed. The same shift should obviously be observed in the values of E_{CT} for the actinoyl ions.

The energies of the $f-f$ transitions are given in Table 1.[69] The energies of transitions of the same kind tend to increase with increase in Z_{An}.

There are few published experimental data on the values of the energies of the $f-f$ transitions for compounds containing actinoyl ions. For example, for the absorption wavenumbers of $Cs_3NpO_2Cl_4$ the ranges 6035–11111, 16437–22309, and 12810–15973 cm^{-1} have been given.[71]

The transitions of greatest interest for analysing the chemical bonding in actinyl compounds are the uranyl-like transitions, whose energies change irregularly along the series UO_2^{2+}, NpO_2^{2+}, PuO_2^{2+}, AmO_2^{2+}, giving an N-type relationship.

3. Redox potentials

The formal potentials E^0 in perchlorate solutions have been determined experimentally for the AnO_2^{2+}/AnO_2^{+} couples; the values obtained are 0.089 ± 0.002, 1.160 ± 0.005, 0.940 ± 0.004, and 1.624 ± 0.009 for An = U, Np, Pu, and Am respectively.[74] Fig. 4 shows that the dependence of E^0 on Z_{An} is irregular (N-type). Comparison of Figs. 3 and 4 shows an analogy in the changes in E_{CT} and E^0 with change in Z_{An}, leading to a linear relationship between E_{CT} and E^0 (Fig. 5).

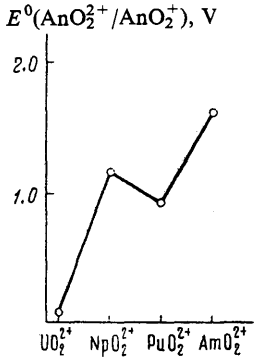


Figure 4. Dependence of the redox potentials (E^0) of AnO_2^{2+}/AnO_2^{+} couples on Z_{An}.

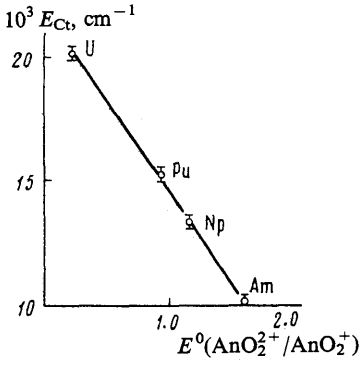


Figure 5. Linear relationship between the calculated energy of the uranyl-like transitions (E_{CT}) of the actinyl ions[123] and the measured redox potentials.[74]

The irregular change in the redox potentials may be due either to the specific features of the electronic structure of the actinyl ions themselves or to the influence of the equatorial ligands; this is again a problem for theoretical study. In any case, it is impossible to avoid semi-empirical MO schemes for an explanation of the irregular changes in the redox properties. From general qualitative considerations it is obvious that the redox potentials increase towards the end of the first half of the series, in particular from the uranyl to the americyl ion. The extremal change in E^0 for the PuO_2^{2+}/PuO_2^{+} couple, however, does not fit into the usual qualitative interpretation.[75–77]

4. Thermodynamic properties

The free energies and enthalpies of the actinyl and actinoyl ions have been discussed.[33,34,49] Fig. 6 shows the dependence of the standard enthalpies of formation of the actinyl (a) and actinoyl (b) ions on the atomic number of the actinide. In both cases the relationship is strictly regular. We noted above that the redox potentials $E^0(AnO_2^{2+}/AnO_2^{+})$ of the chemical reactions

$$(AnO_2^{2+})_{aq} + e \rightarrow (AnO_2^{+})_{aq}\,, \qquad (1)$$

for the same sequence of actinyl ions change irregularly. The change in free energy for reaction (1) can be written as

$$\Delta G_0^0 = FE^0(AnO_2^{2+}/AnO_2^{+}), \qquad (2)$$

where F is the Faraday constant, or

$$\Delta G_0^0 = \Delta G_0^0(AnO_2^{2+})_{aq} - \Delta G_0^0(AnO_2^{+})_{aq}\,. \qquad (3)$$

Comparison of Eqns. (2) and (3) shows that with a regular change in both terms in Eqn. (3), their difference can be represented by an irregular relationship.

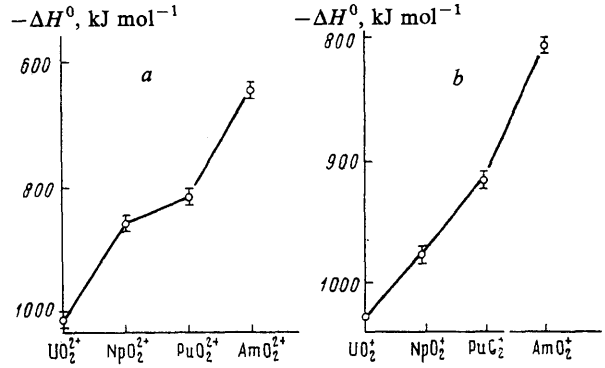


Figure 6. Change in the standard enthalpy of formation of actinyl (a) and actinoyl (b) ions.[30]

Fig. 6b shows that the dependence of $\Delta H^0(AnO_2^{+})$ on Z_{An} is almost linear, whereas the dependence of $E^0(AnO_2^{2+}/AnO_2^{+})$ and $\Delta H^0(AnO_2^{2+})$ on Z_{An} is of the N-type. This important feature,

characteristic of actinyl ions, will be examined below in relation to the electronic structures of these ions.

Finally, the molar polarisability R_M [47] and the refractive index n_d [78] show an identical tendency to undergo an irregular change of the *N*-type with change in Z_{an}. It can be shown that the enthalpy of formation of the actinyl ions and the molar polarisability and refractive index depend on the same parameters related to the electronic structure of the actinyl ions. One of the most important problems in the theory of the structure of the actinyl ions is to find these parameters and identify the fine difference in the electronic structures of the ions which gives an irregular relationship of the *N*-type when revealed in some properties, and a regular relationship when it is not revealed.

5. Extraction of the actinyl ions

There are now extensive published data on the extraction of lanthanides and actinides by various extracting agents.[79–85] Two approaches to the theoretical interpretation of the results may be noted.

A correlation has been noted[80–83] between the change in lg *D*, where *D* is the extraction coefficient for different extracting agents, and the orbital quantum numbers *L* for the normal terms of the *f*-ions. At the same time, a *J*-model has been used,[79] that is it has been shown that in the extraction of tervalent lanthanides by tributyl phosphate (TBP), the change in lg *D* follows the values of the quantum numbers *J* of the normal terms of the free ions, as in the case of the magnetic properties of the lanthanides.

The change in the free energy of extraction

$$\Delta G_e^0 = -RT \lg D ,$$

decreases both with increase in the quantum number *L* and with increase in the quantum number *J*. In the ionic approximation for the series of actinyl ions $U^{6+}(^1S_0)$, $Np^{6+}(^2F_{5/2})$, $Pu^{6+}(^3H_4)$, and $Am^{6+}(^4I_{9/2})$ being considered, the change in the free energy of extraction ΔG_e^0 should decrease regularly from the uranyl ion to the americyl ion if it is assumed that $\Delta G \simeq -L$ or $\Delta G \simeq -J$. In the extraction of the actinyl ions by solutions containing TBP and mineral acids (HNO_3, $HClO_4$, or HCl), the value of ΔG_e^0 when nitric and perchloric acids are added to TBP increases on going from the uranyl to the plutonyl ion, but when hydrochloric acid is added, the value decreases on going from the uranyl to the neptunyl ion and increases on going from the neptunyl to the plutonyl ion.[84] The main conclusion from these experimental data is that the thermodynamic parameters of the extraction of the actinyl ions reflect changes taking place in the electronic structures of these ions on complex formation in the aqueous phase.

6. Complex formation by actinyl ions

Comparison of the values of lg *K* (*K* represents the formation constants of the complexes AnO_2SO_4, $AnO_2(SO_4)_2^{2-}$, $AnO_2(CO_3)_2^{2-}$, $AnO_2(CO_3)_3^{4-}$, AnO_2H^+, $(AnO_2)_2(OH)_2^{2+}$, and $(AnO_2)_3(OH)_5^+$ (in aqueous solution at 25 °C[85–89]) shows two types of lg $K-Z_{An}$ relationships (curves *1*–*7* in Fig. 7).

The first type of relationship is characterised by extremal values of lg *K* for the neptunyl ion (curves *2*–*5* in Fig. 7), and the second corresponds to a regular increase (curve *1* in Fig. 7) or decrease (curves *6* and *7* in Fig. 7) in the values of lg *K*. The change in lg *D* for the actinyl ions, where *D* is the extraction coefficient, shows a regular decrease with increase in Z_{An} for 0.6 M HNO_3 + TBP solution (curve *8* in Fig. 7), and an extremal value for the neptunyl ion in the case of 2 M HCl + TBP solution (curve *9* in Fig. 7).

Thus the change in the thermodynamic parameters in extraction reflects their change on complex formation, that is complex formation is the most important stage determining the thermodynamics of the extraction process. It follows from published data[84] that the entropy term is responsible for the change in ΔG^0 on formation of the di- and tricarbonate complexes of the actinyl ions, and that the enthalpy term is responsible in the case of the mono- and disulphate complexes. In all cases examined except $AnO_2(CO_3)_3^{4-}$, the enthalpy and entropy terms show opposite trends in the change with increase in Z_{An}.

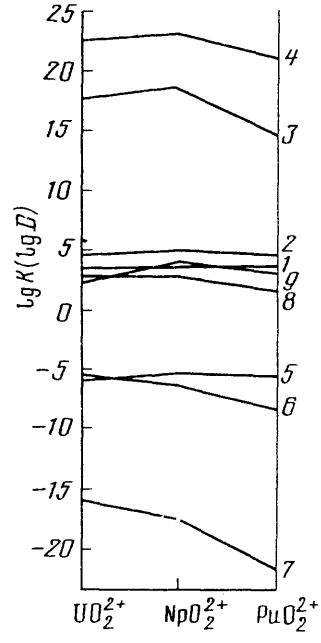


Figure 7. Change in lg *K* (*K* is the equilibrium constant of the reaction $AnO_2^{2+} + X \rightarrow AnO_2X$ in aqueous solution at 25 °C) and ln *D* (curves *8* and *9*) for actinyl ions extracted in 0.6 M aqueous solution by HNO_3 + TBP (*8*) and HCl + TBP (*9*) 25 °C:[84] *1*, AnO_2SO_4;[86] *2*, $AnO_2(SO_4)_2^{2-}$;[86] *3*, $AnO_2.(CO_3)_2^{2-}$;[87] *4*, $AnO_2(CO_3)_3^{4-}$;[88] *5*, AnO_2H^+;[87] *6*, $AnO_2(OH)_2^{2+}$;[89] *7*, $(AnO_2)_3(OH)_5^+$.[89]

The dependence of these thermodynamic parameters on Z_{an} for the extraction of AnO_2^{2+} from HNO_3 + TBP and HCl + TBP solutions shows[84] that in the extraction by nitric acid the trends in the changes in the free energy and the entropy term are the same, whereas in the extraction by hydrochloric acid the trends in the changes in the free energy and the enthalpy term are the same. The experimental data show that in almost all cases examined, the neptunyl ion shows an extremal (or irregular) change in the thermodynamic functions on complex formation or extraction.

In the extraction of the actinyl ions by HNO_3 or $HClO_4$ solution[84] and on formation of the complexes $AnO_2(CO_3)_2^{2-}$ and $AnO_2(CO_3)_3^{4-}$, the free energy and the entropy term change in the same sense with increase in Z_{An}. In the extraction by HCl solution

and on formation of the sulphate complexes AnO_2SO_4 and $AnO_2(SO_4)_2^{2-}$, the free energy and the entropy term change in the opposite sense.[90–95]

III. Electronic structure of the actinyl ions

1. Theoretical studies of actinyl and actinoyl ions

The first model of the molecular orbitals of the uranyl ion, proposed by Eisenstein and Pryce[96] in 1955, was designed to explain the magnetic properties of uranyl compounds. Subsequent studies[65,66,97] were aimed at interpreting the optical spectra of the uranyl ion, and the discussion was based entirely on the MO method. The very first applications of the MO method to the description of the structure of the uranyl ion gave important results. The MO of the uranyl ion were classified on the basis of general symmetry properties; calculations of the overlap integrals made it possible to obtain a measure of the interaction of the atomic orbitals of uranium and oxygen and to determine the principal features of the sequence of the bonding MO of the uranyl ion. The first attempts were made to interpret the magnetic properties and absorption spectra of uranyl compounds.[98–101]

The first quantitative calculations of the molecular orbitals of the uranyl ion were carried out using the theory of the SCF-X_α-method, which makes it possible to obtain a good description of many-electron systems, in particular the complexes of *f*-elements.[102] Calculations carried out up to the present have been restricted mainly to the study of the electronic structure of the uranyl ion by different methods,[103–113] some of which cannot give a clear quantitative picture of the electron density distribution and the structure of the energy levels.[114,115] There is no doubt that it is important to take account of relativistic effects in systems containing heavy atoms.[116–118] There are no published studies, however, of the electronic structure of plutonium and the transplutonium elements, which would make it possible to follow the changes in electronic structure in the actinyl ion series. Until recently there were no published data on the quantum-chemical study of the actinoyl ions, that is there were no published systematic studies of the electronic structure of the series of ions AnO_2^{2+} and AnO_2^{+}. This problem has been examined and reviewed[119–123] using a relativistic version of the X_α-SW method.

2. Calculation procedure

The completely relativistic X_α-SW method is based on the solution of the Dirac equation by the multiple-scattering method.[124]

All the studies have been carried out in the quasi-relativistic (QR) approximation of the SCF-X_α method.[125–133] The essential feature of the QR approximation is the change, for the radial wavefunctions, from the four-component Dirac spinors to two-component spinors with simultaneous exclusion of spin–orbit coupling and neglect of contributions from small components in the construction of the self-consistent central potential and the total electron density. After obtaining self-consistent QR orbitals, spin–orbit coupling was taken into account using perturbation theory and a basis set of QR orbitals, determined with allowance for such relativistic effects as the dependence of mass on velocity and Darwin interaction. The differential equation for the radial function G_{nl} of a large component has the form:

$$[H_{NR} + H_m + BH_D]\, G_{nl} = E_{nl} G_{nl}\,.$$

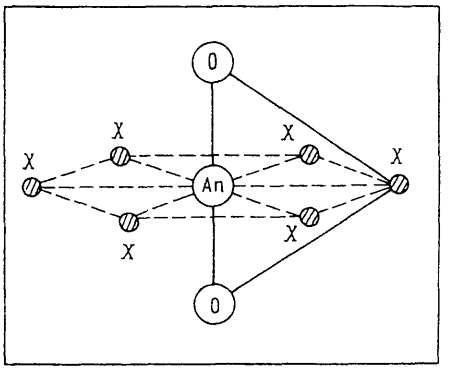


Figure 8. Model of the cluster of an actinyl ion with six ligands X in the equatorial plane of the O–An–O group.

Here, H_{NR} is the standard non-relativistic operator, used to describe the central field (with an exchange $X_\alpha l$-potential), H_m the standard operator for the dependence of the mass of the electron on velocity, and H_D the Darwin operator.[134] The operator B has the form

$$B = \{1 + (\alpha^2/4)[E_{nl} - V(r)]\}^{-1},$$

where $\alpha = 1/137$, and $V(r)$ is the one-electron potential of the central field. The effects of spin–orbit coupling on the molecular orbitals are calculated using perturbation theory in a basis set of self-consistent quasi-relativistic orbitals: $H'_{so} = BH_{so}$, where H_{so} is the standard operator of spin–orbit coupling from Pauli theory.[135–148] As basis orbitals it is possible to use either individual orbitals with a given characteristic value (RX_α-*SO* calculation) or groups of orbitals with similar characteristic values (RX_α-*SO'* calculation, higher orders of perturbation theory).[148–156]

3. Results of the calculations

Model calculations have been carried out[116–120] for the ions AnO_2^{2+} and AnO_2^{+} (An = U, Np, Pu, Am) with interatomic distances R_{An-O} decreasing in accordance with the actinide contraction: 1.73, 1.72, 1.71, 1.70 Å in AnO_2^{2+} and 1.76, 1.75, 1.74, 1.73 Å in AnO_2^{+} for U, Np, Pu, Am respectively. In the works cited, however, no account was taken of the fact that the equatorial ligands X in compounds AnO_2X_y (Fig. 8) have a significant influence on the interatomic distances R_{An-O}, leading, firstly, to their increase with increase in the atomic number of the actinide element, and not to their decrease, as predicted by the effect of actinide contraction and, secondly, to an irregular dependence of R_{An-O} on Z_{An}. We carried out analogous calculations for the actinyl ions in the series of isostructural compounds $NaAnO_2Ac_3$ (a), $Cs_2AnO_2Cl_4$ (b), $RbAnO_2(NO_3)_3$ (c), and $AnO_2(ClO_4)_2$ (d) with different types of dependence of R_{An-O} on Z_{An}. The values of R_{An-O} for all series of compounds with An = U, Np, Pu, and Am respectively (in Å) are given below:

Series	U	Np	Pu	Am
(a)	1.704	1.709	1.721	1.743
(b)	1.1718	1.733	1.731	1.747
(c)	1.683	1.692	1.692	1.712
(d)	1.673	1.670	1.675	1.695

Fig. 9 gives the energy level diagrams for the sequence of doubly-charged AnO_2^{2+} cations, obtained in RX_α-SO′ approximations. The sequence of energy levels remains practically unchanged to the end of the series for different forms of dependence of R_{An-O} on Z_{An}.

The lowest-lying MO ($1\sigma_g - 2\sigma_u$) are formed by the strong covalent mixing of the 6*p*-AO of the actinide and the 2*s*-AO of oxygen, and are inner valence molecular orbitals (IVMO). Above them there is a group of levels formed mainly by the 6*d*- and 5*f*-AO

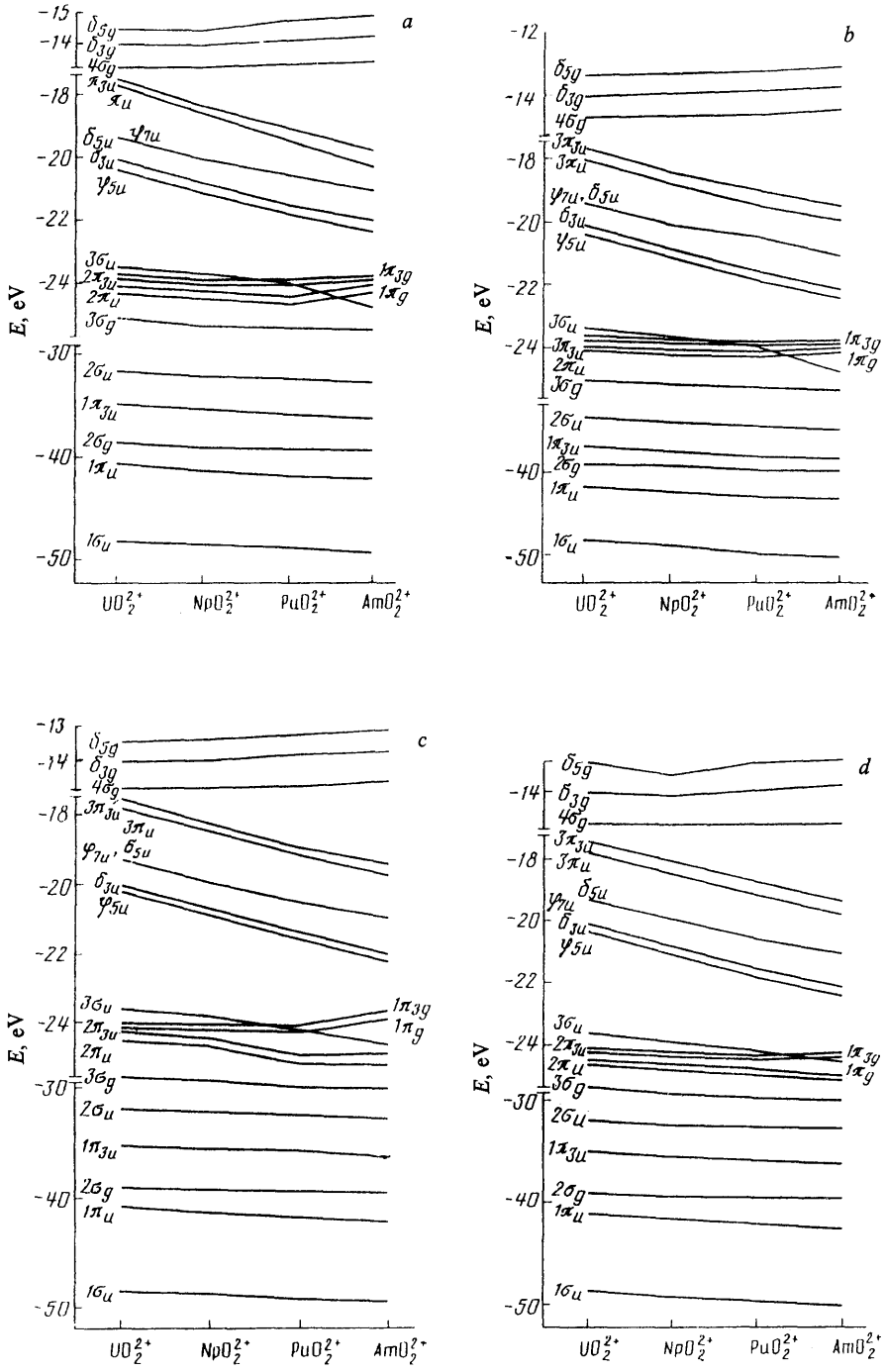


Figure 9. Energies of the MO in actinyl ions calculated by the RX_α-SO′ method: *a*, $NaAnO_2Ac_3$; *b*, $Cs_2AnO_2Cl_4$; *c*, $RbAnO_2 \cdot (NO_3)_3$; *d*, $AnO_2(ClO_4)_2$.

of the actinide and the 2*p*-AO of oxygen, the so-called outer valence MO (OVMO). Even higher, separated by an energy gap (ΔE), are the non-bonding and antibonding levels of 5*f*-character. In the RX_α-SO′ approximation the orbitals φ_{7u} and δ_{5u} are accidentally degenerate. This leads to a qualitative similarity in the electronic structures of the actinyl ions, making it possible to distribute their energy levels of similar composition in groups. In this sense it is possible in the actinyl ions to distinguish the following fragments corresponding to the maximum bonding between various AO: 6*s*(An) + 2*s*(O); 6*p*(An) + 2*s*, 2*p*(O); 5*f*, 6*d*(An) + 2*p*(O); 5*f*(An); and 6*d*(An).

The highest bonding MO (HBMO) for UO_2^{2+} and NpO_2^{2+} is the $3\sigma_u$-MO, but from PuO_2^{2+} and beyond, the π_g-orbital becomes the HBMO. Fig. 9 shows that on going to the heavier actinides, the energies of the non-bonding and anti-bonding MO (of 5*f*-character) gradually decrease, whereas those of the highest bonding MO remain almost unchanged. The greater lowering of the levels of 5*f*-character takes place as a consequence of the gradual increase in the number of electrons localised in them, and also as a consequence of the fact that the energies of the 5*f*-AO decrease with increase in the atomic number of the actinide. The energies of the bonding MO, where the main contribution is made by the AO of oxygen, remain practically unchanged. The magnitude of ΔE decreases along the series from 3.2 eV for UO_2^{2+} to 1.5 eV for AmO_2^{2+}.

Analysis of the electronic structure of the actinyl ions clearly shows the existence of common characteristic groups of levels both in the system of bonding levels and in the system of antibonding levels, corresponding to the interactions 2*s*−6*p*, 2*s*, 2*p*−6*p*, 2*p*−6*d*,5*f* between the valence 2*s*,2*p*-AO of the ligands and the 6*p*, 6*d*, and 5*f*-AO of the actinide atoms from uranium to californium.[122]

Separation of the energy levels into fragments is observed for all the oxygen-containing compounds of the actinides. Comparison of the analogous groups of levels in the isovalent anions and cations, for example in UO_6^{6-} and UO_2^{2+}, NpO_6^{6-} and NpO_2^{2+}, etc., shows, however, that the electrons are more localised in the anions than in the cations. This means that in the anions, in the fragments mainly responsible for their properties, the 2*p*−6*d*,5*f*-electrons are localised to a greater extent in the 2*p*-AO of the oxygen atoms in the bonding levels, and in the 5*f*-AO in the antibonding levels. In the anions, the electronic structure of the fragments is closer to that of the free atoms, that is the bonding levels (2*p*−6*d*,5*f*) approach 2*p*(O), and the antibonding levels (6*d*,5*f*−2*p*) approach 6*d* + 5*f*(An). It can be stated definitely that the series of actinyl ions is described by a set of transferable fragments in such a way that with each of them it is possible to associate a certain energy increment. The cations differ mainly in the electron distributions in the fragments.

In the inner valence MO the most probable distribution of electron density corresponds to its displacement into the 6*s*- and 6*p*-AO of the actinide. In the outer valence MO, the electron density distribution corresponds to covalent bonding.

Finally, in the series of non-bonding and antibonding levels the displacement of electron density corresponds to the direction An←2*p*(O), that is for an anion taken separately the completely "classical" electron density distribution is obtained, and it is preserved in all the actinyl ions. On going from one cation to another, a qualitative modification of the fragments takes place, involving the greater localisation of the 5*f*-electrons with increase in Z_{An} in AnO_2^{2+}, less extensive participation of the 6*d*- and 7*s*-electrons in chemical bond formation, gradual localisation of the core 6*s*- and 6*p*-electrons, and a lowering of the corresponding energy levels.

All this decreases the strength of the An−O bond in the actinyl ions with increase in Z_{An}, and gives a general picture of their qualitative change. This qualitative picture is insufficient, however, for the interpretation of the chemical properties.

Thus the gradual localisation of electrons in the fragments of the actinyl ions with increase in the atomic number of the actinide should have corresponded to a gradual and regular change in their properties.[157–164] The properties of the actinyl ions (from uranyl to americyl), however, generally change in irregular fashion.[1] This means that it is necessary to take account of the difference in the structures of the fragments;[165–170] the transferability of the fragments gives only the zeroth approximation to the qualitative picture.

4. Interpretation of the experimental properties of the actinyl and actinoyl ions, based on the results of SCF-X_α-SW calculations

We shall begin the discussion of the experimental properties with the most important chemical property—the redox potential of the AnO_2^{2+}/AnO_2^{+} couple. The available experimental data give a relationship of the *N*-type for the redox potentials in the series from the uranyl to the americyl ion. To explain this dependence of E^0 on Z_{An}, we can first examine the ionic model, that is the ionisation of the free ions in the gas phase or in solution

$$An^{z+}(f^q) \rightarrow An^{z+1}(f^{q-1}) + e. \quad (4)$$

The oxidation potential of this reaction under equilibrium conditions is written as:

$$E^0 = \frac{0.05916}{n} \ln K_p, \quad (5)$$

where K_p is the chemical ionisation equilibrium constant. The free energy of this reaction ΔG^0 and K_p are related by the familiar expression

$$\Delta G^0 = -RT \ln K_p. \quad (6)$$

At the same time, for standard conditions:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0. \quad (7)$$

Thus each of the quantities ΔG^0, E^0, and $\ln K_p$ can be calculated in terms of the others if they are related to reaction in the same phase, that is solution or gas. Thus, for the chemical equilibrium constant in the gas phase we readily obtain

$$K_p(T) = \frac{g(f^q)}{2g(f^{q-1})} \left(\frac{2\pi}{m}\right)^{3/2} \frac{h^2}{T^{5/2}} \exp(\Delta E/kT), \quad (8)$$

where $g(f^q)$ and $g(f^{q-1})$ are the statistical weights of the normal states of the ions $An^{z+}(f^q)$ and $An^{z+1}(f^{q-1})$, *m* the mass of the ion, *T* the temperature, and ΔE the energy difference between the normal terms of the ions with the f^q- and f^{q-1}-electron configurations.

It can readily be shown that at *T* = constant for all the ions, completely neglecting covalent effects, the change in K_p along the series depends on the ratio $g(f^q)/g(f^{q-1})$, and the change in the free energy of the redox reaction (4) being considered, in accordance with Eqn. (6), depends on the logarithm of this ratio, $\ln[g(f^q)/g(f^{q-1})]$.

The multiplicity of the degeneracy of $g(f^q)$ and $g(f^{q-1})$ depends on the electronic structure of the ions, which also determines the applicability of the *L*- and *J*-models. The dependence of ln K_p on Z_{An} for both models is shown in Fig. 10*b*. The relationship is the typical strictly regular Ω-relationship, that is the ionic model leads to the regular relationship!

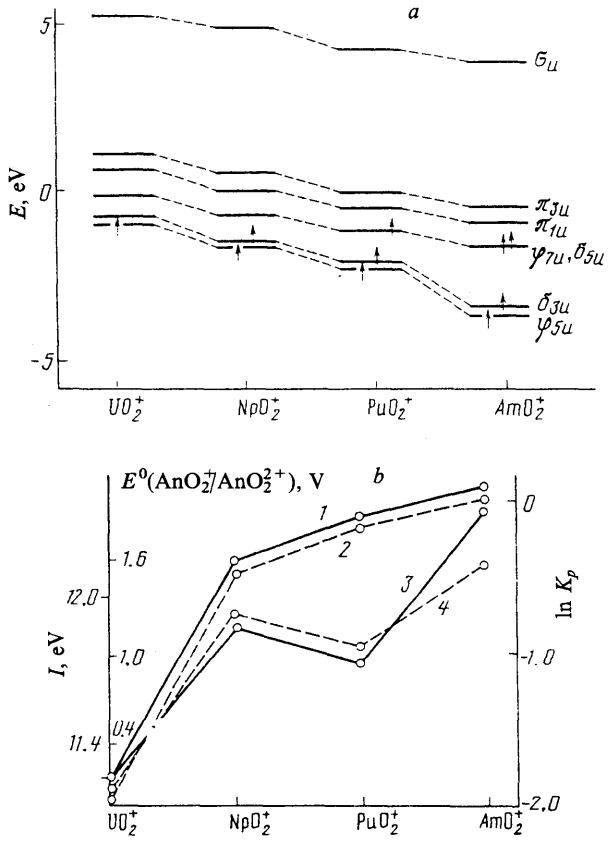


Figure 10. MO diagram for the actinyl ions (*a*) and the dependence of ln K_p [in the *J*-model (curve *1*) and the *L*-model (curve *2*)], the ionisation potentials *I* (curve *3*), and the oxidation potentials E^0 (curve *4*) of the actinyl ions on Z_{An} (*b*).

We can now examine the influence of the crystal field together with spin–orbit coupling. As shown above, the valence 5*f*-AO in the symmetry point group $D_{\infty h}$ are split into δ_u-, φ_u-, π_u-, and σ_u-MO. As a result of spin–orbit coupling, the δ_u- and φ_u-MO are split into δ_{5u}-, φ_{7u}-, δ_{3u}-MO, and π_u into π_{3u} and π_{1u}. Fig. 10*a* shows the filling of these MO with electrons for the actinoyl ions AnO_2^+: $UO_2^+ - \varphi_{5u}^1$; $NpO_2^+ - \varphi_{5u}^1$; $PuO_2^+ - \varphi_{5u}^1\delta_{3u}^1(\varphi_{7u}\delta_{5u})^1$; $AmO_2^+ - \varphi_{5u}^1\delta_{3u}^1(\varphi_{7u}\delta_{5u})^2$. The energy distance between the φ_{5u}- and δ_{3u}-MO is determined mainly by the spin–orbit effect for the free ions, since they are almost pure 5*f*-levels, and the splitting of the π_u-levels is due to the effects of the crystal field and the spin–orbit coupling (CF + SOC) resulting from the considerable mixing with the 2*p*-AO of the oxygen atoms. As a result, the energy distance Δ_1 between the φ_{5u}- and δ_{3u}-MO in AnO_2^+ is about 1500 cm^{-1}, while the distance Δ_2 between the δ_{3u}- and $\varphi_{7u}\delta_{5u}$-MO is greater, and amounts to about 6000 cm^{-1}. In accordance with the scheme adopted for the filling of the MO by electrons and the values of Δ_1 and Δ_2, the change in the ionisation potentials of the actinoyl ions is irregular (Fig. 10*b*); the so-called *N*-relationship is observed. This analysis reveals the reasons for the appearance of a stepwise relationship of the *N*-type. Since the main energy contribution to the oxidation potential $E^0(AnO_2^+/AnO_2^{2+})$ for the chemical reaction $AnO_2^+ \rightarrow AnO_2^{2+} + e$ is associated with the removal of the electron from the AnO_2^+ ion, the corresponding ionisation potentials and the oxidation potential change in the same sense (Fig. 10*b*).

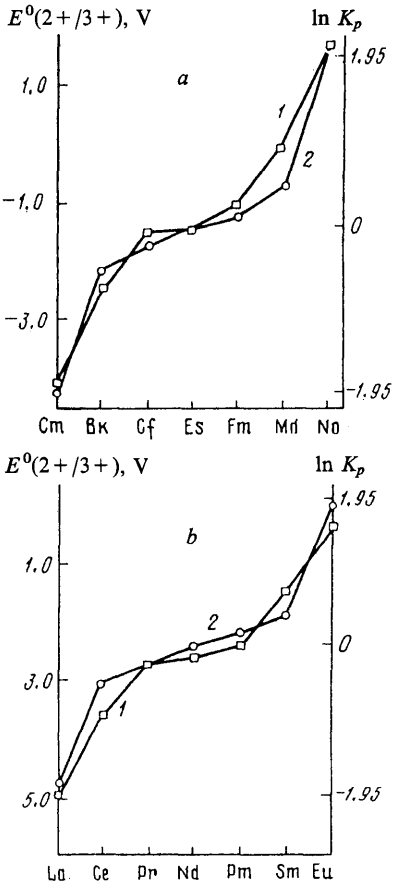


Figure 11. Regular dependence of the potentials $E^0(2+/3+)$ on Z_{An} (*a*) and Z_{Ln} (*b*) (curves *1*), resulting from weak crystal fields and relativistic effects; two Ω-type relationships can be distinguished in each half of the series; the theoretical dependence of ln K_p on *Z* is also given (curves *2*).

Thus when account is taken of strong crystal fields and spin–orbit effects, the Ω-type regular relationship ($K_p - Z_{An}$) in the *L*- or *J*-models becomes an irregular relationship of the *N*-type ($I - Z_{An}$, $E^0 - Z_{An}$).

In other words, it can be stated that the **irregular nature of the dependence of E^0 on the atomic number of the actinide is due largely to strong crystal field and spin–orbit effects.** The opposite is also true: **for weak crystal field and spin–orbit effects, the dependence of E^0 on Z_{An} is regular, of the Ω-type,** like the dependence of K_p on Z_{An}. This is the case for compounds with the electron configurations f^1, f^2, f^3, and f^4 (Fig. 11).

Thus the principal effects responsible for the anomalous properties of the heavy elements are relativistic contraction, spin–orbit splitting, and self-consistent interaction of the orbitals. Relativistic contraction in the case of the *s*-electrons, which have a low density next to the nucleus, leads to a decrease in the radii and an increase in the ionisation potentials of the corresponding ions.

Relativistic effects influence the *p*-AO in the same direction as the *s*-AO, but to a much smaller extent. Finally, relativistic effects influence the *d*- and *f*-electrons in the opposite direction, that is the radii increase and the ionisation potentials decrease. In other words, for an electron configuration $f^q ds^2$ the relativistic effects make the 7*s*-AO more compact and strongly bound, and the 6*d*- and 5*f*-AO more diffuse and weakly bound. In the atom, the relativistic effects for the 5*f*-, 6*d*-, and 7*s*-AO partly compensate one another.

The compounds of actinides in lower oxidation states (3+ and 4+) are practically ionic. This means that in these states the $6d7s^2$-electrons of the actinide are transferred to the ligands, and the 5*f*-electrons are non-bonding. The relativistic effects and crystal field effects increase with increase in the oxidation state.

These postulates can be verified from the values of the redox potentials. In the chemistry of the *f*-elements it is possible to consider two limiting cases: the actinyl and actinoyl ions (strong crystal fields and spin–orbit effects) and the lanthanides and actinides in lower oxidation states 2+ and 3+ (weak crystal fields and spin–orbit effects). Thus in accordance with this approach the oxidation potentials $E^0(2+/3+)$ for the lanthanides and actinides (Figs. 11*a* and 11*b*), with increase in the atomic number of the actinide or lanthanide, change regularly in accordance with the theoretical dependence of ln K_p on Z_{An}. Each half of the series in Fig. 11 shows two relationships of the Ω-type on both the experimental and the theoretical curves. The potentials $E^0(2+/3+)$ for La, Ce, Pr, and Cm were estimated by us, and those for Pm, Bk, Cf, Es, Fm, Md, No [171] and Nd, Sm, Eu [172] were taken from published data. These relationships confirm that the anomalous behaviour of the redox potentials $E^0(AnO_2^{2+}/AnO_2^+)$ corresponding to high oxidation states is due to strong relativistic effects and strong crystal fields.

These conclusions can be verified from the values of the redox potentials $E^0(3+/4+)$ for the actinides. These potentials have been published.[173] Fig. 12*a* gives the relationships for the measured redox potentials and ln K_p, calculated using the model. Fig. 12 shows that the trends in the changes in E^0 and ln K_p from thorium to curium are identical.

For the actinides with oxidation states of 5+ and 4+, the regular dependence of the redox potentials on Z_{An} breaks down. This is related to the formation in acidic solutions of $PaOOH^{2+}$ and AnO_2^+ (An = U, Np, Pu, Am) from Am^{4+}.[173] The dependence of $E^0(4+/5+)$ on Z_{An} is shown in Fig. 12*b*. In accordance with relativistic X_α-SW calculations for the AnO_2^+ ions, the last occupied MO in the ions UO_2^+, NpO_2^+, PuO_2^+, and AmO_2^+ are the orbitals δ_{3u}^1, $(\varphi_{7u}\delta_{5u})^1$, $(\varphi_{7u}\delta_{5u})^2$, and π_{1u}^1 respectively. The energies of these MO can be regarded as providing a measure of the electron affinity (A) of the actinoyl ions. The dependence of A on Z_{An} for these ions is shown in Fig. 12*b*.

The energies of the last occupidd MO in the actinoyl ions and the corresponding redox potentials $E^0(4+/5+)$ increase regularly with increase in Z_{An} for An = U, Np, and Pu, and then decrease for americium. The partly occupied low-lying levels in the actinoyl ions form three groups: $\varphi_{5u}\delta_{3u}$, $\varphi_{7u}\delta_{5u}$, $3\pi_{1u}3\pi_{3u}$. The last level σ_u lies fairly high. Of the three groups of levels, the first two are practically 5*f*-levels, but in the third group of levels there is extensive mixing of 5*f*- and 2*p*-AO.

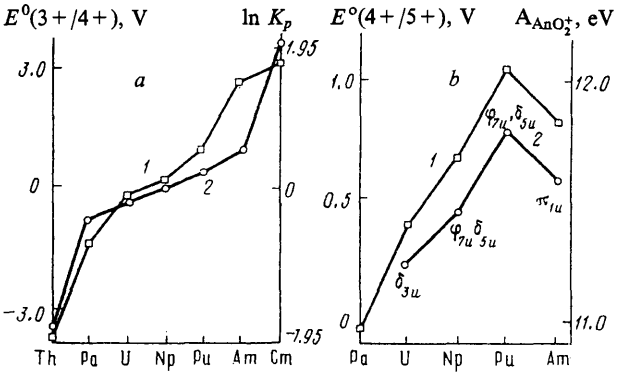


Figure 12. Regular dependence of the redox potentials $E^0(3+/4+)$ for the actinides from Th to Cm, showing agreement with the theoretically expected dependence of ln K on Z (*a*), and the deviation from regularity of the theoretical potentials $E^0(4+/5+)$, corresponding to the change in the electron affinity A (*b*).

The reduction of the actinoyl ions of uranium, neptunium, and plutonium involves the first two groups of levels, and that of americium involves the third group. The replacement of the purely actinide levels taking part in the reduction by levels of mixed character is responsible for the irregular change in the redox potentials (Fig. 12*b*). The correlation between $E^0(4+/5+)$ and A underlines the correctness of the chosen model for explaining the dependence of the redox potentials on Z_{An} within the X_α-SW method.

The same approach can be used to explain the irregular change in $E^0(AnO_2^{2+}/AnO_2^+)$ with change in Z_{An}. In the oxidation of AnO_2^+, the last occupied MO loses an electron; in UO_2^+ and NpO_2^+ it belongs to the first group, and in PuO_2^+ and AmO_2^+ it belongs to the second group. The change in the levels responsible in a given case for the oxidation again breaks down the regularity of the dependence of E^0 on Z_{an}, but now for plutonium.

Thus the satisfactory qualitative interpretation of the redox properties provides support for the key model assumption that the increasing effects of spin–orbit coupling and the crystal field with increase in the oxidation state are responsible for the chemical anomalies in the redox potentials of the actinides.

We can now consider the changes in the electronic absorption spectra of the actinyl ions. X_α-methods give good agreement with experiment in the range of X-ray photoelectron excitation. It is also possible to obtain satisfactory agreement for the visible range of the spectrum, however. Table 2 gives the energies of the electronic

charge-transfer transitions which we obtained for UO_2^{2+}. Comparison of our data with published data[57,58] shows that for the uranyl ion the calculations give effectively the energy distance between the last occupied and the first unoccupied MO.

Table 2. Energies of the electronic charge-transfer transitions for UO_2^{2+} (cm^{-1}).

Transition	UO_2^{2+}					Transition	$CsUO_2Cl_4$	
	(Ref.123)	Series *					(Ref.57)	(Ref.58)
		(a)	(b)	(c)	(d)			
$3\sigma_u-\varphi_{5u}$	20404	25243	24679	26211	26453	$3\sigma_u-\delta_{3u}$	20095	20406
$3\sigma_u-\delta_{3u}$	22017	26937	26292	27905	28147		20097	21310
$3\delta_u-\varphi_{7u}, \delta_{5u}$	28227	33227	32663	34195	34437	$3\sigma_u-\varphi_{5u}$	22026	22410
$3\sigma_u-3\pi_{1u}$	37986	46938	43712	46454	47099		22076	22750
$3\sigma_u-3\pi_{3u}$	40970	47583	46454	49357	49841	$3\sigma_u-\varphi_{7u}$	26197	27719
							26247	27758

*Here and subsequently (in Tables 3–5) the data are given from a series of calculations for the compounds $NaAnO_2Ac_3$ (*a*), $Cs_2AnO_2Cl_4$ (*b*), $RbAnO_2(NO_3)_3$ (*c*), $AnO_2(ClO_4)_2$ (*d*).

Naturally, it is impossible to interpret a large number of lines using a one-electron model. In each case, therefore, the energy of the electron transitions which we obtained corresponds to the weighted-mean energy of several many-electron excited states.

Table 3 gives our calculated energies of the "uranyl-like" transitions for the first four actinyl ions in the actinide series, for compounds with the different types of dependence of R_{An-O} on Z_{An} given earlier. In our calculations, the last occupied orbital is the $3\sigma_u$-MO for UO_2^{2+} and NpO_2^{2+}, and the π_g-MO for PuO_2^{2+} and AmO_2^{2+}, and the "uranyl-like" transitions take place from these MO into unoccupied orbitals of 5*f*-character. The energies of these transitions decrease with increase in the atomic number of the actinide as a result of the lowering of the energy levels of 5*f*-character.

Experimental studies of the neptunyl ion have established that the excited state is described by the electron configuration $3\sigma_u^1\delta_u^1\varphi_u^1$, which leads to the appearance in the spectrum of bands with energies 13918, 16072, 16092, 17967, and 19510 cm^{-1} [70] or 13239, 15239, 15678, 16795, and 19371 cm^{-1}.[71] Similar results were obtained in other studies.[61,62] The charge-transfer bands (E_{CT}) in the actinyl ions correspond to electron transfer for the $3\sigma_u$-MO to the φ_{5u}- and δ_{3u}-MO in the uranyl and neptunyl ions, and from the π_g- to the $\varphi_{7u}\delta_{3u}$, $\varphi_{7u}\delta_{3u}$-MO in the plutonyl and americyl ions respectively. Although the absolute values of E_{CT} differ from the experimental values, the *N*-type of the relationship is clearly revealed. It can be stated that the irregular character of the dependence of E_{CT} on Z_{An} is due to the strong crystal field combined with the spin–orbit effect. Both of these effects are revealed in such properties, different at first sight, as the energies of the uranyl-like transitions and the oxidation potentials, and are responsible for the linear relationship between the potentials $E^0(AnO_2^+/AnO_2^{2+})$ and E_{CT} for these ions. Thus these two properties apparently depend on the same MO.

Table 3. Energies of the "uranyl-like transitions for AnO_2^{2+} (cm^{-1})

Transition	UO_2^{2+}	NpO_2^{2+}	PuO_2^{2+}	AmO_2^{2+}	Series
$3\sigma_u-\varphi_{5u}$	25243	21549	16936*	11533*	(a)
	24679	20485	16291*	11291*	(b)
	26211	22259	18953	13550*	(c)
	26453	23153	19678	15000*	(d)
$3\sigma_u-\delta_{3u}$	26937	23308	18985*	13791*	(a)
	26292	22259	18307*	13468*	(b)
	27905	24437	21049	15726*	(c)
	28147	25009	21775	17259*	(d)
$3\sigma_u-\varphi_{7u}, \delta_{5u}$	33227	30485	26937*	22582*	(a)
	32663	29356	26211*	22259*	(b)
	34195	31131	28953	24517*	(c)
	34437	32106	29598	25969*	(d)
$3\sigma_u-3\pi_u$	46938	41212	36534*	30898*	(a)
	43712	39357	35566*	30646*	(b)
	46454	43631	39597	33792*	(c)
	47099	44204	40808	35970*	(d)
$3\sigma_u-3\pi_{3u}$	47583	44276	39921*	34518*	(a)
	46454	42421	38873*	34195*	(b)
	49357	44034	42905	37502*	(c)
	49841	47268	44196	39599*	(d)

Note. Transitions for the π_g-orbital are marked with an asterisk.

In fact, the oxidation potentials $E^0(AnO_2^+/AnO_2^{2+})$ are determined by the ionisation potential of the actinoyl ion $I(AnO_2^+)$ or the electron affinity $A(AnO_2^{2+})$. The values of E_{CT} depend mainly on the electron affinity of the AnO_2^{2+} ions. It is not the whole set of MO, but only individual MO, that make the main contribution to the vlalues of E^0 and E_{CT} and are responsible for the identical (*N*-type) dependence of these properties on Z_{An}.

The classical object for the study of the energy of *f*–*f* transitions is the neptunyl ion, which contains one electron in the φ_{5u}-level. Table 4 compares our calculated energies of the *f*–*f* electron transitions for the neptunyl ion with experimental data,[59,71,73] and Table 5 gives the energies of the *f*–*f* transitions in the actinyl ions. These data indicate that the centres of gravity of bands corresponding to transitions of the same kind are displaced along the actinyl ion series towards an increase in their energies. As noted above, the spectra of the *f*–*f* transitions reflect two trends in the

change in the energies of the MO: the decrease in the splitting of the 5*f*-AO by the crystal field of the ligands along the series, and the increase in their splitting as a result of spin–orbit coupling. Thus in the uranyl ion the splitting of the 5*f*-AO by the crystal field is twice their splitting by spin–orbit coupling, whereas towards the end of the series the two effects are of almost equal magnitude.

Table 4. Energies of the *f*–*f* electron transitions in NpO_2^{2+} compounds (cm^{-1}).

Transition	Calculated for the series				Experiment			
	NpO_2^{2+}				$Cs_2NpO_2Cl_4$		$Cs(NpO_2)(NO_3)_3$	
	(a)	(b)	(c)	(d)	(Ref.59)	(Ref.71)	(Ref.59)	(Ref.73)
δ_{3u}–φ_{7u}	7178	7097	6693	7097	6880	6890	6459	6750
δ_{3u}–δ_{5u}	7178	7097	6693	7097	7990	7880	9420	8180
δ_{3u}–$3\pi_{1u}$	17904	17098	19093	19194	17241	17241	17843	18000
δ_{3u}–$3\pi_{3u}$	20969	20153	19597	22259	20080	–	20816	21000

The splitting by the crystal field and spin–orbit coupling is much smaller in the actinoyl ions than in the actinyl ions.[119]

Overall, in the actinyl and actinoyl ions, increase in the atomic number of the actinide displaces transitions of the same kind into the ultra-violet range of the spectrum.

To interpret the redox properties and electronic absorption spectra of the actinyl and actinoyl ions we used individual MO, responsible for the ionisation potentials, their electron affinity, energy transitions, etc. Other properties, for example the thermodynamic properties, depend not on the energy of the last occupied MO but on the energies of the whole set of MO for the compound or ion that is on their sum.

We can write an expression for the standard enthalpy of formation of AnO_2^{2+} using the ionic approximation

$$\Delta H^0(AnO_2^{2+}) = \Delta H^0(An^{6+}, \text{gas}) + A(R_{An^{6+}} + R_{O^{2-}})^{-1} + B, \quad (9)$$

where

$$\Delta H^0(An^{6+}, \text{gas} = \Delta H^0(An, \text{gas}) + \sum_{z=1}^{6} I_z + 15RT. \quad (10)$$

Here, A and B are constants, and $R_{An^{6+}}$ and $R_{O^{2-}}$ the ionic radii of An^{6+} and O^{2-}. The error in the calculation of $\Delta H^0(AnO_2^{2+})$ is due to the neglect of the interaction of the 5*f*-, 6*d*-, and 7*s*-AO with the 2*p*-AO of the oxygen atoms. This is a crude and approximate calculation scheme, so that we shall restrict ourselves to qualitative estimates of the thermodynamic quantities.

The trend in the change in the enthalpies of formation of the actinyl ions is determined by the second term in Eqn. (10), that is by the sum of the ionisation potentials of the actinide atom, and not by the last ionisation potential, as in the case of the redox potentials. The sum of the first two ionisation potentials remains almost unchanged for U, Np, Pu, and Am, and has the values 17.58, 17.58, 17.50, and 17.633 eV respectively. Thus the trend in the change in $\sum_{z=1}^{6} I_z$ is determined by the sum $\sum_{z=3}^{6} I_z$, and that for $\sum_{z=1}^{5} I_z$ is determined

Table 5. Energies of the *f*–*f* electron transitions for AnO_2^{2+} (cm^{-1}).

Transition	NpO_2^{2+} in the series				PuO_2^{2+} in the series				AmO_2^{2+} in the series			
	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
φ_{5u}–δ_{3u}	1758	1774	2178	1855	2048	2016	2097	2097	2258	2178	2178	2258
φ_{5u}–φ_{7u}	8936	8871	8871	8952	10000	9920	10000	7823	11049	10968	10968	10968
φ_{5u}–δ_{5u}	8936	8871	8871	8952	10000	9920	10000	7823	11049	10968	10968	10968
φ_{5u}–$3\pi_{1u}$	19662	18872	21371	21049	19598	19280	20646	21130	19356	19356	20243	20967
φ_{5u}–$3\pi_{3u}$	22727	21937	21775	24114	22985	22582	23953	24517	22985	21904	23953	24598
δ_{3u} – φ_{7u}	7178	7097	6693	7097	7952	7904	7904	7823	8791	8791	8790	8710
δ_{3u} – δ_{5u}	7178	7097	6693	7097	7952	7904	7904	7823	8791	8791	8790	8710
δ_{3u} – $3\pi_{5u}$	17904	17098	19093	19194	17549	17259	18549	19033	17098	17178	18065	18711
δ_{3u} – $3\pi_{3u}$	20969	20153	19597	22259	20936	20565	21856	22420	20727	20727	21775	22340

by the sum $\sum_{z=3}^{5} I_z$. From Eqn. (8) we can write the sum of the ionisation potentials $\sum_{z=3}^{5} I_z$ in the form:

$$\sum_{z=3}^{5} I_z = \sum_{z=3}^{5} \ln \frac{2L_z\left(f^{q-1}\right)+1}{2L_z\left(f^{q}\right)+1}, \qquad (11)$$

where the values of $L(f^{q-1})$ and $L(f^q)$ correspond to the reaction

$$\mathrm{An}(f^q) \rightarrow \mathrm{An}(f^{q-1}) + \mathrm{e},$$

and are determined from the values of the normal terms of the actinide ions

	U	Np	Pu	Am
An^{2+}	*I*	*H*	*F*	*S*
An^{3+}	*I*	*I*	*H*	*F*
An^{4+}	*H*	*I*	*I*	*H*
An^{5+}	*F*	*H*	*I*	*I* .

(12)

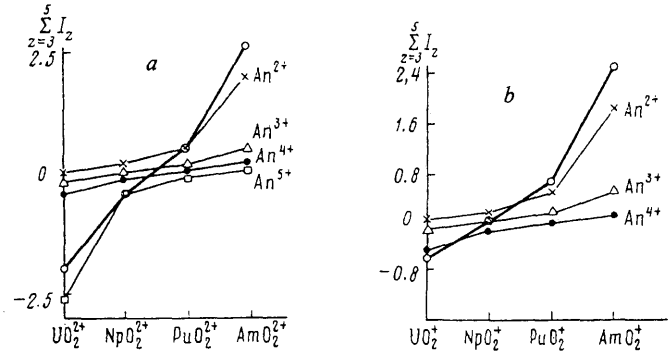


Figure 13. Qualitative trend in the change in the dependence of the sum of the ionisation potentials of the actinide atoms An^{5+} [Eqn. (11)] $\sum_{z=3}^{5} I_z$ on Z_{An}, determining the change in the enthalpy of formation of the actinyl (*a*) and actinoyl (*b*) ions (thick line); the thin lines show the trend in the change in the successive ionisation potentials of An^{2+}, An^{3+}, etc.

The trends in the changes in the separate ionisation potentials of An^{2+}, An^{3+}, etc., and also their sums, determined from Eqn. (11) with allowance for the values of the normal terms, with change in the atomic number of the actinide are shown in Fig. 13. The complete analogy between the experimental relationship for the enthalpies of formation (Fig. 6) and the theoretical relationship (Fig. 13) shows that the trend in the change in the enthalpies of formation is determined by the sum of the first six ionisation potentials for the actinyl ions, and by the sum of five ionisation potentials for the actinoyl ions. In the sum of the ionisation potentials, the spin–orbit contribution is small compared with the electron–electron interaction energy, so that it does not determine the trend in the change in properties, in contrast to the redox potentials, where relativistic corrections make a significant contribution to the values.

It is of interest to consider the relationship obtained for the redox properties by examining them using the purely ionic model, that is using not the ionisation potentials of the actinoyl ions $I(AnO_2^+)$ but the ionisation potentials of the free ions, namely $U^{5+}(^2F,f^1)$, $Np^{5+}(^3H,f^2)$, $Pu^{5+}(^4I,f^3)$, and $Am^{5+}(^5I,f^4)$. The dependence of the redox potentials calculated in the ionic approximation on Z_{An} will be regular, and of the Ω-type and not the *N*-type, as observed experimentally.

Fig. 14 shows the dependence of the effective charges on the actinide ions (An = U, Np, Pu, and Am) on Z_{An}. The relationship is of the Ω-type. For the actinyl ions the larger the distance R_{An-O}, the smaller the effective charge on the actinide atom, that is for an infinitely large distance R_{An-O} the charge on An tends to +2, corresponding to the presence of the free actinide ion An^{2+} and oxygen atoms.

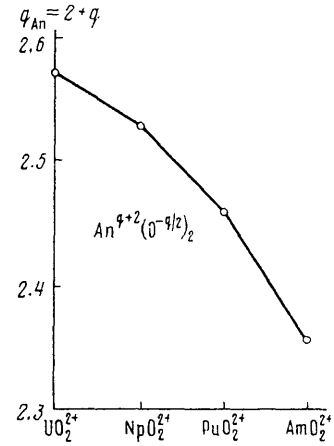


Figure 14. Dependence of the effective charges in the actinyl ions on the atomic number of the actinide.

From the electron density distribution in the actinyl ions it follows that the effective electron configuration of the actinide atoms in the bonding levels is $5f^{2.6-3.2}6d^1$. This electron configuration corresponds approximately to a double bond in the uranyl ion. The 6*s*- and 6*p*-AO will increase the U–O bond order slightly.[40]

It may be concluded that the Ω-type dependence of q_{An} on Z_{An} for the actinyl ions from UO_2^{2+} to AmO_2^{2+} will lead to an Ω-type dependence of R_{An-O} on Z_{An} (see Fig. 1). At the same time, there is a linear relationship between q_{An} and R_{An-O}. This conclusion applies either to the free ions AnO_2^{2+} or to compounds AnO_2X_y in which the ligands X do not have a significant influence on the electronic structure of the actinyl ions.

If, as is usually done in chemistry, the reactivity of ions is characterised by the ionisation potentials and electron affinity, and the electronegativity is defined as $F = I + A$, it is found that the values of I, A, and F change irregularly according to a relationship of the N-type (Fig. 15), that is a relationship of the type already encountered for various properties of the actinyl and actinoyl ions, such as the internuclear distances, bond force constants, molecular polarisabilities, refractive index, etc. Since the irregular relationships for I, A, and F are due to relativistic effects and the crystal field, it may be concluded that the properties of the N-type of the actinyl complexes determined by these parameters will also be due to these effects. The N-type of relationship is determined by the electronic structure of the actinyl ions, and the ligands X increase or decrease the strength of this type of relationship, by donating or accepting electron density. Here, there are two possibilities.

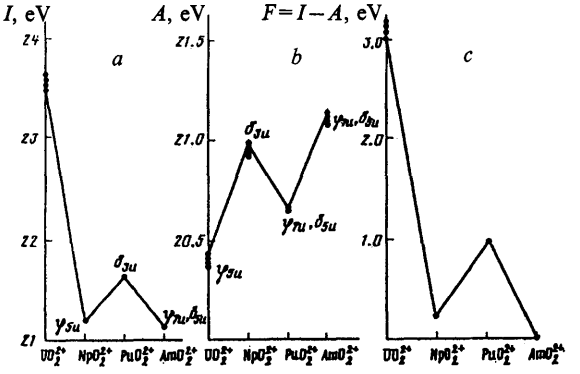


Figure 15. Irregular N-shaped change in the ionisation potentials (a), electron affinity (b), and electronegativity (c) of the actinyl ions on Z_{An}; the MO responsible for the change in these quantities in each ion are shown.

1. The ligands X in the equatorial plane decrease the strength of the An−O bond, which becomes more ionic, and the effects of the crystal field decrease. The L-model begins to "operate". The dependence of the properties on the atomic number of the actinide is of the Ω-type.

2. The ligands X increase the strength of the An−O bond, the effects of the crystal field increase, and the dependence of the properties on Z_{An} remains of the N-type, as for the free AnO_2^{2+} ions.

If it is assumed that complex formation by AnO_2^{2+} ions with ligands X involves the reaction of unoccupied and partly occupied levels of the 5f-type, and also occupied σ- and π-levels mainly of oxygen atoms, it is possible to explain why the enthalpy of formation of the complexes AnO_2X_y will have an extremal value on going from the neptunyl to the plutonyl compounds. This also applies to the enthalpy of extraction. The strong crystal field, combined with the spin−orbit effect, also determines these important chemical characteristics, giving a dependence of the N-type. If the An−O bonds are sufficiently weakened by the ligands X, these properties change according to a relationship of the Ω-type.

The effects of spin−orbit coupling and the crystal field divide the actinyl ions of the first half of the series into two tetrads sharing the americyl ion: UO_2^{2+}, NpO_2^{2+}, PuO_2^{2+}, AmO_2^{2+} and AmO_2^{2+}, CmO_2^{2+}, BkO_2^{2+}, CfO_2^{2+}. In the approximation of free sextuply-charged actinide ions, this division corresponds to the normal terms $^1S_0$, $^2F_{5/2}$, $^3H_4$, $^4I_{9/2}$ for the first tetrad, and $^4I_{9/2}$, $^3H_4$, $^2F_{5/2}$, $^1S_0$ for the second tetrad.

Similarly, the actinoyl ions form two tetrads, from PaO_2^+ to PuO_2^+ and from PuO_2^+ to BkO_2^+.

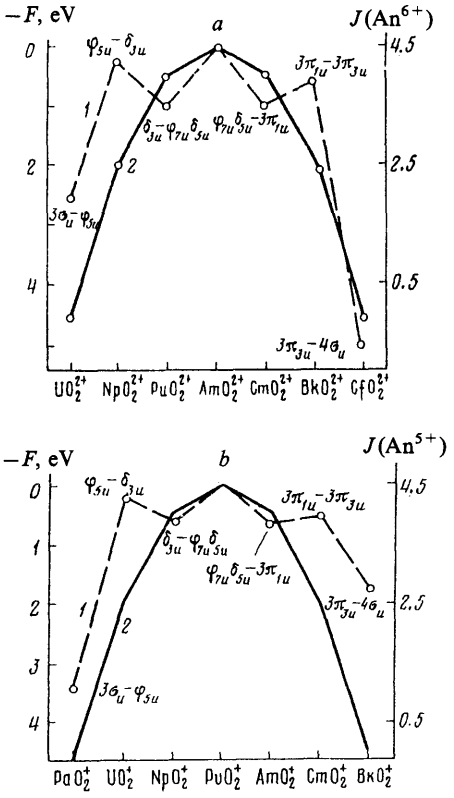


Figure 16. Dependence of the electronegativity $F = -I + A$ for the actinyl (a) and actinoyl (b) ions (curve 1) and the quantum numbers J (curve 2) for the normal terms of the sextuply-charged (a) and quintuply-charged (b) ions on Z_{An}; the MO determining the quantities I and A are shown on the dependence of F on Z for each ion.

Figure 16 shows the dependence of the electronegativities of the ions AnO_2^{2+} (Fig. 16a) and AnO_2^+ (Fig. 16b) on Z_{An}. The dependence of the quantum numbers J for the free sextuply-charged An^{6+} and quintuply-charged An^{5+} ions on the atomic number of the actinide is given for comparison. The "saw-tooth" dependence of F on Z_{an} for the actinyl and actinoyl ions has the general character of bell-shaped curves and is similar to the dependence of the quantum numbers J on Z_{An} for the quintuply- and sextuply-charged ions. This means that there should be a qualitative

correlation between various properties of the actinyl and actinoyl ions and the quantum numbers J for the free ions An^{6+} and An^{5+}. These are tetrads in the J-model, but not in the L-model. It follows from Fig. 16 that the values of F in both tetrads change with increase in Z_{An} according to an N-relationship. Curves of this type are observed when the properties of the actinyl and actinoyl ions depend on definite MO, and not on the entire set of MO as a whole. Thus the electronegativity of the uranyl ion is determined by the energy corresponding to the charge-transfer band $F_{UO_2^{2+}} = E_{3\sigma_u} - E_{\varphi_{5u}}$; the electronegativity of the neptunyl ion is smaller, since it depends on the energy of spin–orbit splitting $F_{NpO_2^{2+}} = E_{\varphi_{5u}} - E_{\delta_{3u}} \simeq \zeta$; for the plutonyl ion, the value is $E_{PuO_2^{2+}} = E_{\delta_{3u}} - E_{\varphi_{7u},\delta_{3u}} \simeq 2.5\zeta$; finally, for AmO_2^{2+}, $F \simeq 0$, since the degenerate φ_{7u},δ_{5u}-MO contains one electron. The irregular $F_{AnO_2^{2+}}$ relationship is responsible for the appearance of relationships of the N-type in each of the tetrads from the uranyl to the americyl ion and from the americyl to the curyl ion.

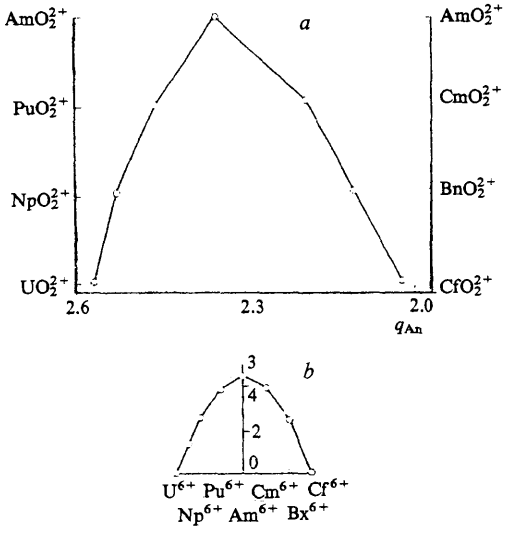


Figure 17. Dependence of the effective charges on the actinide atoms in the actinyl ions (*a*) and the corresponding dependence of the quantum numbers J of the total angular momenta for the sextuply-charged ions An^{6+} in the ground electronic state (*b*) on Z_{An}.

In the so-called summative properties which depend on all the MO, such as the electron density distribution, a relationship of the Ω-type is observed. This type of relationship is shown in Fig. 17*a* for the effective charges on the actinide atoms in the actinyl ions. The two tetrads for the change in q_{An} are completely analogous to the two tetrads for the values of the quantum numbers J of the normal terms of the sextuply-charged actinide ions in Fig. 17*b*.

IV. Summary

Before summarising the interpretation of the physicochemical properties of the actinyl and actinoyl ions based on X_α-SW calculations, we ask the question: is the chemistry of compounds of this class enriched by new chemical ideas as a result of these calculations, or do they provide a basis only for the quantitative interpretation of the properties? We have never been under the illusion that calculations for a particular molecule, no matter how well they are carried out, that is using the entire arsenal of computer techniques, will open the gates of the unknown. We have emphasised this idea many times (see for example our earlier review[174]). The calculation for a series of molecules or ions of the same type, as in the present case, has made it possible to determine the reasons for the irregular change in a number of properties along the series, and this cannot be done by restricting the calculation to one ion, for example the uranyl ion, as has been the practice until now. The calculations should not be restricted to the simple Hückel method, since it has been found that the irregularity is a manifestation of relativistic effects combined with the crystal field effect. X_α-SW calculations have made it possible to understand why some properties change regularly while others change irregularly.

The division of MO into fragments is not a new idea in chemistry. In the case of the actinide compounds, however, there is a characteristic specific reason for this division, related to the division of the AO of the actinide atoms into three groups, according to the energy values: $6s + 6p$, $5f$, and $6d + 7s$. This gives a characteristic fragmented system of energy levels; in the fragments, individual MO of the same type have similar AO compositions.

Finally, there is considerable debate in the literature on the existence of the tetrad and double–double effects and their interpretation and limits of applicability.[47,80–84] In fact, at first sight it appears strange that such "down to earth" properties of the compounds of the lanthanides and actinides as the extraction constants or complex-formation constants of the f-ions correlate with the quantum numbers L and J of the normal terms, not to mention that there is no difference between them, that is the logarithms of the extraction coefficients of the lanthanides for a given extracting agent in some sources correlate with the quantum numbers J and in others with L.[84,85] By using the methods of statistical physics combined with calculations for the entire series of observed and hypothetical ions AnO_2^{2+} and AnO_2^{+}, we have been able for the first time to go beyond simple "property–quantum number" correlations and have been able to show why and when these correlations are significant, and also that these correlations determine the trend in the change in properties, but no more. Without a series of calculations it was impossible to suggest (and nobody has done it!) that the effective charges on the actinide ions in actinyl compounds obey the tetrad relationship. Moreover, it can be stated that in isovalent compounds of the actinide series, for example in $AnHal_6$, where An = U, Np, ..., Bk, the relationships observed will be of the same type as for the actinyl ions (strictly regular, regular, and irregular relationships). These questions will be examined in later papers, but here we point out that the relationship is general and provide an explanation. Thus the problem of determining the electronic structure of the actinyl and actinoyl ions, formulated in the Introduction, can be regarded as solved. In the carrying out of systematic series of calculations for systems of the same type we see the optimum use of the methods of computational quantum chemistry for analysing experimentally observed relationships and predicting new ones.

References

1. G V Ionova *Usp. Khim.*, 1990, **59**(1) 66 [English translation in *Russ. Chem. Rev.*, 1990(1)]
2. G V Ionova, V G Pershina, V I Spitsyn *Elektronnoe Stroenie Aktinidov* (The Electronic Structure of the Actinides), Nauka, Moscow, 1986, 232 pp
3. G V Ionova, V G Vokhmin, V I Spitsyn *Zakonomernosti Izmeneniya Svoistv Lantanidov i Aktinidov* (Regularities in the Change in the Properties of the Lanthanides and Actinides), Nauka, Moscow, 1990, 238 pp
4. W H Zachariasen *Acta Crytallogr.*, 1948, **1** 277
5. M Atoji, M J McDermott *Acta Crystallogr.*, 1970, **26** 1550
6. T K Keenan *Inorg. Nucl. Chem. Lett.*, 1968, **4** 381
7. I L Jenkins, F H Moore, M J Waterman *J. Inorg. Nucl. Chem.*, 1965, **27** 77
8. N C Jayadevan, D M Chackraburty *Acta Crystallogr., Sect. B*, 1972, **28** 3178
9. M P Mefod'eva, M S Grigor'ev, T V Afanas'eva, E B Kryukov *Radiokhimiya*, 1981, **23**(5) 697
10. V M Vdovenko *Sovremennaya Radiokhimiya* (Modern Radiochemistry), Atomizdat, Moscow, 1969, 308 pp
11. N K Dalley, M H Mueller, S H Simonsen *Iorg. Chem.*, 1971, **10** 323
12. V M Vdovenko, E V Stroganov, A P Sokolov, G Lungu *Radiokhimiya*, 1962, **4**(1) 39
13. J C Taylor, M H Mueller *Acta Crystallogr.*, 1965, **19** 389
14. D Hall, A D Rae, T N Waters *Acta Crystallogr.*, 1965, **19** 399
15. V M Vdovenko, V A Vodovatov, L G Mashirov, D N Suglobov *Dokl. Akad. Nauk SSSR*, 1973, **209**(2) 352
16. V M Vdovenko, V A Vodovatov, L G Mashirov, D N Suglobov *Radiokhimiya*, 1974, **16**(5) 717
17. V A Golovnya, G V Ellert, R N Shchelokov *Kompleksnye Soedineniya Urana (Complexes of Uranium)* (Edited by I E Chernyaev), Nauka, Moscow, 1964, 232 pp
18. C Musikas, J H Burns *Actinides-74: Abstracts*, Karlsruhe, 1975, p. 30
19. S S Malcic *Bull. Inst. Nucl. Sci. Bris Kidrich*, 1958, **8** 99
20. R Graziani, G Bombieri, E Forsellin *J. Chem. Soc., Dalton Trans*, 1972, 2059
21. F Weigel, G Hoffmann, R Marquart *Actinides-81: Abstracts*, California, 1982, p. 192
22. N W Alcock *J. Chem. Soc., A*, 1968, **6** 1588
23. G A Barclay, T M Sabine, J C Taylor *Acta Crystallogr.*, 1965, **2** 205
24. Yu F Volkov, I I Kapshukov *Radiokhimiya*, 1976, **1**(2) 284
25. W H Zachariasen, H A Plettinger *Acta Crystallogr.*, 1959, **12** 526
26. M S Fred, J Blaise *The Chemistry of the Actinide Elements* (Edited by J J Katz, J T Seaborg, L R Morss), Chapman and Hall, New York, 1986, p. 1–102
27. L H Jones *J. Chem. Phys.*, 1955, **23** 2105
28. W H Zachariazen *Acta Crystallogr.*, 1954, **7** 783
29. C E Thalmayer, D Cohen *Actinide Chemistry*, Pergamon Press, New York, 1967, p. 256
30. D Hall, A D Rae, T N Waters *Acta Crystallogr.*, 1966, **29** 160
31. Yu N Mikhailov, V G Kuznetsov *Nauchnaya Konferentsiya, Posvyashchennaya 50-letiyu IONKh AN SSSR: Tezisy Dokladov* (Summaries of Papers Presented at the Scientific Conference Dedicated to the Fiftieth Anniversary of the Institute of General and Inorganic Chemsitry of the USSR Academy of Sciences), Nauka, Moscow, 1968, p. 68
32. V A Glebov *Elektronnaya Struktura i Svoistva Uranil'nykh Soedinenii* (The Electronic Structure and Properties of Uranyl Compounds), Energoatomizdat, Moscow, 1983, 88 pp
33. J Fuger, F L Oetting *The Chemical Thermodynamics of Actinide Elements and Compounds. Part 2. The Actinide Aqueous Ions*, Intern. Atomic Energy Agency, Vienna, 1976, p. 64
34. F David *J. Less Common Metals*, 1986, **121** 27
35. L H Jones, R A Penneman *J. Chem. Phys.*, 1965, **21** 5
36. G V Ionova, V I Spitsyn *Effektivnye Zaryady v Soedineniyakh Aktinidov* (Effective Charges in Compounds of the Actinides), Nauka, Moscow, 1988, 270 pp
37. T K Keenan, F H Kruse *Inorg. Chem.*, 1964, **3** 1231
38. Yu F Volkov, G I Visyashcheva, S V Tomilov *Radiokhimiya*, 1981, **23**(2) 237
39. Yu F Volkov, G I Visyashcheva, S V Tomilov *Radiokhimiya*, 1981, **23**(2) 243
40. A Cousson, S Dabos, H Abazli, et al. *Inorg. Chim. Acta, A*, 1983, **3** 89
41. G V Ionova, V I Spitsyn *Radiokhimiya*, 1980, **22**(4) 473
42. R J Gillespie *Molecular Geometry* (Translated into Russian), Mir, Moscow, 1975, p. 216
43. C L Rollinson *Comprehensive Inorganic Chemistry* (Edited by J C Bailar), Pergamon Press, New York, 1973, p. 737
44. F A Cotton, G Wilkinson *Advanced Inorganic Chemistry* (Translated into Russian), Vol. 1, Mir, Moscow, 1969, p. 388
45. J Jove, G Ionova *Radiochim. Acta*, 1990, **143** 73
46. K Tatsumi, R Hoffmann *Inorg. Chem.*, 1980, **19** 2656
47. L P Fuks, PhD Thesis, Warsaw University, 1986
48. G Bombieri, P de Giovanni *Handbook on the Physics and Chemistry of the Actinides* (Edited by A J Freeman, et al.), Elsevier Sci. Publ., Amsterdam, 1985, p. 75–141
49. L R Morss *The Chemistry of the Actinide Elements* (Edited by J J Katz, L R Seaborg, L Morss), Chapman and Hall, New York, 1986, p. 1279
50. S P McGlynn, J K Smith, W C Neely *J. Chem. Phys.*, 1961, **35** 105
51. J A Burns, C Musikas *Inorg. Chem.*, 1977, **16** 1619
52. A A Lychev, L G Mashirov, Yu I Smolin *Radiokhimiya*, 1980, **22**(1) 43
53. V A Vodovatov, I N Ladygin, A A Lychev *Radiokhimiya*, 1975, **17**(6) 884
54. T K Keenan *Inorg. Chem.*, 1965, **4** 1500
55. L B Asprey, F H Ellinger, W H Zachariasen *J. Am. Chem. Soc.*, 1954, **76** 5235
56. G I Visyashcheva, Yu F Volkov, G A Simakin, I I Kapshukov *Radiokhimiya*, 1984, **26**(2) 171
57. R G Denning, T R Snellgrove, D R Woodwark *Mol. Phys.*, 1976, **32** 419
58. R G Denning, T R Snellgrove, D R Woodwark *Mol. Phys.*, 1979, **37** 1129
59. D R Denning, J O W Norris *Mol. Phys.*, 1982, **46** 287
60. D N Suglobov, V M Vodovatov, L G Mashirov *Radiokhimiya*, 1976, **18**(5) 710
61. A F Leung, E Y Wong *Phys. Rev.*, 1970, **187** 504

62. O M Stafsudd, A F Leung, E Y Wong *Phys. Rev.*, 1969, **180** 339
63. J C Eisenstein, M H L Pryce *J. Res. Nat. Bur. Stand., Sect. A*, 1965, **69** 217
64. J C Eisenstein, M H L Pryce *J. Res. Nat. Bur. Stand., Sect. A*, 1966, **70** 165
65. S P McGlynn, J K Smith *J. Mol. Spectros.*, 1961, **6** 164
66. S P McGlynn, J K Smith *J. Mol. Spectrosc.*, 1961, **6** 188
67. R L Belford, G Belford *J. Chem. Phys.*, 1961, **34** 1330
68. J B Newman *J. Chem. Phys.*, 1965, **43** 1691
69. J T Bell *J. Inorg. Nucl. Chem.*, 1969, **31** 703
70. R G Denning, J O W Norris, D Brown *Mol. Phys.*, 1982, **46** 325
71. N G Gorshkov, Candidate's Thesis, NIIAR, Leningrad, 1987
72. N G Gorshkov, L G Mashirov *Radiokhimiya*, 1985, **27**(5) 552
73. C K Joergensen, R Reisfeld *Struct. Bonding (Berlin)*, 1982, **50** 121
74. C Riglet, P Vitorge *Inorg. Chim. Acta*, 1987, **133** 323
75. I A Lebedev *Radiokhimiya*, 1978, **20**(5) 645
76. I A Lebedev *Radiokhimiya*, 1979, **21**(6) 802
77. F David *Handbook on the Physics and Chemistry of the Actinides* (Edited by F J Freeman, et al.), Elsevier Sci. Publ., Amsterdam, 1986, p. 97–128
78. T K Keenan *Inorg. Nucl. Chem. Lett.*, 1968, **4** 381
79. D F Peppard, C A A Bloomquist, E P Horwitz, et al. *J. Inorg. Nucl. Chem.*, 1970, **32** 339
80. I Fidelis, S Siekiersli *J. Inorg. Nucl Chem.*, 1966, **28** 185
81. I Fidelis, S Siekiersli *J. Inorg. Nucl. Chem.*, 1966, **29** 2629
82. I Fidelis *Inorg. Nucl. Chem. Lett.*, 1976, **12** 475
83. L Fuks, I Fidelis *J. Radioanal. Nucl. Chem. Lett.*, 1987, **118** 361
84. S Sinha *Systematics and the Properties of the Lanthanides* NATO, Sci. Affairs Division, New York, 1983, p. 71–122
85. W J Ullman, F Schreiner *Radiochim. Acta*, 1988, **43** 37
86. W J Ullman, F Schreiner *Radiochim. Acta*, 1986, **40** 179
87. B S Jensen *Migration Phenomena of Radionuclides in the Geosphere. A Critical Review of Available Information,* Harward Acad. Publ., London, 1982, 337 pp
88. M Aaberg, D Ferri, J Glaser, et al. *Inorg. Chem.*, 1983, **22** 3981
89. M Woods, M L Mitchell, J C Sullivan *Inorg. Nucl. Chem. Lett.*, 1978, **14** 465
90. L D Landau, E M Lifshits *Statisticheskaya Fizika* (Statistical Physics), Nauka, Moscow, 1964, 412 pp
91. W T Carnall *Systematics and the Properties of the Lanthanides*, NATO, Sci. Affairs Division, New York, 1983, p. 215
92. G V Ionova, B I Spitsyn *Proc. II^{es}* Journees des Actinides, Jesolo Lido, Italy, 1981, p. 212
93. S G Bratsch, J J Lagowski *J. Phys. Chem.*, 1985, **89** 3310
94. S Fraga, K M S Saxena *Atomic Data*, 1971, **3** 323
95. J C Krupa, M Hussonnois, M Genet, et al. *J. Chem. Phys.*, 1982, **77** 154
96. J C Eisenstein, M H L Pryce *Proc. R. Soc., London, A*, 1955, **229** 20
97. J B Newman *J. Chem. Phys.*, 1967, **47**(1) 85
98. P F Walsh, D F Ellis *J. Chem. Phys.*, 1976, **65** 2387
99. C Goerller-Walrand, S De Jaegere *Spectrochim. Acta, Part A*, 1972, **28** 257
100. C Goerller-Walrand, L G Vanquickenborne *J. Chem. Phys*, 1971, **54** 4178
101. C Goerller-Walrand, L G Vanquickenborne *J. Chem. Phys.*, 1972, **57** 1436
102. M Boring, J H Wood, J W Moskowitz *J. Chem. Phys.*, 1974, **63** 638
103. C Y Yang, K H Johnson *J. Chem. Phys.*, 1978, **68** 1001
104. M Boring, J H Wood *J. Chem. Phys.*, 1979, **71** 392
105. J H Wood, M Boring, S B Woodruff *J. Chem. Phys.*, 1981, **74** 5225
106. P Pyykko, L L Lohr *Inorg. Chem., 1981,* **20** 1950
107. C K Joergensen *Chem. Phys. Lett.*, 1982, **89** 445
108. R G Denning, D N P Foster, T R Snellgrove *Mol. Phys.*, 1979, **37** 1089
109. N B Borkovskii, A B Kovrikov, D S Umreiko *Koord. Khim.*, 1984, **10**(11) 1526
110. S Larsson, P Pyykko *Chem. Phys.*, 1986, **101** 355
111. R L DeKock, E J Baerends, P H Boerrigter, et al. *J. Chem. Phys. Lett.*, 1984, **105** 308
112. A L Gubskii, A P Kovtun, Yu A Teterin, et al. *Preprint No. 4053112*, Kurchatov Institute of Atomic Energy, Moscow, 56 pp
113. V I Sergienko, L N Ignat'eva, G L Gutsev, et al. *Zh. Strukt. Khim.*, 1985, **26**(1) 131
114. M A Makhyoun *Inorg. Chem.*, 1987, **26** 3592
115. M A Makhyoun, A A Hasanein *Gazz. Chim. Ital.*, 1988, **118** 145
116. C Yang, S Rabii *Phys. Rev., A*, 1975, **12** 362
117. C Yang *Chem. Phys. Lett.*, 1976, **41** 558
118. C Yang *Proceedings NATO Adv. Study Inst. Vancouver, 10–21 Aug. 1981,* New York, Lonndon, 1983, p. 335
119. G V Ionova, V G Pershina, N I Suraeva *Radiokhimiya*, 1989, **31**(1) 11
120. G V Ionova, V G Pershina, N I Suraeva *III Vsesoyuznaya Kofnerentsiya "Khimiya Neptuniya i Plutoniya": Tezisy Dokladov* (Summaries of Papers Presented at the Third All Union Conference on the Chemistry of Neptunium and Plutonium), Nauka, Leningrad, 1987, p. 17
121. G V Ionova, V G Pershina, N I Suraeva, A V Nikolaev *III Vsesoyuznaya Konferentsiya "Khimiya Neptuniya i Plutoniya": Tezisy Dokladov* (Summaries of Papers Presented at the Third All Union Conference on the Chemistry of Neptunium and Plutonium), Nauka, Leningrad, 1987, p. 99
122. G V Ionova, V G Pershina, N I Suraeva *Radiokhimiya,* 1989, **31**(4) 19
123. V G Pershina, G V Ionova, N I Suraeva *Radiokhimiya*, 1989, **31**(4) 26
124. A Messiah *Quantum Mechanics* (Translated into Russian), Nauka, Moscow, 1979, 478 pp
125. D E Ellis, A Rosen, P E Walch *Int. J. Quantum Chem. Symp.*, 1975, **9** 351
126. D E Ellis, G L Goodman *Int. J. Quantum Chem. Symp.*, 1984, **25** 1
127. J H Wood, M Boring *Phys. Rev., B*, 1978, **16** 2701
128. A Rosen *Chem. Phys. Lett.*, 1978, **55** 311
129. M Boring, J H Wood *J. Chem. Phys.*, 1979, **71** 32
130. M Boring, J H Wood *J. Chem. Phys.*, 1979, **5** 342
131. G Thornton, N Roesch, N M E Edelstein *Inorg. Chem.*, 1980, **19** 1304
132. J D Bjorken, S D Drell *Relativistic Quantum Mechanics* (Translated into Russian), Nauka, Moscow, 1978, 295 pp
133. R D Cowan, D C Griffin *J. Opt. Soc. Am.*, 1976, **66**(10) 1010
134. H A Bethe *Quantum Mechanics* (Translated into Russian), Mir, Moscow, 1965, 333 pp
135. P Pyykko *Adv. Quantum Chem.*, 1978, **2** 353

136. I B Bersuker *Elektronnoe Stroenie i Svoistva Koordinatsionnykh Soedinenii* (The Electronic Structure and Properties of Coordination Compounds), Khimiya, Leningrad, 1986, 288 pp
137. H Chermette, A Goursot *Proc. Symp.* Copenhagen, New York, London, 1984, p. 635
138. J Karkowski, J Kobus *Int. J. Quantum Chem.*, 1985, **28**(6) Pt. 1 741
139. J B Danese, J W D Connoly *Int. J. Quantum Chem. Symp.*, 1973, **7** 279
140. J B Danese, J W D Connoly *J. Chem. Phys.*, 1974, **61** 3063
141. J B Danese *J. Chem. Phys.*, 1974, **61** 3071
142. J B Danese *Chem. Phys. Lett.*, 1977, **45** 150
143. I F Janak, V L Moruzzi, A R Williams *Phys. Rev., B*, 1975, **12** 1257
144. F Herman, A R Williams, K H Johnson *J. Chem. Phys.*, 1974, **61** 3508
145. N Roesch, W G Klemperer, K H Johnson *Chem. Phys. Lett.*, 1973, **23** 149
146. D R Salahub, R P Messmer, K H Johnson *Mol. Phys.*, 1976, **31** 529
147. J Weber, M Geoffroy *Theor. Chim. Acta*, 1977, **43**(4) 299
148. I A Topol', A I Dement'ev *Zh. Strukt. Khim.*, 1980, **21**(2) 3
149. I A Topol', A I Dement'ev *Zh. Strukt. Khim.*, 1980, **21**(2) 13
150. R P Messmer, D R Salahub *J. Chem. Phys.*, 1976, **65** 779
151. I A Topol', A I Dement'ev *Zh. Strukt. Khim.*, 1980, **16**(2) 154
152. A S Chesnyi, I A Topol', S L Bazhenov *Teor. Eksp. Khim.*, 1980, **16**(2) 154
153. K H Johnson *Adv. Quantum Chem.*, 1973, **7** 143
154. J W D Connoly, K H Johnson *Chem. Phys. Lett.*, 1971, **10** 616
155. J C Slater *The Self-Consistent Field for Molecules and Solids* (Translated into Russian), Mir, Moscow, 1978, 662 pp
156. I A Topol', B I Zhilinskii *Teor. Eksp. Khim.*, 1984, **20**(4) 406
157. K Schwarz, J W D Connoly *J. Chem. Phys.*, 1971, **55** 4710
158. E A Kmetko *Phys. Rev., A*, 1970, **1** 37
159. K Schwarz *Phys. Rev., B*, 1972, **5** 2466
160. M Berrondo, O Goscinski *Phys. Rev., A*, 1969, **1** 10
161. I Lindgren, K Schwarz *Phys. Rev.*, 1972, **5** 542
162. K H Johnson, F C Smith *Phys. Rev., B*, 1972, **5** 831
163. J G Norman *J. Chem. Phys.*, 1974, **61**(11) 4630
164. J G Norman *Mol. Phys.*, 1976, **31** 1191
165. J Weber, V A Gubanov *J. Inorg. Nucl. Chem.*, 1979, **41** 6
166. F M Michel-Calendini, H Chermette, J Weber *J. Phys.*, 1980, **13** 1427
167. M R Cook, M Karplus *J. Chem. Phys.*, 1985, **83** 6344
168. D A Case, M Karplus *Chem. Phys. Lett.*, 1976, **39** 33
169. W R Wadt, *J. Am. Chem. Soc.*, 1981, **103** 6053
170. B W Veal, D J Lam, W T Carnall, H R Hoekstra *Phys. Rev., B*, 1976, **12**(12) 5651
171. N B Mikheev *Radiochim. Acta*, 1983, **32** 69
172. L R Morss *Standard Potentials in Aqueous Solutions* (Edited by A J Bard, et al.), Chapman and Hall, New York, 1989, p. 20
173. L R Morss *The Chemsitry of the Actinide Elements* (Edited by J J Katz, et al.), Chapman and Hall, New York, 1986, Vol. 2, p. 1279–1360
174. G V Ionova, V I Spitsyn *Usp. Khim.*, 1984, **43**(8) 1249 [English translation in *Russ. Chem. Rev.*, 1984(8)]

Received 27th March 1992

Translated from *Uspekhi Khimii* **61** 1687–1719 (1992) U.D.C. 541.128.3+543.422.27

Solid state reactions as a method of introducing transition metal cations into high-silica zeolites

A V Kucherov, A A Slinkin
Zelinskii Institute of Orgnanic Chemistry, Russian Academy of Sciences

ABSTRACT. Solid state reactions can be used to introduce one or more multivalent transition metal cations into high-silica zeolites. Most such cations cannot be introduced into these matrices by other methods. The influence of various factors on the processes of stabilisation of the cationic species in the zeolite channels is analysed. Pentasil-based systems with distinct, isolated centres form unique subjects for studying the relationship between the catalytic properties of the transition metal cation and the local structure of the centre. Highly active and stable catalysts for the complete oxidation of alkanes and for the decomposition of nitrogen oxides can be obtained by solid-state modification of the pentasils.

The bibliography comprises 65 references.

Contents

I. Introduction 925
II. Procedure for carrying out exchange in the solid state and methods for studying the products 925
III. Introduction of transition metal ions into the cationic sites in HS-zeolites by means of solid state reactions 926
IV. The role of the gas phase and the anionic part of the salt in solid state exchange in HS-zeolites 939
V. Transition metal cations in an H-ZSM-5 matrix as isolated catalytic centres 940
VI. Conclusion 942

I. Introduction

The introduction of different ions into zeolites is one of the methods of modifying their adsorption and catalytic properties and there is therefore great interest in this topic. For wide-pore zeolites, e.g. those of the faujasite type, exchange from the liquid phase (usually from aqueous solution) is a universal method for introducing any ion into the cationic sites. The results obtained by using ion exchange for such zeolites have been reviewed.[1,2]

However, ionic exchange from the liquid phase has very limited potentialities for zeolites of the pentasil type because the channels are too small for diffusion of multiply charged ions in their solvation shells. For this type of zeolite only singly charged, and some doubly charged, ions can be introduced by exchange methods but most transition metal ions, which are precisely those of greatest interest from the point of view of oxidation-reduction catalytic properties, cannot be introduced into the channels by this means. Modified high-silica (HS) zeolites particularly have unique potentialities for the catalytic processes to be analysed at the atomic-molecular level because it is possible to produce in them a distinct set of isolated centres whose topography and structure are determined by the type of zeolite lattice and whose spatial environment is determined by the structure of the channels.

HS-zeolites have a framework that is thermally highly stable and this enables us to use topochemical methods of introducing cations by means of solid state reactions with various transition metal compounds. The present review is devoted to an analysis of this particular line of research, which only started to be developed in the last decade.

Our aim was to summarise the data on the introduction of transition metal ions into HS-zeolites by means of solid state reactions and to discuss the nature of the oxidation-reduction centres formed and the catalytic processes involving them. The subject matter is to a large extent a review of our own work because we have a great interest in the topic under discussion and have carried out systematic research in this field since 1984.

II. Procedure for carrying out exchange in the solid state and methods for studying the products

The typical procedure for exchange in the solid state is very simple, involving heating a mechanical mixture of the zeolite with a transition metal oxide (or salt) in a stream of inert gas, under vacuum, or in air. Soluble compounds can be deposited on the outer surface of the zeolite more uniformly by the "dry" impregnation method and this makes the subsequent solid state reaction more rapid.

The temperature at which the solid-state exchange reaction reaches an appreciable rate depends on the type of cation and anion. Under sufficiently drastic conditions the degree of exchange reaches the maximum possible for a given zeolite and the excess of the transition metal compound remains in the mixture as a separate phase.

A number of methods can be used to study solid-state exchange reactions with the NH_4- or H-forms of zeolites: i.r. spectroscopy, RFES [probably X-ray photoelectron spectroscopy (Ed. of Translation)], thermogravimetric analysis, and analysis of the gaseous products liberated (HCl in the case of metal chlorides, H_2O for oxides). However EPR is extremely sensitive and informative for transition metal cations. For cations such as Cu^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}, V^{4+}, Cr^{5+}, and Mo^{5+} EPR data not only enable the process of dispersion of the ions in the zeolite matrix to be recorded but also provide a safe estimate of the coordination environment of isolated cations and the changes in it on reaction with various molecules.

In the early 1970's some interesting results were obtained which showed that solid state reactions between a zeolite and alkali metal salts can be accompanied by ion exchange. For example, Rabo and co-workers[3–5] observed replacement of the residual protons by Na^+ cations when mixtures of the zeolites NaY, CaY, BeY, and LaY with NaCl are heated (at 575–675 K). HCl was evolved during the reaction and the catalytic activity of the zeolites in reactions catalysed by acidic groups decreased sharply. After CaY and LaY had been heated with NaCl their i.r. spectra showed a reduction in the intensities of the bands due to acidic OH groups. A solid state reaction with NaCl has been used to remove the residual acidic groups in a Y zeolite.[3–5]

In the preparation of specimens for EPR studies, evolution of HCl and stabilisation of ions in the cationic centres of zeolites of types A, X, and Y occurred as a result of solid state reactions of the H-forms of these zeolites with zinc, cobalt, nickel, and chromium chlorides.[6]

This line of research, related to the modification of the acid-base properties of zeolites by alkali metal and alkaline-earth metal salts, has recently been extended to HS-zeolites (mordenite, H-ZSM-5). Detailed studies in this area have been made by a group under the direction of Professor Karge (see Ref. 7 for a summary of their results). In the present review we shall not be concerned with the modification of the acid-base properties of zeolites by alkali metals but shall concentrate on systems with transition metal cations.

Table 1. Specimens studied by Kucherov and Slinkin.[11]

Zeolite	Si_2O_2/Al_2O_3	Exchange of Na^+ by H^+, %	Zeolite	Si_2O_2/Al_2O_3	Exchange of Na^+ by H^+, %
NaM	10	0	pentasil-140	140	95
HNaM	10	50	pentasil-280	280	95
HM	10	95	amorphous alumino-silicate ($S = 360\ m^2\ g^{-1}$)	14	—
HNa-ZSM-5*	69	40			
H-ZSM-5	69	95			

*Obtained by baking out the organic cations from a specimen with 40% deficiency of Na^+.

III. Introduction of transition metal ions into the cationic sites in HS-zeolites by means of solid state reactions

The first papers in which the migration of transition metal ions through zeolite crystals was discussed were Ref. 6 and also Refs. 8–10, in which reduction–reoxidation processes in the ion-exchange zeolites of CuY, CuM, and AgY were investigated. With CuY specimens reduced in hydrogen two types of Cu^0 crystals are formed:[8] inside large cavities in the zeolite and on the outer surface. Reoxidation of small Cu^0 crystals takes place easily and is accompanied by the reappearance of Cu^{2+} in the cationic sites of the zeolite. When CuM specimens are reduced no Cu^{2+} ions are left in the mordenite channels but Cu^0 particles ~200 Å in diameter are formed on the outer surface.[9] However, reoxidation of the specimens does not lead to the formation of CuO crystals on the outer surface but to migration of Cu^{2+} ions which are then trapped in the mordenite channels. Thus in the H-forms of the zeolite there can be diffusion from the outer surface to the cationic sites in an oxidising atmosphere. Similar effects were observed by Beyer, et al.[10] who found that the reoxidation of AgY can be regarded as a solid state reaction between the H-form of the zeolite and an Ag/Ag_2O phase situated on the outer surface of the crystals.

The papers quoted above naturally provided an impetus to detailed studies of solid state reactions in HS-zeolite–transition metal oxide (or salt) mechanical mixtures. Research was carried out first on copper-containing systems because Cu^{2+} ions (unlike most transition metal ions) can be introduced into HS-zeolite by ion exchange. The detailed studies of ion-exchange specimens carried out recently form an excellent basis for a comparative analysis.

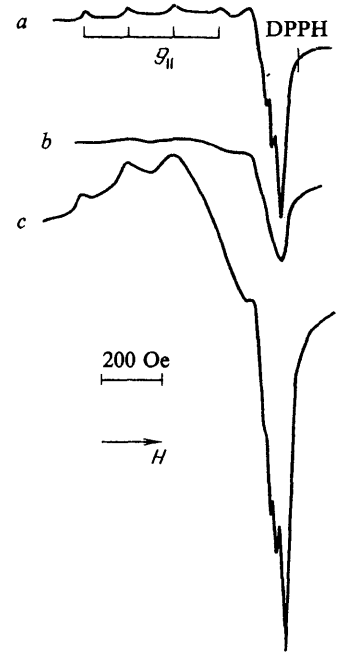


Figure 1. EPR spectra (at 20 °C) of an [HM + BCC] mixture heated in air:[11] *a*, 550 °C, 1 h, specimen evacuated at 20 °C; *b*, air admitted; *c*, 700 °C, 1 h + 800 °C, 1 h, specimen evacuated t 20 °C. [DPPH = diphenylpicrylhydrazine.]

1. Topochemical reactions of copper compounds with mordenite and pentasils

The introduction of Cu^{2+} cations using solid state reactions at 400–800 °C between copper compounds [CuO, basic copper carbonate (BCC), copper metal, $CuCl_2$, CuF_2, $Cu_3(PO_4)_2$, Cu_2S] and various mordenite and pentasil specimens has been investigated thoroughly[11,12] (Table 1).

The EPR spectra of Cu^{2+} ions in an [HM + BCC] mixture heated at various temperatures are shown in Fig. 1. Access of air at 20 °C leads to reversible broadening of the hyperfine-structure (HFS) lines in the spectra and the disappearance of the splitting in the perpendicular component (Fig. 1*b*). On oxidative heating of the [HM + Cu^0] mixture a complex pattern of EPR signals is observed. The only difference is that after heating for an hour at 550 °C the EPR signal is ~5 times weaker than the spectrum in Fig. 1*a* (the HFS agrees completely). However, raising the temperature to 700 °C leads to a considerable increase in the intensity of the signal and after heating at 800 °C for an hour the signal for the [HM + Cu^0] mixture (Fig. 1*c*) agrees with that for the [HM + BCC] mixture in both shape and intensity.

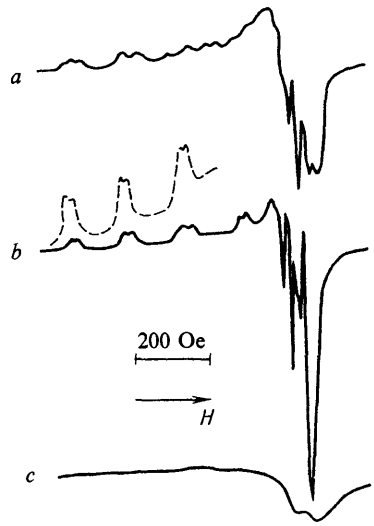


Figure 2. EPR spectra (at 20 °C) of an [H-ZSM-5 + Cu^0] mixture heated in air:[11] *a*, 550 °C, 1 h, specimen evacuated at 20 °C; *b*, 800 °C, 1 h, specimen evacuated at 20 °C; *c*, air admitted.

There are qualitatively no differences between the processes accompanying the oxidative heating of the mixtures of zeolites with BCC, CuO, and Cu^0. In all three cases the reaction of course involves copper(II) oxide which, at the temperatures used, is formed rapidly from both BCC and Cu^0. However, the degree of dispersion of the CuO has a marked effect on the rate of the reactions. In the most heterogeneous system, where Cu^0 powder with a particle size measured in tens of microns is used, the rate of formation of isolated ions, which give the EPR signal, is substantially lower. However it is of fundamental importance that, when the various mixtures are heated under sufficiently drastic conditions, the intensity of the EPR signal from the dispersed Cu^{2+} ions reaches the maximum possible for the given zeolite specimen.

EPR signals from Cu^{2+} do not appear when an [NaM + BCC] mixture is heated at 550–800 °C in air, i.e. there is no exchange of Na^+ by Cu^{2+}; protonic centres are necessary for the stabilisation of Cu^{2+} ions.

The EPR signals produced when an [H-ZSM-5 + Cu^0] mixture is heated in air are shown in Fig. 2. The HFS of the EPR signal (Fig. 2*b*) shows no change and the intensity does not increase when the heating time at 800 °C is increased to 4 h. Admitting O_2 to the specimen at 20 °C causes pronounced reversible broadening of the Cu^{2+} lines in the EPR spectrum (Fig. 2*c*).

The EPR signals obtained when HNa-ZSM-5 is heated with CuO have different parameters (Table 2) and the maximum intensity of the EPR signal from Cu^{2+} is appreciably smaller in this case than for H-ZSM-5. Clearly the Na^+ cations present in the zeolite block those centres that are capable of binding Cu^{2+} cations in H-ZSM-5.

Table 2. Parameters of the EPR spectra due to Cu^{2+}.[11]

Specimen	Heated at (°C)	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$, Oe	$A_{\perp}$, Oe
HM+CuO	550	2.325	2.055	144	19
HNa-ZSM-5+CuO	550 and 800	2.37	2.075	135	—
H-ZSM-5+CuO	550	2.33	2,07	142	17,5
		2.27	2,045	175	29
H-ZSM-5+CuO	800	2.31	2.06	153	
		2.29	2.05	156	23
H-ZSM-5+CuF_2 or $Cu_3(PO_4)_2$	500 and 700	2.31		153	
		2.29		156	
		2.37		120	
		2.38		120	

The reaction of CuO with pentasil specimens with various modules gives EPR spectra with almost the same shape but a different maximum intensity. The intensity of the Cu^{2+} EPR signal is linearly dependent on the aluminium content of the zeolite, providing clear confirmation that the Cu^{2+} is located at the sites of the cationic vacancies formed by the Al^{3+} in the framework.

Heating a mixture of H-ZSM-5 with anhydrous $CuCl_2$ under vacuum at 400 °C for 30 min gives the Cu^{2+} EPR spectrum shown in Fig. 3*a*. Heating the mixture at 550 °C for an hour causes a considerable increase in the signal intensity and heating in air at 800 °C for an hour gives the signal shown in Fig. 3*b*. Heating mixtures of H-ZSM-5 with CuF_2 and $Cu_3(PO_4)_2$ under vacuum at 550–800 °C also gives EPR signals from isolated Cu^{2+} ions. Admitting air leads to reversible broadening of the EPR lines. X-Ray analysis shows that there is no disruption of the zeolite framework when H-ZSM-5 is heated with CuF_2 at 800 °C for 2 h. The parameters of the EPR spectra of Cu^{2+} ions in specimens studied by us previously[11,12] are given in Table 2.

Analysis of the results obtained greatly facilitates detailed comparisons with the data for copper-containing zeolites prepared from the same specimens by ion exchange and studied thoroughly previously,[13,14] and also with data for CuH-ZSM-5.[15,16] When markedly heterogeneous mechanical mixtures of the H-forms of mordenite and pentasil with CuO are heated there is evidently considerable dispersion and migration of some of the Cu^{2+} ions into the zeolite channels. The ions in mordenite and pentasil are located at the same cationic sites as are found in the corresponding

specimens obtained by ion exchange. Thus the EPR signal produced when HM is heated with BCC under fairly mild conditions (Fig. 1*a*) is almost the same as the spectrum of an ion-exchange specimen of CuHM with a small degree of exchange [1 Cu^{2+} ion for each 3 unit cells (u.c.)], where almost all the copper introduced occurs as isolated ions with square pyramidal coordination. The broadening of the components of the Cu^{2+} ion EPR spectrum due to dipole-dipole interaction with O_2 molecules present in the first coordination sphere indicates 100% dispersion of the Cu^{2+} cations in the zeolite channels. When the thermal treatment of HM with CuO is made more severe the EPR spectrum increases in intensity and its shape changes, indicating an interaction between the Cu^{2+} ions. The spectrum shown in Fig. 1*c* is characteristic of weak association of interacting Cu^{2+} ions and is identical in shape and intensity to the spectrum of an exchange specimen of CuHM containing two Cu^{2+} ions to one unit cell. Thus the pattern of changes in the EPR signals accompanying the solid state reaction of HM with CuO is identical to that observed on increasing the concentration of exchanged Cu^{2+} cations in HM. Hence as the migration of Cu^{2+} ions in HM increases they occur first as isolated cations and then as they increase in number in the channels weak associates are formed and a maximum possible concentration is reached (notwithstanding the large excess of CuO on the outer surface).

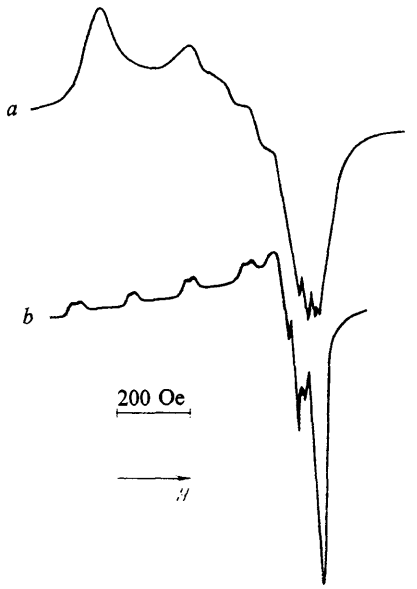


Figure 3. EPR spectra (at 20 °C) of a mixture of H-ZSM-5 with $CuCl_2$ heated under vacuum:[12] *a*, 400 °C, 30 min; *b*, 800 °C, 1 h.

In order to compare the amounts of Cu^{2+} introduced into mordenite by different methods, the oxidative heating of a mixture of BCC with an ion-exchange specimen of CuHM with the maximum degree of exchange was investigated.[12] No increase in the intensity of the Cu^{2+} EPR signal was obtained by heating at 700–800 °C. Hence for mordenite the maximum number of Cu^{2+} cations is not significantly dependent on the method of introduction but is determined by the number of accessible sites in which they can be located. This number is only half of the total cation capacity.

For pentasil-type zeolites the Cu^{2+} introduced by exchange in aqueous solution can be ~20% of the amount of aluminium in the framework and after heating at 500 °C all the copper occurs as two types of isolated, coordinately unsaturated cations with square pyramidal ($g_{||}$ = 2.31, $A_{||}$ = 155 Oe) and square planar ($g_{||}$ = 2.27, $A_{||}$ = 175 Oe) coordination. On increasing the ignition temperature to 800 °C two types of location are retained (square pyramids with a degree of distortion towards square planar). The EPR spectra obtained by heating mechanical mixtures (Fig. 2, *a* and *b*) agree completely with the spectra of the Cu^{2+} cations in the exchange specimen CuH-ZSM-5 which has been heated at 550 °C and 800 °C respectively. The effect of O_2 on the HFS of the EPR spectra is equally pronounced for both the exchange specimen and the heated mechanical mixtures.

Thus for pentasil also, the diffusion of Cu^{2+} ions from the outer surface leads to their being trapped in the cationic sites that are characteristic of the exchange specimens. In spite of the large excess of CuO on the outer surface of the pentasil the number of Cu^{2+} ions dispersed singly reaches a constant value and formation of associates does not take place. The maximum degree of occupation of the cationic vacancies in H-ZSM-5 by Cu^{2+} ions diffusing from the surface has been estimated as 30–40% of the total capacity.[12] When a mixture of the ion-exchange specimen CuH-ZSM-5 (20% exchange) with BCC is heated oxidatively at 700–800 °C the intensity of the EPR signal from isolated Cu^{2+} ions increases by a factor of ~1.5; this also indicates an increase in the degree of exchange to 30%. Thus, for pentasil solid state reactions lead to a somewhat greater degree of exchange than does ion exchange in aqueous solution.

It should be emphasised that the ion-exchange specimens and the specimens prepared by heating mechanical mixtures with CuO are identical as regards adsorption of various substances from the gaseous phase. All the changes in the coordination of the isolated Cu^{2+} ions are absolutely identical for the two types of specimen. This applies both to adsorption of strong ligands (NH_3, pyridine C_3H_6 [17,18]) and to the effects produced by the physical adsorption of hexane and xenon.[19,20]

2. Changes in the ligand environment of Cu^{2+} on adsorption of various molecules in H-ZSM-5

The number of states in which the Cu^{2+} cations occur in the zeolite ZSM-5 depends on the thermal treatment conditions and the Cu^{2+} cation concentration in the zeolite. Anderson and Kevan[15] introduced Cu^{2+} cations by ion exchange into the zeolite NaH-ZSM-5 which is obtained by decomposition of NaTPA-ZSM-5 under vacuum at 600 °C. After the exchange the zeolite contained approximately one Cu^{2+} cation per 10^3 tetrahedra. Dehydration of this zeolite at 400 °C gave an EPR signal from Cu^{2+} ions present in only one state ($g_{||}$ = 2.310, $g_{\perp}$ = 2.052, $A_{||}$ = 172 × 10^{-4} cm^{-1}). The concentration of Cu^{2+} cations in this zeolite was 1 cation per 10 u.c. According to Sendoda and Ono[16] there are ~6 Cu^{2+} cations in 10 u.c. of the zeolite and the EPR spectrum of a specimen which has been dehydrated under vacuum at 400 °C contains three signals corresponding to three Cu^{2+} cation states ($g_{||}^1$ = 2.31, $A_{||}^1$ = 164 × 10^{-4} cm^{-1}; $g_{||}^2$ = 2.30, $A_{||}^2$ = 163 × 10^{-4} cm^{-1}; $g_{||}^3$ = 2.27, $A_{||}^3$ = 176 × 10^{-4} cm^{-1}). When dehydration under vacuum is carried out at 550 °C one of the states of the Cu^{2+} ions disappears and the two remaining states have almost the same EPR parameters

($g_{\|}^1$ = 2.31, $A_{\|}^1$ = 170 × 10^{-4} cm^{-1}; $g_{\|}^2$ = 2.30, $A_{\|}^2$ = 175 × 10^{-4} cm^{-1}). In other studies[11–14,19,20] the amount of Cu^{2+} in H-ZSM-5 reached ~1 cation to 1 u.c., with the zeolite containing two types of Cu^{2+} cation (see Table 2), and the specimens obtained by exchange and by a solid state reaction were identical.

There is an important aspect of the behaviour of Cu^{2+} ions in the zeolite H-ZSM-5 during vacuum conditioning. The intensity of the EPR signal decreases significantly after conditioning of the specimen under vacuum at various temperatures for 3 h.[16] However this effect is not observed if the specimen undergoes oxidative thermal treatment immediately before evacuation.[11–14] It is not impossible that the reduction in intensity is due to the presence of small quantities of adsorbed organic impurities in the specimen. Judging from their results, Sendoda and Ono[16] made no observation of oxidative treatment of the specimen before the vacuum conditioning.

Adsorption of NH_3 at 20 °C does not lead to a significant change in $A_{\|}$ [17,18] and, in contrast to other reports,[15,16] splitting due to interaction with the nuclear spin of the atoms in the coordinated NH_3 molecules was not observed in the $g_{\perp}$ region. This may be due to steric hindrance in the reaction of the NH_3 molecules with the Cu^{2+} cations trapped in the ZSM-5;[16] the steric hindrance probably increases as the concentration of Cu^{2+} cations in the zeolite increases.[15] The two types of Cu^{2+} cation react differently with NH_3.[16,17] The reaction of the Cu^{2+} in the zeolite ZSM-5 with pyridine is more hindered than that with NH_3.[16] In accordance with this the parameter of the EPR spectrum of the Cu^{2+} cations change even less[17,18] and no HFS component due to interaction with the nuclear spin of the nitrogen atom is observed in the $g_{\perp}$ region.

There is a vigorous reaction between $(CH_3)_2O$ molecules and the Cu^{2+} cations in ZSM-5.[17,18] Both types of Cu^{2+} cations are evidently involved in this reaction with formation of two types of complex which probably contain different numbers of $(CH_3)_2O$ molecules in the coordination sphere.[15] Several adsorption complexes with different numbers of molecules are also produced in the reaction of CH_3OH with Cu^{2+} in the zeolite ZSM-5. It is found that the type of change in $g_{\|}$ and $A_{\|}$ in the reaction of Cu^{2+} cations with $(CH_3)_2O$ and CH_3OH molecules ($g_{\|}$ increases and $A_{\|}$ decreases compared to the values for the Cu^{2+} cations in the initial specimen) is similar to the changes in these parameters on hydration of the Cu^{2+} cation;[15] this confirms that the complex-formation reaction takes place with escape of the complexes into a straight channel or to the point of intersection of the channels.

Substantial additions to the information on the stereochemistry of paramagnetic Cu^{2+} complexes in H-ZSM-5 were obtained by using pulsed spin-echo spectroscopy as well as EPR.[15,16]

Anderson and Kevan[15] consider that in the initial hydrated specimen the Cu^{2+} is octahedrally coordinated by 6 water molecules and this complex is located at the intersection of the channels. Evacuation at 20 °C is found to be sufficient for the removal of three molecules of water while activation at 400 °C leads to complete removal of H_2O and formation of Cu^{2+} species with restricted accessibility from the large channel in the zeolite, i.e. situated in a five-membered ring. Adsorption of polar molecules (H_2O, NH_3, pyridine, alcohols) causes rapid migration of Cu^{2+} to positions in the large channels and the formation of Cu^{2+} complexes coordinated to two CH_3OH molecules, three C_2H_5OH or pyridine molecules, or four ammonia molecules. The reaction of Cu^{2+} with the non-polar molecules ethylene and benzene is considerably worse.

The absence of modulation by ^{27}Al in spin-echo spectra shows that the Cu^{2+} cations are not located preferentially on the negatively charged AlO_2^- units in the lattice (the Cu–Al distance is not less than 6 Å). The Cu^{2+} concentration in the zeolite may play an important role in the formation of Cu^{2+} ions coordinated in different ways.[15] For example, for a specimen containing 7 times more copper two types of species were detected after evacuation at 20 °C.[16] It was also found that on adsorption of pyridine a Cu^{2+} complex with two, not three, molecules is formed.

The coordination and location of the Cu^{2+} are affected not only by a low copper concentration in the zeolite but also by the presence of sodium.[11–14] Na^+ ions in the zeolite occupy most of the sites securely, blocking them from coordination with Cu^{2+}. This can only be avoided by using the initial H- or NH_4-forms of ZSM-5.

This was confirmed by Sendoda and Ono[16] who compared the ability of Cu^{2+} in H-ZSM-5, Na-ZSM-5, K-ZSM-5, and Ca-ZSM-5 to form complexes with methanol and ethanol. This ability was found to depend on the presence of the second cation and it is suggested that complexes with 4 molecules of the alcohol are formed in H-ZSM-5 but with only 3 molecules of the alcohol in the other specimens. Furthermore the EPR spectroscopic parameters quoted for Cu^{2+} in pure H-ZSM-5 are similar to our values[11–14] ($g_{\|}$ = 2.27, $A_{\|}$ = 180 Oe; $g_{\perp}$ = 2.05) and are markedly different from those for Cu^{2+} in a zeolite containing Na^+ (see Table 2).

3. Physical adsorption of n-hexane and xenon

In studies of the interaction of isolated Cu^{2+} cations with various molecules in the channels in ZSM-5 it was found that not only unsaturated and polar molecules affect the coordination of the Cu^{2+} but the adsorption of n-hexane is also accompanied by measureable changes in the EPR spectra. We have made a detailed analysis of the effects produced by the physical adsorption of alkanes (n-hexane) and inert gases (Ar, Xe) in the channels in CuH-ZSM-5.[19,20] The EPR signal from the initial CuH-ZSM-5 which has been heated at 800 °C is a superposition of two spectra from isolated Cu^{2+} ions: $g_{\|}^1$ = 2.30, $A_{\|}^1$ = 159 Oe, and $g_{\|}^2$ = 2.31, $A_{\|}^2$ = 156 Oe. The perpendicular components were not completely resolved but the analysis gave the values $g_{\perp}^1$ = 2.05, $A_{\perp}^1$ = 23.5 Oe, and $g_{\perp}^2$ = 2.06, $A_{\perp}^2$ = 22.5 Oe. These values show that the specimen contains two distinct types of isolated Cu^{2+} cations located in square pyramids with appreciable distortion towards square planar.

Adsorption of argon (~150 mm Hg) on to the CuH-ZSM-5 specimen at 20 °C did not produce measureable changes in the Cu^{2+} EPR spectrum. However, sorption of xenon (200 mm Hg) was accompanied by an appreciable and reversible effect on one of the two sets of EPR lines.

Sorption of n-hexane (at 20 °C and saturated vapour pressure) was also accompanied by changes in the HFS of one of the Cu^{2+} EPR signals. A slow increase in temperature to 200 °C with continuous evacuation (to 10^{-6} mm Hg) was accompanied by slow changes in the Cu^{2+} EPR spectrum and after evacuating at 200 °C for 30 min the EPR spectrum reverted almost completely to the original spectrum.

Thus appreciable changes in the EPR parameters on adsorption were found for only one of the two types of Cu^{2+} cation ($\Delta g_{\|}$ = 0.03–0.04, $\Delta g_{\perp}$ = 0.01, $\Delta A_{\|}$ = 9–12 Oe, $\Delta A_{\perp}$ ~ 3 Oe). Hence the Cu^{2+} cations located in two distinct sites which differ very little in their type of coordination show a significant difference in their ability to interact with adsorbed molecules of xenon or hexane. For one type of ion the changes in the coordination are negligibly small but for the other type sorption causes an appreciable reduction in the distortion of the square pyramidal coordination of the Cu^{2+}.

Changes in the symmetry of the Cu^{2+} ion due to formation of a coordinate or covalent bond are common for most compounds (unsaturated and polar molecules). However it is difficult to imagine the formation of bonds between Cu^{2+} ions and a non-polar saturated molecule (hexane) and even more so with an inert gas atom (xenon). It is known that the sorption of hexane in H-ZSM-5 at 20 °C can be described as filling of the channels with the liquid hydrocarbon. The sorption does not take place at specific centres but the whole volume of the channels is filled with the condensed phase. In our opinion[19,20] the results obtained indicate some geometrical displacement of the Cu^{2+} ions to one of the types of cationic site due to a dispersion interaction with the adsorbate molecules (or atoms) occupying the channels in the zeolite.

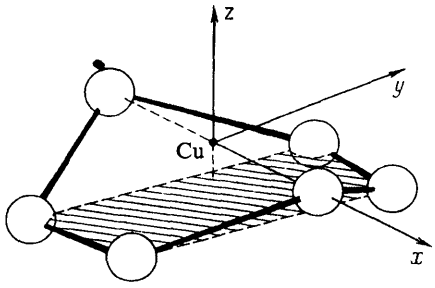


Figure 4. $[Cu^{2+}(O_b^{q-})_6]^{Q}$ **cluster model for an isolated** Cu^{2+} **ion in a structural unit in H-ZSM-5,[17] as determined by X-ray diffraction.[21]**

4. Quantum-chemical analysis of the interaction of molecules with isolated Cu^{2+} cations in H-ZSM-5

There is only one instance where the position of a transition metal cation (Ni^{2+}) in the zeolite H-ZSM-5 has been determined by X-ray diffraction.[21] The ions were found to be located in two sites: (1) in a straight channel close to the wall, and (2) inside a $T_{14}O_{20}$ unit composed of five-membered rings. The cation in the straight channel is bonded to only 3 oxygen atoms in the network but it must have oxygen ligands outside the network. The second site is less accessible and the cation in this site has 6 network ligands. The geometry of this site is shown in Fig. 4. Aspects of the location of the copper cation have been analysed using quantum-chemical calculations.[17,18] The components of the g tensor g_{qq} calculated by the standard method using the Stown approximation agree well with the components of the experimental spectrum. The almost equal components g_{11} and g_{22} are close to the value $g_{\perp} = 2.05$ and the theoretical value g_{33} agrees satisfactorily with the experimental $g_{||}$. However, the most interesting result is that small displacements of the Cu^{2+} ion in the chelate site under discussion can cause marked changes in the parameters of the g factor. Even a negligibly small displacement of the ion ($\Delta z = 0.01$ Å) will lead to appreciable changes in the components g_{qq} (especially g_{33}). There is also a marked dependence of the calculated parameters of the EPR spectrum on changes in the donor-acceptor properties of the ligand environment of the Cu^{2+} when $\Delta z = 0$.

Quantum-chemical calculations of the components of the g tensor[17,18] were also used to assess the interaction of Cu^{2+} in this centre (see Fig. 4) with ammonia. The EPR parameters of complexes with 1 or 2 NH_3 molecules situated on the z axis above and below the Cu^{2+} ion with typical $Cu^{2+}-NH_3$ distances can easily be calculated. However, the differences between the calculated and observed parameters are very large. For complexes with one NH_3 molecule above the cluster $g_{11} = 2.003$, $g_{22} = 2.383$, and $g_{33} = 2.493$, and for those with two NH_3 molecules $g_{11} = 2.003$, $g_{22} = 2.057$, and $g_{33} = 2.090$. Hence either the interaction with ammonia takes place with removal of the Cu^{2+} from such a site or the NH_3 molecule is located sufficiently far away from the cluster under consideration.

Thus it is possible for some of the Cu^{2+} ions in H-ZSM-5 to be located in positions where the EPR parameters are very sensitive to both small geometrical displacements of the ion and small changes in the donor-acceptor properties of the ligand environment. The results of the quantum-chemical calculation confirm that it is possible for the weak effects of physical adsorption of xenon or hexane to cause measurable changes in the Cu^{2+} EPR parameters, as mentioned above.

5. Aspects of the reaction of H-ZSM-5 with various copper compounds

Results published by us[11,12] show that protonic centres in HS-zeolites can be regarded as powerful energy traps for migrating ions. From this point of view the topochemical reaction under discussion can be described as the reaction of CuO with an acid (the protonic centres) and formation of a sort of "salt" of a weak base and a strong acid. The reaction of CuO with H-ZSM-5 at 550–800 °C under vacuum (10^{-6} mm Hg) takes place exactly the same as in air, i.e. the absence of O_2 from the gaseous phase has no effect on the migration and location of Cu^{2+} ions in H-ZSM-5.

It was noted above that H-ZSM-5 can react in the solid state with various compounds. High-temperature reactions of H-ZSM-5 under vacuum with $Cu_3(PO_4)_2$, $CuCl_2$, and CuF_2, like the reaction with CuO, give EPR signals from isolated Cu^{2+} ions (see Figs. 3 and 4). However, the marked differences in the HFS of the EPR spectra in these cases clearly demonstrate the effect of the anion which will act as a ligand, for the isolated Cu^{2+} cations trapped in the zeolite, which is outside the framework (see Table 2).

The appreciable migration of Cu^{2+} at 400 °C in a mixture of $CuCl_2$ with H-ZSM-5 is due to the low stability of the $CuCl_2$ lattice (m.p. 596 °C). Differences occur in the types of coordination of Cu^{2+}, due to the presence of different anionic fragments. For example, in the heated systems (H-ZSM-5 + CuF_2) and [H-ZSM-5 + $Cu_3(PO_4)_2$] at least 4 types of coordination can be distinguished. Two of these are entirely the same as the types found for (CuO + H-ZSM-5) but the other two correspond to a crystal field with octahedral symmetry. It therefore appears that a significant proportion of the isolated Cu^{2+} cations in the zeolite channels interact with the strong ligands F^- and PO_4^{3-} which are outside the framework.

Studies of the reaction of H-ZSM-5 with a copper(I) compound such as Cu_2S [12] show that isolated Cu^+ ions can also migrate to cationic sites in the zeolite after the mixture has been heated under vacuum and their subsequent oxidation produces isolated Cu^{2+} ions.

Thus, using copper-containing high-silica zeolites as an example,[11,12] it has been shown that, due to the thermal stability of the framework of the HS-zeolite and the characteristics of the protonic centres present in them, it is possible to introduce cations by solid state reactions. Not only physicochemical studies but also catalytic data, which will be discussed in a later section, confirm that the specimens obtained are identical to ion-exchange specimens.

In addition to the research on copper-containing HS-zeolites a whole series of papers has been published in which the potentialities of solid state reactions are analysed using a number of other transition metals as examples.

6. Reactions of mordenite and pentasils with chromium compounds

Solid state reactions of mordenite and pentasils (see Table 1) with chromium oxides at 500–820 °C have been studied thoroughly.[22–26]

Heating mechanical mixtures of the H-forms of zeolites with CrO_3 and Cr_2O_3 gives EPR signals of isolated Cr^{5+} ions. When different mixtures are heated under sufficiently drastic conditions the intensities of these signals reach a limit which is determined by the concentration of acidic centres in the zeolite. Heating mixtures containing NaM to 820 °C does not give EPR signals representing isolated ions.

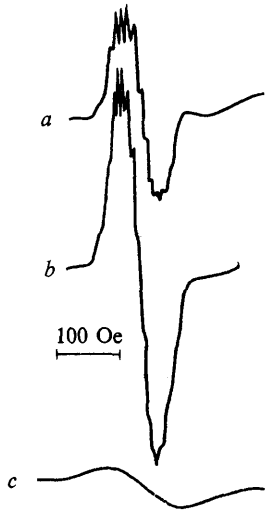


Figure 5. EPR spectra (at 20 °C) of Cr^{5+} ions introduced into H-ZSM-5 by a reaction with CrO_3:[23] *a*, specimen heated in air at 550 °C for 1 h and evacuated at 20 °C for 5 min; *b*, specimen heated at 800 °C for 1 h and evacuated at 20 °C for 5 min; *c*, air admitted to specimen (*b*).

The EPR spectra produced by heating a mechanical mixture of H-ZSM-5 with CrO_3 in air and under vacuum are shown in Fig. 5. Cooling the specimen to –196 °C under vacuum increases the intensity of the signal (Fig. 5*b*) without changing its form (ΔH = 50 Oe, g_0 = 1.98). Admitting air at 20 °C causes a marked, but reversible, broadening of the signal (Fig. 5*c*).

For the initial mixture of H-ZSM-5 with 1.2 mass% Cr_2O_3 the EPR spectrum at 80 °C is a broad symmetrical line (ΔH = 460 Oe) characteristic of bulk antiferromagnetic α-Cr_2O_3. Heating this mixture in air leads to a considerable reduction in the intensity of this signal from the Cr_2O_3 phase and the appearance of a sharp line observed at 20 °C which is identical to the spectrum shown in Fig. 5*b*.

Thus copper is not exceptional and similar processes involving the migration and redistribution of ions in the solid state can occur for other transition metals.

Results published by us[22–25] indicate unequivocally that Cr^{5+} ions are trapped in the H-forms of mordenite and pentasils. In the pentasils the ions occur as isolated, coordinately unsaturated cations which are accessible to molecules from the gas phase. When air is admitted a dipole-dipole interaction with O_2 molecules leads to a marked, reversible broadening of the HFS lines in the spectrum (Fig. 5*c*).

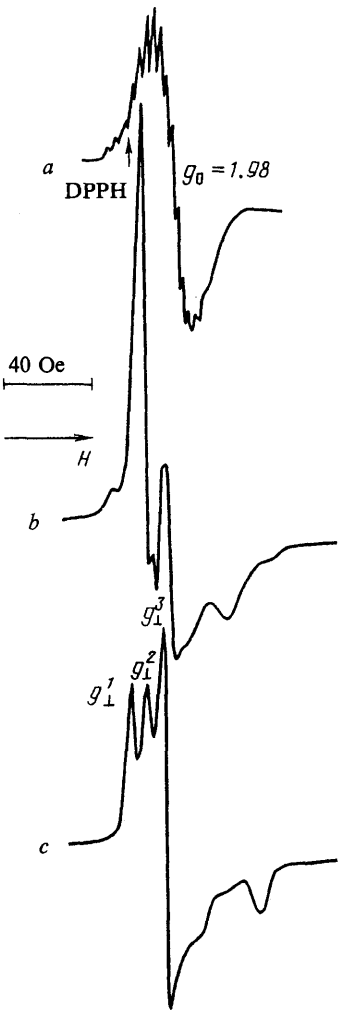


Figure 6. EPR spectra (at 20 °C) of Cr^{5+} ions introduced into H-pentasil-280:[24] *a*, specimen evacuated at 20 °C for 5 min; *b*, after admitting NH_3; *c*, after admitting pyridine; [$g_\perp^1$ = 2.00; $g_\perp^2$ = 1.99; $g_\perp^3$ = 1.98; $g_\parallel^1$ = 1.95; g^2 = 1.93; $g_\parallel^3$ = 1.91].

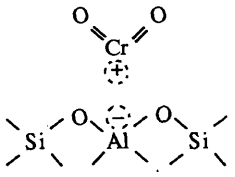
An important aspect of the Cr/HS-zeolite system needs emphasising: the chromium ions in the cationic sites are stabilised in the chromium(V) state when the reaction is carried out in an oxidising medium using both chromium(VI) (CrO_3) and

chromium(III) (Cr_2O_3) compounds. Thus stabilisation of the chromium cations in the matrices of HS-zeolites makes the valence state Cr^V stable.

It is difficult to imagine that, in the HS-zeolites, highly charged pentavalent ions are trapped as cations with no ligands outside the framework and we have therefore suggested[23,24] that the ions stabilised in the cationic sites of the pentasil are not isolated Cr^{5+} ions but isolated CrO_2^+ species balancing the single charge on the framework. The maximum concentration of the CrO_2^+ species depends on the concentration of acidic centres in the specimen.[23,24]

The extra hyperfine structure (EHFS) in the Cr^V EPR spectra (see Fig. 5) provides direct evidence for interaction of the ionic species with an Al^{3+} ion in the framework, creating a cationic vacancy.[23,24] EHFS was also observed for Cr/H-Y.[27,28] In reactions of specimens with NH_3 and pyridine the EHFS disappears and two or three anisotropic signals from Cr^V are superimposed (Fig. 6), i.e. the interaction with these strong ligands leads to a considerable change in the coordination sphere of the cations.[23,24]

The splitting by an aluminium atom situated nearby in itself again confirms the cationic location of Cr^V in the zeolite. However our interpretation of the spectrum with HFS[23,24] was not definitive because, from a formal point of view, an EPR signal with ~15 components obtained in the *X*-band may not be interpreted in terms of splitting by one ^{27}Al nucleus but by two or three aluminium atoms side by side. Although such close alignment of the aluminium atoms in the framework of the ZSM-5 zeolite is improbable, this interpretation of the spectrum (see Fig. 5) is still possible. The problem has been solved by Hemidy, et al.:[29,30] the EPR spectrum of the same Cr^V/ZSM-5 specimen is recorded in the *Q*-band (λ = 8 mm) for comparison (Fig. 7*a*). Using recording in the *Q*-band the anisotropic nature of the spectrum becomes considerably more marked. The groups of lines can be divided into parallel and perpendicular components (6 lines) with slightly different splittings. It is clear from this spectrum that in this system there is an interaction of an isolated Cr^{5+} cation with one Al^{3+} ion in the framework, creating a cationic vacancy. The small magnitudes of the splittings (6–7.5 Oe) indicate that the Al^{3+} is situated in the second coordination sphere of the Cr^{5+} cation and the following mutual arrangement, which allows an interaction between the unpaired electron and the ^{27}Al nuclear spin, is proposed:



The dependence of the distribution of chromium cations in different valence states in a ZSM-5 type zeolite (Si/Al = 20) on the chromium concentration and the conditions of the oxidation-reduction treatment has been studied in detail using chromium concentrations from 0.8 to 3.5 mass%.[25,26] It was shown that at different stages of the thermal treatment of impregnated Cr–TsVM specimens containing 0.8 and 1.8 mass% Cr the Cr^{5+} cations can have different coordination environments. After impregnation and drying in air at 140 °C the major part of the chromium in the specimens occurs as chromates. However even heating at this temperature is sufficient for some of the Cr^{5+} cations to be stabilised within the zeolite channels as hydrated octahedral complexes. When the thermal treatment in air is more drastic the concentration of isolated, coordinately unsaturated Cr^{5+} cations in the zeolite channels increases and aluminium atoms are found in their coordination sphere. The concentration of this type of cation is determined by the concentration of chromium introduced at the impregnation stage.

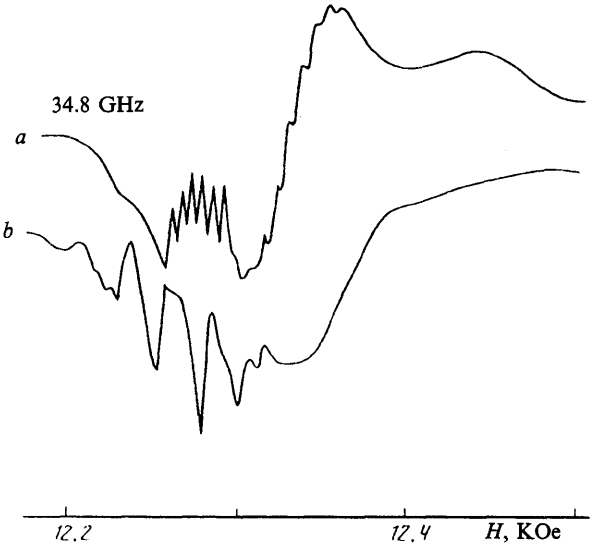


Figure 7. EPR spectra recorded in the *Q* band at 20 °C due to Cr^{5+} cations[28] in: *a*, H-ZSM-5; *b*, H-[Ga]ZSM-5.

A further increase in the concentration of chromium in the chromium–zeolite system leads to new features in its distribution. For example, for specimens containing 2.5 and 3.5 mass.% Cr no EPR spectra due to Cr^{5+} cations were observed either after drying (at 140 °C) or after heating in air at 500 °C for 10 min. This indicates that fairly large crystals of a chromium-containing phase are formed on the outer surface of the zeolite and diffusion of chromium cations from this phase and their stabilisation in the zeolite channels as Cr^{5+} take place slowly. However, heating for an hour is sufficient for this concentration to become high. On passing through the Néel point (314 K), in addition to the signal due to Cr^{5+} cations, an intense broad EPR signal due to formation of large antiferromagnetic crystals of α-Cr_2O_3 on the outer surface of the zeolite is produced. For the specimen containing 3.5 mass% Cr the proportion of Cr^{5+} cations formed is only 20% of the total number of chromium cations in the specimen because a considerable amount of the chromium is stabilised as Cr^{3+} cations in the α-Cr_2O_3 crystals. In other words, these results[25,26] show that the Cr^{5+} cations in an H-ZSM-5 type zeolite may be trapped in several types of centre with different symmetries and with some of the ligands in the first coordination sphere not belonging to the zeolite framework. The results also indicate that, in spite of the considerable variation in the total chromium content and the treatment conditions, it is not possible to introduce more than $(9-10) \times 10^{19}$ Cr^{5+} cations per 1 g of zeolite, i.e. ~0.8 mass% Cr and corresponding to a Cr/Al ratio of ~0.2.

Using a 2.5% Cr–TsVM specimen an investigation was also made of the consistency of the distribution of the different forms of chromium on repetition of the oxidation-reduction treatment at 500 °C.[25,26] It was found that the distribution of the components obtained on preparation of the specimen is very stable and repeating the oxidation-reduction treatment 20 times does not lead to any irreversible changes in the distribution of Cr^{5+} and Cr^{3+} cations in the channels and on the outer surface of the zeolite. An analysis of the EPR spectra due to Cr^{3+} confirms that heating the specimens in hydrogen at 500 °C has no effect on that part of the chromium occurring in the Cr–TsVM in the form of α-Cr_2O_3 crystals. However the Cr^{5+} cations are reduced very easily and quantitatively, most probably to form Cr^{2+} ions.

The results in Refs. 23–26, where the chromium is introduced into H-[Al]ZSM-5, can be compared with more recent research[31] where aspects of the stabilisation of chromium in H-[Cr]ZSM-5, a chromium-silicate with the pentasil structure which contains no aluminium, are discussed. In this matrix, which has the same lattice geometry, some of the Cr^{3+} ions enter the zeolite framework in the synthesis. After the specimens have been heated in air the major part of the chromium introduced is aggregated into an inert Cr_2O_3 phase on the surface of the zeolite but a small proportion of the chromium ions are firmly stabilised by the zeolite as isolated Cr^{5+} ions with a low coordination. However, these ions, which remain grafted to the framework of the H-[Cr]ZSM-5, have properties which differ markedly from those of the CrO_2^+ cationic species that are the counter-ions of the framework aluminium in H-[Al]ZSM-5.

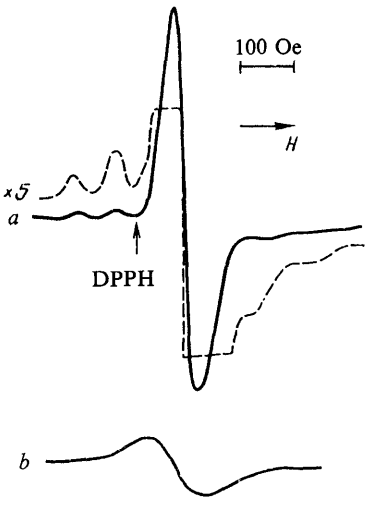


Figure 8. EPR spectra of Mo^{5+} ions introduced into H-ZSM-5 by a reaction with $MoCl_5$ at 450 °C under vacuum:[23] *a*, under vacuum; *b*, in air.

7. Introduction of Mo^{5+} cations into HS-zeolites

Studies have been made of the solid state reactions of mordenite and pentasils with molybdenum compounds.[24,25] The processes of migration of ions into HS-zeolites (see Table 1) when mechanical mixtures with MoO_3 and $MoCl_5$ are heated in air or under vacuum at 150–820 °C have been discussed. Heating mechanical mixtures of the H-forms of zeolites with $MoCl_5$ gives EPR signals from isolated Mo^{5+} ions (Fig. 8). As in the case of Cu^{2+} and Cr^{5+}, when the heating is under sufficiently drastic conditions the intensities of these signals reach a limit which is determined by the concentration of the acidic centres. No isolated molybdenum ions are produced in reactions with NaM up to 820 °C.

Heating mechanical mixtures of the zeolites with MoO_3 or ammonium paramolybdate in air or under vacuum does not give an EPR signal due to Mo^V nor does subsequent reduction in hydrogen give appreciable quantities of Mo^{5+}.[24,25] The reason given for the failure to introduce molybdenum cations by this means is that MoO_3 forms large polymeric fragments even in the vapour phase and does not give cationic species,[24,25] i.e. Mo^{6+} ions do not penetrate into the zeolite channels at all on heating in air.

The reaction of various zeolite specimens with $MoCl_5$ under vacuum is different. Fragments of this volatile compound (b.p. 268 °C) migrate extremely easily both on HS-zeolites and on an amorphous aluminosilicate. The EPR spectrum observed at 20 °C (Fig. 8*a* and *b*) is characteristic of isolated Mo^{5+} ions and the weak HFS lines (6 components with a splitting of ~80 Oe) are due to splitting at the ^{95}Mo and ^{97}Mo nuclei which have a nuclear spin of 5/2 (~24%). The cations are considerably more strongly bound to the zeolites than to the amorphous aluminosilicate. This is shown by experiments in which the specimens are heated at temperatures considerably above the volatilisation temperature of $MoCl_5$. On the amorphous carrier the concentration of cations starts to decrease noticeably at 450 °C and they are removed from the surface quantitatively by heating at 550 °C for 30 min. On zeolites the same thermal treatment does not remove more than one-third of the Mo^{5+} cations. Thus the cationic sites in HS-zeolites are powerful energy traps for Mo^{5+} ions (or rather $MoCl_4^+$ specimes which diffuse easily into the zeolite channels in the reaction with $MoCl_5$).

8. Aspects of the introduction of vanadyl cations into HS-zeolites

Reactions of HS-zeolites with V_2O_5 and the properties of the systems obtained have been studied.[24,25,32–34] Topochemical migration into the cationic sites in the zeolites was shown to be characteristic also of vanadium ions. The reaction of H-ZSM-5 with V_2O_5 at 550–800 °C gives a typical EPR signal from isolated V^{4+} cations ($g_{\|} = 1.93$, $g_{\perp} = 2.00$, $A_{\|} = 198$ Oe, $A_{\perp} = 85$ Oe).[32] Admitting O_2 to the specimen at 20 °C leads to a marked, but reversible, broadening of the lines in the spectrum. As with the other transition metals studied, the maximum concentration of isolated vanadyl ions depends on the concentration of acidic centres in the zeolite.

An important and unusual aspect of the stabilisation of vanadyl cations is their extraordinary stability in both reducing and oxidising media: almost the same EPR signal from V^{4+} ions in H-ZSM-5 is obtained when the specimens are heated at 800 °C in H_2 and in O_2.[24,25]

As the vanadyl ion, with the configuration $3d^1$, is electronically analogous to the Cr^V ion, we may expect EHFS in the EPR spectra for the vanadyl cations in V-H-ZSM-5, as for systems containing chromium.[23,25] EHFS was in fact found in the spectra by a careful EPR study of this system in the temperature range from –196 to 300 °C.[33] The HFS lines in the spectrum of isolated V^{IV} ions (Fig. 9*a*) undergo additional splitting due to EHFS coupling (Fig. 9*b* and *c*). The resolution of the EHFS components ($\Delta H \approx 7$ Oe) is considerably dependent on the temperature at which the spectrum is

recorded. At −196 °C EHFS is almost absent and at 20 °C the poor resolution makes it impossible to determine the number of components. As the temperature is increased the EHFS lines become narrower and signals with a fairly well resolved EHFS can be obtained at 200−300 °C (see Fig. 9*b* and *c*).

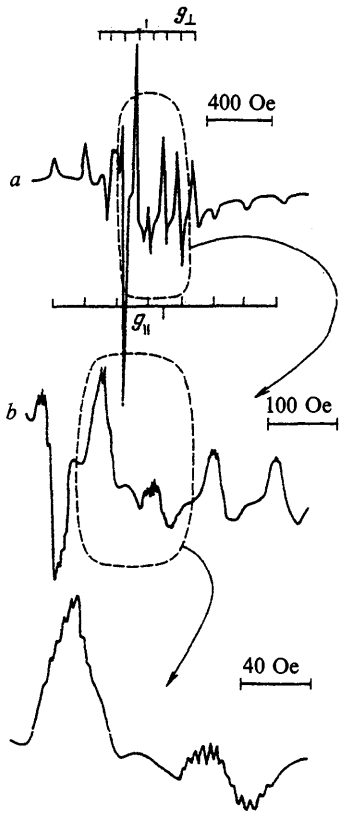
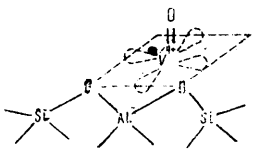


Figure 9. EPR spectra of isolated vanadyl cations ($^{51}V^{IV}$, $3d_1$, I = 7/2) introduced into H-ZSM-5:[33] *a*, complete spectrum recorded at 20 °C; *b* and *c*, parts of spectrum (*a*) recorded at 200 °C.

The detection of EHFS at a ^{27}Al nucleus in the V^{IV} EPR spectra (see Fig. 9) provides unambiguous evidence for an electronic interaction between the vanadyl cation and an Al^{3+} ion in the framework of the zeolite. The mutual disposition of the two ions will pave the way for an interaction between their outer electron shells and this will place limitations on the spatial arrangement of the vanadyl ions in the H-ZSM-5 channel. By taking into consideration the small magnitude of the EHFS splitting, which indicates that the Al^{3+} ion is in the second coordination sphere of the V^{IV}, and also that the unpaired electron is in the d_{xy} orbital of the V^{IV}, the following arrangement of the ions has been proposed:[33]



Solid state reactions of the H- and Ca-forms of ZSM-5 with V_2O_5 have also been shown to give paramagnetic vanadium species that are amenable to reactions with H_2O and O_2.[34] The number of V^{4+} ions formed is less for the Ca-form than for pure H-ZSM-5, the Ca-form having a smaller concentration of protonic acidic centres. The use of spin-echo spectroscopy as well as EPR[34] enabled the mutual arrangement of the vanadium and aluminium ions to be deduced from echo data at 4 K. The distance from the V^{4+} to the nucleus of the framework aluminium was found to be not more than 5 Å. The effect of the conditions under which the zeolite is heated with V_2O_5 was also investigated[34] and the possible reduction of V^{4+} with hydrogen was proposed. This conclusion was based on very small changes in the parameters of the EPR spectrum from paramagnetic vanadium and also changes in the colour of the specimens from yellow to grey. However these arguments are not very convincing in view of the fact that mixtures containing 4 mass% V_2O_5 were used in this work. This is a large excess compared to the amount required to fill all the cationic vacancies in the zeolite channels, i.e. some of the V_2O_5 will remain on the outer surface of the zeolite in the form of a phase, the changes in which will account for the observed effects.

In order to investigate thoroughly the distributiom of V^{IV} cations in the structure of the zeolite H-ZSM-5 and to analyse the properties of the vanadyl cations introduced by the solid state reaction, the changes in the parameters of the EPR spectra due to V^{4+} occurring on adsorption of various molecules (NH_3, pyridine, 2,4,6-trimethylpyridine *p*-xylene, nitrobenzene) were studied.[32] The adsorption of these molecules (with the exception of 2,4,6-trimethylpyridine) leads to splitting of the initial EPR spectrum into two, indicating that there are two types of VO^{2+} cation in the zeolite structure. Since adsorption of the sterically hindered 2,4,6-trimethylpyridine molecules has no effect on the parameters of the spectrum it is clear that the two types of cation are located inside the zeolite structure and not on the outer surface. It was shown previously that the zeolite CuH-ZSM-5 contains two types of Cu^{2+} cation, one of which is probably located in a channel and the other in a five-membered ring adjacent to a channel, with square pyramidal coordination. We have suggested[32] that a similar situation may apply to the trapping of VO^{2+} in H-ZSM-5. When a weak ligand such as *p*-xylene is adsorbed there is almost no change in the parameters of the EPR spectrum due to V^{4+} but there is some narrowing of the components and disappearance of the EHFS due to interaction of VO^{2+} with the framework Al^{3+}. By analogy with the effects of weak ligands on Cu^{2+} cations in H-ZSM-5 [20,21] there may be a small displacement of the VO^{2+} cations in the chelate site due to the effect of occupation of the channels in H-ZSM-5 by the *p*-xylene molecules.[32] The *p*-xylene molecules react not only with the cationic centres but also with the oxidation-reduction centres, giving an intense EPR signal from cation-radicals in the region of g = 2.004. Thus the introduction of VO^{2+} cations into the zeolite does not suppress the one-electron transfer centres in the zeolite.

The adsorption of pyridine, NH_3, and nitrobenzene is accompanied by considerable changes in the EPR spectral parameters due to the entry of these strong ligands into the coordination sphere of the VO^{2+}. An analysis of the spectra suggests that, on adsorption of pyridine and NH_3, delocalisation of the unpaired electron from the d_{xy} orbital to the ligand orbitals takes place, leading to increased covalency of the bonds. On the other hand, on adsorption of nitrobenzene the electron delocalisation is reduced and the V=O bonds become more polar.

As was mentioned above, the valence state of a VO^{2+} cation trapped in the zeolite H-ZSM-5 is extremely stable under high-temperature oxidation-reduction conditions: there is no oxidation of this cation to V^{5+} even on heating in a stream of air at 800 °C. This feature has been discussed using ideas put forward in a paper by us[32] where it was shown that the value of $B = \Delta g_{\|}/\Delta g_{\perp}$ characterises the strength of the V=O bond. For example, for V^{4+} cations deposited on Al_2O_3 and SiO_2 B has the values 2.1 and 2.4 respectively but after further reduction it decreases to 1.1 for the V^{4+}/Al_2O_3 system, i.e. the V=O bond becomes weaker, but it increases to 3.1 for the V^{4+}/SiO_2 system, i.e. the V=O bond becomes stronger. However in these instances the B values are small, i.e. on these carriers the V=O bond is not very strong and the V^{4+} cations will undergo oxidation-reduction changes. For VO^{2+} cations stabilised on H-ZSM-5 the B values calculated[32] vary from 8 to 15 and hence in these instances the V=O bond is considerably stronger than for deposition of vanadium cations on Al_2O_3 and SiO_2. However the physical reasons for this are not clear. The question as to which features of the structure of H-ZSM-5 and the location of the VO^{2+} cations guarantee such a high vanadyl bond strength remains undecided.

The solid state reaction of V_2O_5 with the zeolite NaY in air at 420–480 °C has been studied using a combination of methods (X-ray analysis, EPR, ^{29}Si and ^{129}Xe NMR, electron microscopy).[36] When the vanadium concentration is appreciable [R = V/(Al + Si) = 0.2] the lattice of the Y zeolite breaks down and the structure collapses. However, when R = 0.005 or 0.05 the zeolite structure is retained although the V_2O_5 phase disappears during the reaction. Some of the entrances to the zeolite cavities are blocked by a compound which contains V^{4+} ions. It is suggested that the reation of V_2O_5 with Na^+ may lead to formation of a vanadium bronze of the $NaV_5^{V}V^{IV}O_{15}$ type but there is no direct confirmation of this. However it is significant that in this case also,[36] where the zeolite NaY was used, there is an intense solid state reaction between the zeolite and V_2O_5 at fairly low temperatures.

9. Introduction of manganese cations into ZSM-5 zeolites

A number of methods (EPR, RFES†, adsorption of Ar, thermal desorption of NH_3, catalytic testing) have been used to study thoroughly the possible introduction of Mn^{2+} ions into H-ZSM-5 and Na-ZSM-5, both by ion exchange and by solid state reactions with MnO, $MnCl_2$, and $MnSO_4$.[37–39] It was shown that during a solid state reaction with H-ZSM-5 at 430–650 °C the manganese salts or MnO disappear from the surface of the zeolite and manganese ions are uniformly distributed throughout the zeolite crystals. The introduction of the ions is accompanied by a reduction in the number of strong Brønsted acid centres. There is no reaction with the Na-form of the zeolite. Hence, as with the other ions discussed above, stabilisation of the manganese is due to the presence of free protonic centres. However, note that the replacement of the strong acidic centres in H-ZSM-5 reaches a limit of only ~50%.[37,38] Using $MnCl_2$ an exchange reaction takes place to an appreciable extent even on heating at 300 °C for 1 h.[38] Under identical conditions the degree of exchange decreases in the order: $MnCl_2 > Mn_3O_4 > MnSO_4$.[39] Some of the manganese cations are stabilised in the zeolite as manganese(II), which is very stable and undergoes no changes on oxidation-reduction treatment in a stream of oxygen or hydrogen. The properties of the isolated Mn^{2+} cations do not depend on the method of introduction into the zeolite (ion exchange or solid state reactions). However the specimens may also contain manganese in other oxidation states which will complicate the analysis of their properties.

There is another feature of the Mn^{2+}–H-ZSM-5 system: only hydrated specimens give a typical EPR signal in the X-region with HFS due to isolated Mn^{2+} ions (6 components, g = 2.00); in the absence of H_2O molecules the signal is markedly broader.[37–39] This phenomenon has been analysed in detail for Mn^{2+} ions in Y zeolites.[40,41]

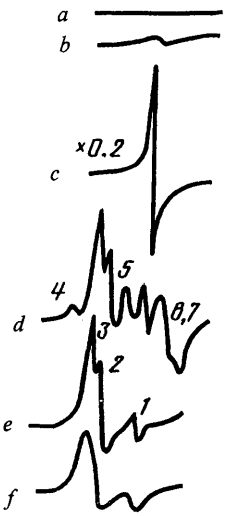


Figure 10. Changes in the EPR spectrum occurring when a mixture of $FeCl_3$ with H-ZSM-5 is heated:[42] *a*, specimen 1; *b* and *c*, specimen 2; *d*, specimen 3 evacuated for 2 min; *e*, specimen 4 evacuated for 2 min; *f*, adsorption of O_2 (100 torr) by specimen 4. Spectra (*c*) and (*d*) were measured at −196 °C. g values: *1*, 4.27; *2*, 5.65; *3*, 6.25; *4*, 9.1; *5*, 4.95; *6*, 3.7; *7*, 3.4

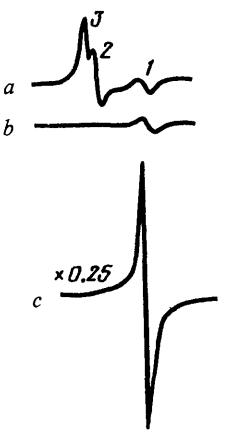


Figure 11. Effect of adsorption of NH_3 on the EPR signal from specimen 4:[42] *a*, initial signal at 20 °C; *b*, after adsorption at 20 °C; *c*, specimen (*b*) at −196 °C. g values; *1*, 4.27; *2*, 5.65; *3*, 6.25.

†Probably X-ray photoelectron spectroscopy (Ed. of Translation).

10. Reactions of H-ZSM-5 with iron compounds

Reactions between iron compounds and H-ZSM-5 have been studied thoroughly by the EPR method.[42,43] The location, coordination and properties of Fe^{3+} in this zeolite were investigated and comparisons made with a Y type zeolite, and also with a ferrisilicate analogue of the ZSM-5 zeolite (H-[Fe]ZSM-5) containing Fe^{3+} in the framework tetrahedra.

The initial mixtures of H-ZSM-5 with iron oxides give EPR spectra having only a very broad line with $g \simeq 2.0$. No new EPR signals due to Fe^{3+} are obtained by heating the mixtures to 800 °C under vacuum or in air. Heating specimens prepared by exchange with $(NH_4)_4Fe(CN)_6$ does not give any lines due to Fe^{3+}. However, the situation is different when $FeCl_3$ is used.[42,43]

The EPR spectrum of the initial mechanical mixture of H-ZSM-5 with $FeCl_3$ (specimen 1)[43] is shown in Fig. 10*a*. Heating this specimen under vacuum at 300 °C for 2 h (specimen 2) leads to the formation of the signal shown in Fig. 10*b*. Cooling specimen 2 to −196 °C produces an anomalous increase in the intensity of the EPR line with $g = 4.27$ [by a factor of more than 100: $I = (2-3) \times 10^{19}$ spins g^{-1}]. There are no changes in this signal when specimen 2 is heated under vacuum at 300−400 °C for a longer time.

The subsequent heating of specimen 2 in air at 300 °C for 30 min (specimen 3) leads to a decrease in the intensity of the line with $g = 4.27$ and a considerably more complicated EPR spectrum (Fig. 10*d*). When the sample is heated at 550 °C (specimen 4) the intensities of the two low-field lines ($g = 5.65$ and 6.25) continue to increase, the intensity of the line with $g = 4.27$ decreases considerably, and the lines with g factors equal to 9.1, 4.95, 3.7, and 3.4 disappear (Fig. 10*e*). No further changes in the spectrum result from increasing the time of oxidation of specimen 4 at 550 °C to 4 h or raising the temperature of oxidation (to 750 °C, 30 min). Measuring the EPR spectra of specimen 4 at −196 °C increases the intensities of all the lines in the spectrum (Fig. 10*d*) by a factor of only 2.5−3, i.e. there are no anomalous changes in intensity on cooling as were observed for the line with $g = 4.27$ for specimen 2 (see Fig. 10*b* and *c*). Admitting dry oxygen to specimen 4 at 20 °C causes a significant reversible broadening of the low-field lines in the spectrum (Fig. 10*f*). Adsorption of NH_3 or pyridine on specimen 4 at 20 °C leads to complete disappearance of the lines with g equal to 5.65 and 6.25 (Fig. 11*a* and *b*) and after adsorption the intensity of the line with $g = 4.27$ starts to show an anomalous dependence on temperature (Fig. 11*b* and *c*). On the adsorption of H_2O on specimen 4 the intensities of the lines with g equal to 5.65 and 6.25 decrease by a factor of approximately 3 and there is a similar increase in the intensity of the low-temperature line with $g = 4.27$.

Thus these results[42,43] show that solid state reactions do not give isolated Fe^{3+} ions in all cases. Nevertheless this method can be used to introduce Fe^{3+} into H-ZSM-5 but the part played by the anionic fragment is a controlling factor.

The data on the reaction of iron oxides with H-ZSM-5 are inconsistent: we found[42,43] that reactions with FeO and Fe_3O_4 do not proceed at an appreciable rate up to 800 °C but in other work[37] a reaction with Fe_2O_3 led to the introduction into the zeolite of Fe^{3+} ions giving an EPR signal with $g = 4.27$ and readily amenable to reduction. These peculiarities may be due to the different stabilities of the lattices of the iron oxides. When $FeCl_3$, whose lattice is considerably less stable (m.p. 309 °C), is used[42,43] the migration and redistribution of Fe^{3+} is observed at 250−300 °C. The appearance of the EPR signal with $g = 4.27$ (Fig. 10*b* and *c*) unambiguously indicates the occurrence of isolated Fe^{3+} ions in a strong crystal field of low symmetry. In the case of iron[42,43] the ion stabilised is not likely to be Fe^{3+} but the singly charged species $FeCl_2^+$ and FeO^+ which balance the single charge on the framework. The changes in the EPR spectrum on oxidative heating of specimen 2 (Fig. 10*b*−*e*) are precisely due to a gradual change from $FeCl_2^+$ type cationic species to FeO^+. The disappearance of the anomalous signal with $g = 4.27$ and the appearance in its place of lines with g equal to 6.25 and 5.65 can be interpreted in terms of a further reduction in the symmetry of the Fe^{3+} crystal field.

The reversible broadening of the lines in the EPR spectrum occurring when oxygen is admitted (see Fig. 10*f*), which is due to a dipole-dipole interaction with the O_2 molecules, indicates that the Fe^{3+} ions giving the EPR signals with $g = 6.25$ and 5.65 are accessible to molecules in the gas phase. The changes in the spectra due to Fe^{3+} occurring when strong ligands such as NH_3 and pyridine are adsorbed on specimen 4 (see Fig. 11) confirm the suggestions made above. The interaction of coordinately unsaturated Fe^{3+} ions with these ligands will lead to an increase in the crystal-field symmetry of the Fe^{3+} and a shift of the EPR lines towards lower g values, as has been observed.[42,43]

A comparison of the optical spectra shows[43] that the lines in the u.v. region (250 and 320 nm) are due to the presence in the specimen of Fe^{3+} ions with low coordination. Adsorption of NH_3 raises the coordination of the Fe^{3+} and leads to disappearance of these bands.

Reduction of specimen 4 by the adsorbed NH_3 does not take place up to 300 °C.[42,43] More drastic thermal treatment (550 °C, 30 min) is accompanied by the complete disappearance of Fe^{3+} and the appearance of iron metal species which give a ferromagnetic resonance (FR) spectrum. The broad FR line is characteristic of fairly large Fe^0 particles which may be located on the outer surface of the zeolite crystals.

Reoxidation of the reduced iron-containing H-ZSM-5 is accompanied by the complete disappearance of the FR line due to Fe^0, but it does not lead to full restoration of the EPR spectrum due to isolated Fe^{3+} ions.[43] The concentration of such ions is 3−5 times lower than the original even after reoxidation at 750 °C for an hour. There are two possible reasons for this irreversible decrease in their concentration due to the reduction-oxidation treatment: (1) the number of centres in which the Fe^{3+} ions are located is reduced, and (2) there is no reduction in the number of centres in the channels but migration of the oxide species occurring on the outer surface of the zeolite crystals takes place with great difficulty (as with mechanical mixtures of H-ZSM-5 with iron oxides). An experiment involving the reintroduction of $FeCl_3$ into this specimen[43] shows that the second suggestion is correct. The migration of mobile $FeCl_2^+$ species leads to refilling of all the vacant cationic sites in the zeolite and the concentration of isolated Fe^{3+} ions reaches the original value.

The changes in the EPR spectra due to the Fe^{3+} in H-ZSM-5 occurring on reaction with weak ligands such as H_2O and *p*-xylene[42,43] indicate that there is considerable coordination unsaturation of the Fe^{3+} in the specimens. Furthermore effects due to the weak interaction of coordinately unsaturated Fe^{3+} cations with xenon and n-hexane physically adsorbed in the channels in H-ZSM-5 have been observed.[20] The sorption of xenon or hexane at 20 °C causes appreciable broadening of the lines with $g^2 = 5.8$ and $g^3 = 6.3$ in the EPR spectrum due to Fe^{3+} ions.[20] In addition, the sorption of n-hexane results in an anomalous variation of intensity with temperature for the lines with $g^1 = 4.3$; the original evacuated specimen does not show this anomaly. This effect may indicate some reduction in the disortion of the environment for some of the Fe^{3+} cations, caused by displacement of the cation due to a dispersion interaction with the hexane molecules occupying the

channel. The broadening of the low-field lines at 20 °C[20] may also indicate some changes in the conditions of the spin-lattice interaction due to changes in the symmetry of the environment. Such an effect is significant only for Fe^3 ions located in a very strong crystal field with low symmetry.

The set of properties of the Fe^{3+} cations in H-ZSM-5 described above enable them to be distinguished quite clearly from the isolated Fe^{3+} ions introduced isomorphously into the H-ZSM-5 framework on synthesis. Although the isolated tetrahedral Fe^{3+} ions in the zeolite lattice give very similar low-field EPR spectra, they are quite insensitive to interactions with various molecules (even including strong ligands) and differ in being very difficult to reduce.

11. Introduction of Ni^{2+} ions into H-ZSM-5

Solid state reactions of H-ZSM-5 with NiO, $NiCl_2$, $NiSO_4$, and $Ni(CH_3COO)_2$ have been investigated.[38,39] When $NiCl_2$ is used heating in a stream of dry oxygen at 500 °C for 6 h leads to complete replacement of the strongly acidic OH groups in the zeolite (on the basis that an Ni^{2+} cation replaces 2 acidic protons). Subsequent reduction of the specimen with hydrogen at 450 °C or exchange with NH_4NO_3 leads to the complete reduction of the initial concentration of the acidic centres. When nickel sulphate is used the reaction with H-ZSM-5 is less effective and there is no reaction at all with nickel acetate and NiO. Thus for nickel ions also, the anionic fragments have an important role in the solid state reactions.

12. Reactions of H-ZSM-5 with zinc and gallium oxides

The modifying effect of ZnO and Ga_2O_3 on the catalytic properties of H-ZSM-5 has been mentioned in many studies but in the present review we shall concentrate on a group of papers[44–47] in which attempts have been made to observe the physicochemcial changes in [ZnO + H-ZSM-5] and [Ga_2O_3 + H-ZSM-5] mixtures during heating by employing a number of methods (RFES, TPR, thermal desorption of NH_3, i.r. spectroscopy). Thermal treatment leads to migration of Zn^{2+} ions from the outer surface into the zeolite channels and to a decrease in the concentration of Brønsted acid centres.[44] The Zn^{2+} ions in H-ZSM-5 are more easily reduced than is the ZnO phase.[44] Migration into the pores of H-ZSM-5 has also been observed for gallium oxide,[45,47] the gas phase having a decisive role. Using oxidative heating the Ga_2O_3 phase is located on the outer surface of the zeolite crystals and the features of the introduction affect only its degree of dispersion.[47] However treatment in a hydrogen or hydrocarbon atmosphere results in the Ga-phase entering the zeolite channels, the gallium introduced having an oxidation state appreciably less than three.[45,46] Migration of Ga_2O species and their stabilisation in the vicinity of Brønsted acid centres in the zeolite channels has been proposed.[47]

13. Aspects of the introduction of transition metal cations into H-ZSM-5 (and of their properties) resulting from isomorphous replacement of framework Al^{3+} ions by Ga^{3+} or Fe^{3+}

It is known that the properties of the acidic centres in high-silica zeolites can be changed by isomorphous replacement of the framework Si^{4+} ions by other triply charged ions instead of Al^{3+}. Conclusive evidence for the possible synthesis of gallosilicates and ferrosilicates with the ZSM-5 structure has been published and the lower strength of the acidic centres in such structures (H-[Al]ZSM-5 > H-[Ga]ZSM-5 > H-[Fe]ZSM-5) and the changes in the catalytic properties in acid-base reactions resulting from this have been demonstrated. The stabilisation of cations in the same zeolite matrix, but at weaker acidic centres, is naturally of considerable interest. In addition changing from Al^{3+} ions (nuclear spin $I = 5/2$) to Ga^{3+} ($I = 3/2$) will lead to changes in the EHFS of the spectra of Cr^V and V^{IV} due to interaction of the unpaired electron on the cationic species with the nucleus of the framework ion creating the cationic vacancy.

Solid state reactions of H-[Ga]ZSM-5 with CuO, $FeCl_3$, CrO_3, V_2O_5, and $VO(NO_3)_2$ at 300–800 °C have been studied and the results obtained compared with data for the zeolite H-ZSM-5.[27,28] The migration of Cu^{2+} ions in H-[Ga]ZSM-5 is identical to that observed for H-ZSM-5. The results obtained[27,28] indicate conclusively that the concentration and coordination of isolated Cu^{2+} cations in H-ZSM-5 and H-[Ga]ZSM-5 are very similar. Specimens heated at 550 °C contain two distinct types of Cu^{2+} coordination: square planar and square pyradmidal. These two types are retained in specimens heated at 800 °C (the square pyramids showing considerable distortion towards square planar). A comparison of H-ZSM-5 and H-[Ga]ZSM-5 shows only very small differences in the degree of distortion of the environment.

The changes in the EPR spectra due to the interaction of Cu^{2+} with various adsorbates show that the Cu^{2+} cations in H-ZSM-5 and H-[Ga]ZSM-5 are equally accessible to molecules from the gas phase. For example, adsorption of O_2 causes broadening of the lines in the spectrum due to dipole-dipole interactions, and adsorption of ammonia changes the parameters of the spectrum, indicating some reduction in symmetry. In the case of the physical non-localised adsorption of xenon some geometrical displacement of the Cu^{2+} cations due to dispersion forces is observed, as in CuH-ZSM-5.

Thus the replacement of Al^{3+} ions by Ga^{3+} in a zeolite framework with the ZSM-5 structure causes no appreciable changes in the concentration, coordination, and reactivity of the Cu^{2+} ions introduced into the cationic sites in the zeolite by solid state reactions.[27,28]

The same conclusion was reached for iron:[27,28] the processes of solid state introduction of Fe^{3+} into the cationic sites in H-[Ga]ZSM-5 and H-ZSM-5 are identical. The properties of the cations introduced into the two zeolites are almost the same. For the Fe^{3+} ions in H-[Ga]ZSM-5 location in crystal fields with low symmetry is also found. Adsorption of NH_3 increases the symmetry of the Fe^{III} environment (the lines with $g = 5.7$ and 6.3 disappear) and changes the spin-lattice relaxation conditions (the anomalous temperature dependence for the line with $g = 4.3$ appears).

The processes of introducing chromium into H-ZSM-5 and its gallosilicate analogue are similar and interesting features are observed in the EHFS of the EPR spectra due to Cr^{5+}.[27,28] Heating H-[Ga]ZSM-5 with CrO_3 at 420 °C for an hour gives an anisotropic EPR signal from isolated Cr^{5+} ions (two quartets with the parameters $g_\perp = 1.99$, $A_\perp = 28$ Oe, $g_{||} = 1.94$, and $A_{||} = 26.5$ Oe). Heating at 700 °C gives a signal with $g_0 = 1.97$ and $A \sim 24$ Oe. Chemisorption of NH_3 causes an immediate change in the EPR signal with disappearance of the EHFS and the appearance of anisotropic lines; this indicates a considerable change in the coordination of the Cr^{5+} due to attachment of an additional strong ligand. This EPR spectrum is identical to the signal observed in the reaction of Cr^V/H-ZSM-5 with NH_3 (see Fig. 6).

Thus the Cr^{5+} cations have the same coordination in the presence of NH_3 in the channels of H-ZSM-5 and its gallosilicate analogue (two distinct Cr^V positions with different distortions of the coordination symmetry). One of the two types of Cr^{5+} ion is more easily reduced when the specimens with adsorbed NH_3 are heated. The changes in the EHFS of the Cr^V EPR spectra resulting from the change from Al^{3+} to Ga^{3+} in the ZSM-5 framework are shown in

Fig. 7. The signals in the Q-band are more markedly anisotropic (see Fig. 7), making their interpretation easier. The following conclusion is drawn by reference to theory: the EHFS is due to interaction of a CrO_2^+ cation with one framework Al^{3+} ion ($I = 5/2$) and changing to Ga^{3+} (which has $I = 3/2$) reduces the number of EHFS components from 6 to 4. However there is a marked increase in the splitting constant (from 6 to 24 Oe), i.e. the unpaired electron of the CrO_2^+ has a much stronger interaction with a Ga^{3+} nucleus than with an Al^{3+} nucleus. This change cannot be attributed to a difference in the nuclear magnetic moments: whereas for ^{27}Al $\mu_I/\mu_K = +3.64$, for ^{69}Ga $\mu_I/\mu_K = +2.00$ and for ^{71}Ga $\mu_I/\mu_K = +2.55$. The change in the magnitude of the splitting most likely indicates a small change in the geometry of the cation site since the ionic radius of Ga^{3+} (0.62 Å) is appreciably larger than that of Al^{3+} (0.50 Å).

Comparison of the zeolites H-ZSM-5 and H-[Ga]ZSM-5 containing Cr^V or Fe^{III} shows a marked difference in their thermal stabilities: the Ga^{3+} ion is less strongly bound in the lattice than the Al^{3+} ion. In H-ZSM-5 there is no noticeable disruption of the cationic sites at 750–800 °C. In H-[Ga]ZSM-5 this temperature is sufficient for fairly rapid irreversible disappearance of the sites of the isolated Cr^{5+} or Fe^{3+} cations although X-ray diffraction data indicate that the crystallinity of the zeolite is preserved.[27,28] The disappearance of the sites in which cations are trapped is evidently due to Ga^{3+} escaping from the framework. The isolated cations migrate to the outer surface and are aggregated to form oxides. For Fe^{3+} this is confirmed by EPR data.

In addition to the acidic centres in H-[Ga]ZSM-5 being thermally less stable traps for cationic species than the centres in H-ZSM-5, in the gallosilicate the strength of these centres is insufficient for stabilisation of isolated vanadyl cations. In contrast to H-ZSM-5, the reaction of H-[Ga]ZSM-5 with V_2O_5 at 400–800 °C gives hardly any isolated V^{4+} ions.[27,28] Nor are such ions produced by heating H-[Ga]ZSm-5 under vacuum with compounds such as $VO(NO_3)_2$.

In the ferrisilicates H-[Fe]ZSM-5, which have even weaker and thermally less stable acidic centres, it is not possible to stabilise even such transition metal cations as Cu^{2+} and Cr^{5+}. A comparison of the properties of H-ZSM-5 and H-[Fe]ZSm-5 using a highly sensitive EPR method[38,39] showed that isolated Cu^{2+} ions are not stabilised in a ferrisilicate matrix with the ZSM-5 structure.

14. The concurrent introduction of highly charged ions into H-ZSM-5

EPR has been used to investigate the possible introduction of the ions $[Cu^{2+} + CrO_2^+]$, and also $[Cu^{2+} + VO^{2+}]$, into H-ZSM-5 in the solid state and to study the effect of the thermal treatment conditions on these processes.[48,49] In a number of instances it is possible to replace one highly charged ion by another, and also to introduce two different cations simultaneously. It is significant that the different ions are found to have the same location sites and the processes of their location are competitive and depend on the conditions under which the solid state reaction is carried out.

For example, the reaction of H-ZSM-5 with $CuCrO_4$ at 550–800 °C gives a superposition of two EPR spectra due to Cu^{2+} and Cr^{5+} ions. The well resolved HFS of the spectra indicates that the Cu^{2+} and Cr^{5+} ions are isolated and their coordination is the same as when they are introduced individually. It is suggested[48,49] that the copper and chromium ions are distributed statistically in the cationic sites in H-ZSM-5. Estimation of the intensities of the EPR signals indicates that the concentrations of these isolated ions in the specimen are comparable ($Cu^{II}/Cr^V \simeq 2-3$). It is interesting to compare this specimen with the double mixture [(H-ZSM + 1% CrO_3) + 5% CuO] in which the reactions with the oxides were carried out consecutively.[48,49]

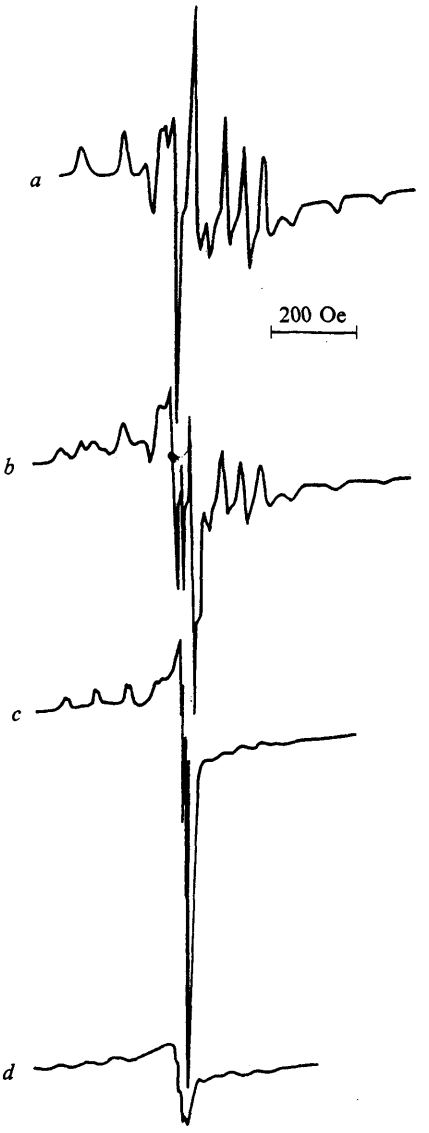


Figure 12. EPR spectra of a [(H-ZSM-5 + V_2O_5) + CuO] mixture under vacuum:[49] *a*, (H-ZSM-5 + CuO) mixture heated in air at 800 °C for 1 h; *b*, the triple mixture heated in air at 500 °C for 1 h; *c*, the same mixture heated in air at 800 °C for 1 h; *d*, after reduction of the specimen in H_2 at 400 °C for 2 h.

Heating H-ZSM-5 with CrO_3 at 800 °C for an hour leads to replacement of the accessible cationic sites in the zeolite by isolated Cr^{5+} ions, giving an intense EPR signal (see Fig. 5*b*). In the subsequent reaction with CuO there are two simultaneous processes:

the intensity of the signal due to Cr^{5+} decreases and that of the signal due to Cu^{2+} increases. It is clear from the changes in the spectra that there is replacement of one ion by the other in the cationic sites, giving a Cu^{II}/Cr^{V} ratio of $\sim 20-30$. It is likely that the equilibrium obtained on heating to a high temperature is dynamic and is dependent on the ratio of the concentrations of the two ions on the outer surface, which in the present case is equal to 5. Reduction of the specimens containing Cu^{2+} and Cr^{5+} ions with hydrogen leads to a rapid disappearance of their EPR signals.

The studies of the reaction of H-ZSM-5 with V_2O_5 and CuO in different media[48,49] are of great interest because Cu^{2+} is easily reduced in hydrogen at 400 °C but VO^{2+} is stable in both oxidising and reducing media up to 800 °C. The maximum concentration of isolated V^{4+} ions in the cationic sites is obtained by heating H-ZSM-5 with V_2O_5 at 800 °C, as is shown by the EPR signal in Fig. 12*a*. A subsequent reaction with CuO in air leads to a gradual decrease in the intensity of the EPR signal due to V^{4+} and the simultaneous appearance of a signal due to Cu^{2+} which increases in intensity (Fig. 12*b* and *c*). The intensity ratio of the signals shows that more than 90% of the V^{IV} in the cationic sites in H-ZSM-5 is replaced by Cu^{II}. Since both oxides were introduced in excess and are present in similar concentrations on the outer surface it is concluded[48,49] that VO^{2+} is appreciably less strongly bound in the cationic sites in H-ZSM-5 than Cu^{2+}. Presumably, during the reaction with CuO the V^{4+} ions are removed to the outer surface of the crystallites and undergo aggregation, with possible conversion to V^{5+}.

An experiment involving the subsequent reduction of the specimen in hydrogen at 400 °C enabled the location of the ions to be determined more accurately. This temperature is high enough for fairly rapid reduction of Cu^{2+} to Cu^0 yielding the metal on the outer surface but it is too low to ensure diffusion of the V^{4+} ions which takes place at an appreciable rate above 500 °C. If V^{5+} ions were in the immediate vicinity of the cationic sites within the zeolite, we would expect the removal of Cu^{2+} from their sites in the reducing atmosphere to be accompanied by conversion of V^{5+} to V^{4+} and the appearance of the corresponding EPR signal (Fig. 12*a*). However no signal due to vanadyl ions is observed; there is merely a considerable reduction in the intensity of the signal due to Cu^{2+} (Fig. 12*d*). It is only when the temperature is increased to 800 °C, and rapid diffusion of V^{4+} ions occurs again, that they again migrate from the outer surface to the cationic sites and their concentration reaches the same maximum limit as in the initial (H-ZSM-5 + V_2O_5)/800 °C specimen. Repeating the oxidising treatment, in which the formation and migration of Cu^{2+} ions occur, again leads to replacement of almost all the isolated VO^{2+} ions by Cu^{2+}.

The replacement of one transition metal cation by another in H-ZSM-5 was also observed very clearly in the reaction of Fe^{3+}-H-ZSM-5 with CuO.[42,43] After a specimen of FeH-ZSM-5, which contains isolated Fe^{3+} cations, was heated with CuO at 550–750 °C the intensities of the signals due to Fe^{3+} with different coordinations (g = 6.25, 5.65, and 4.27) decreased almost by a factor of 1000 and signals due to Cu^{2+} appeared in their place, i.e. more than 99% of the isolated Fe^{3+} cations were replaced by Cu^{2+}. It is emphasised[42,43] that both the concentration and the coordination of the isolated Cu^{2+} ions are the same as in a CuH-ZSM-5 specimen, i.e the Cu^{2+} ions which replace the Fe^3 are introduced into the same cationic sites as are found in H-ZSM-5.

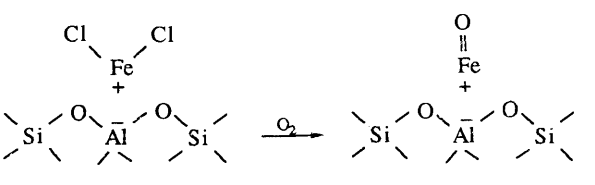
The results obtained demonstrate the complex nature of the processes of migration and redistribution of transition metal ions in HS-zeolites occurring when they are heated to high temperatures. This complexity is due to the differences in the strength of binding of the ions in the cationic site.

IV. The role of the gas phase and the anionic part of the salt in solid state exchange in HS-zeolites

The overwhelming majority of solid state reactions between HS-zeolites and transition metal compounds have been carried out in air in the presence of water vapour and the possible hydrating effect of H_2O molecules cannot be discounted. However the cation migration processes also take place effectively when compounds that are insoluble in water, such as CuO, Cr_2O_3, and V_2O_5, are used. In many instances (V_2O_5, CuO, $CuCl_2$, $FeCl_3$, $MoCl_5$) the reactions take place under high vacuum ($\sim 10^{-5}$ torr), i.e. in the absence of H_2O. Hence the presence of water is not a necessary condition for solid-state ion exchange in HS-zeolites. A similar conclusion was reached regarding solid state processes involving the introduction of alkali metal cations.[7]

A comparison of solid state exchange under vacuum and in air indicates that in the majority of cases (CuO and copper salts, V_2O_5, CrO_3) oxygen has almost no effect on the migration of ions in the zeolite. However in the case of Cr_2O_3 the reaction will not take place under vacuum up to 820 °C but can be carried out in air.[23,24] This peculiarity is probably related to the very high stability of the lattice of the initial oxide (m.p. 2340 °C). It is likely that more labile fragments capable of migrating into the zeolite at 550–800 °C are only formed on the surface of the Cr_2O_3 in the presence of oxygen.

It is clear that the temperature of the reaction can be reduced and the potentialities of the solid-state exchange method extended by using compounds (salts) of a given element which have considerably different labilities. However it must be stressed that the anionic part of the salt, which facilitates the migration, also acts as a ligand for the highly charged cation in the zeolite which is outside the framework, i.e. it changes the symmetry of the crystal field of the cationic centre. In some instances (Cl^-) the ligand can be replaced by heating in air:



but in many cases (PO_4^{3-}, SO_4^{2-}, F^-) the ligand is bonded to the centre very strongly and cannot be removed even by heating the specimens in air at 800 °C.

Clearly, when using transition metal compounds in which the anionic ligand can be replaced by oxygen, the reaction must be carried out under vacuum or in an inert gas. An example of this is the reaction of H-ZSM-5 with $FeCl_3$.[42,43] The reaction with this low-melting salt under vacuum leads, even at 250–300 °C, to stabilisation in the zeolite of isolated $FeCl_2^+$ cationic species. If the specimen is subsequently heated in air the symmetry of the Fe^{3+} environment is reduced, evidently due to conversion to an FeO^+ species.

The effect of a reducing medium (H_2, hydrocarbons) on the state of the cations in HS-zeolites (including those introduced by a solid state reaction) has been studied in many papers. For ions which can be reduced to the metal fairly easily (Cu, Ni, Fe) replacement of the cations within the channels by H^+, migration of the metal atoms, and formation of fairly large metal particles on the outer surface of the zeolite are usually observed. For such metals there is clearly no point in carrying out the solid state exchange in a reducing medium. Reactions with other transition metals in a hydrogen or hydrocarbon atmosphere have hardly been studied but exceptions to this are research involving V^{4+} ions[24,25,32] and gallium ions.[45–47] The solid-state migration of gallium from Ga_2O_3 into the zeolite H-ZSM-5[45–47] takes place only in a reducing medium and the stabilised cations have a charge less than 3+. Vanadyl cations are stable in a reducing medium and they will migrate into the cationic sites in the H-ZSM-5 in a hydrogen atmosphere. For the binary system (Cu + V)/H-ZSM-5, in an oxidising medium the Cu^{2+} ions are bonded to the cationic vacancies much more strongly than the VO^{2+} ions but in hydrogen the Cu^{2+} ions are reduced, Cu^0 drifts to the outer surface, and VO^{2+} cations are stabilised in the sites that have been freed.[48,49]

Thus the possibilities for solid state exchange in HS-zeolites can be extended by varying the transition metal salt and the atmosphere in which the reaction is carried out. However the results obtained indicate a possible substantial redistribution of the modifying components when the atmosphere is altered, e.g. under the conditions of a catalytic reaction.

V. Transition metal cations in an H-ZSM-5 matrix as isolated catalytic centres

In this section a full analysis of all the catalytic data for transition metal/HS-zeolite systems has not been undertaken. Primarily, examples of the oxidation-reduction catalytic properties of HS-zeolites modified by solid state reactions are given and some results obtained for ion-exchange specimens are quoted for comparison.

An important feature of HS-zeolites with the ZSM-5 structure is the stabilisation of isolated cationic species in coordinately unsaturated ligand environments (in fields with low symmetry) and in consequence the high reactivity of such cations with various classes of substances. For example, the H-ZSM-5 matrix provides stabilisation for Cu^{2+} with square planar coordination,[11,12] Fe^{3+} ions in crystal fields with very low symmetries,[42,43] and chromium and vanadium ions in the normally unstable oxidation states Cr^V and V^{IV}.[23–25] Such ions interact not only with the molecules of strong ligands (NH_3, pyridine, H_2O) but also with physically adsorbed molecules of n-hexane and *p*-xylene, and even xenon atoms, which occupy the channels in the zeolite.[20,21,32] In other types of zeolite the cationic centres do not have such a high coordination unsaturation. Furthermore, an important characteristic of the ZSM-5 matrix is that the cationic centres are well separated from each other, i.e. isolated active centres are formed (but only 2–3 distinct types). The coordination of the cations can be altered to a considerable extent by introducing additional anionic ligands.

Thus the cationic centres stabilised by a ZSM-5 matrix provide a unique method for investigating the relationship between the catalytic and physical properties of isolated transition metal ions. In other words, these structures can be regarded as "inorganic analogues of enzymes", in which the isolated active centre is situated in the topologically defined internal space of the zeolite channel. For most transition metals these are oxidation-reduction centres because the ions can easily change their oxidation state. Of course, for ZSM-5 type zeolites, in which the [Si]/[Al] ratio is not less than 16–20, the concentration of isolated centres in 1 g cannot be very large (not more than 1–1.5 mass% of the transition metal compound can be dispersed into the channels and stabilised in the cationic sites created by the framework Al^{3+} ions). However, the abnormally high specific reactivity of the centres suggests that the system is not only of importance theoretically but also has possible practical applications.

Among the oxidation-reduction reactions on modified pentasils the decomposition of NO_x and the burning of hydrocarbons have recently attracted attention.

1. The decomposition of NO and its reduction by hydrocarbons on Cu-H-ZSM-5

The catalytic decomposition of NO on various types of cation-containing zeolites has been studied in a number of papers.[50–58] Cu-containing zeolites display considerable activity and the specific activity of Cu-H-ZSM-5 is unusually high.[50,51] The dependence of the specific activity on the copper content is an S-shaped function. This may indicate the presence of two types of Cu^{2+} ion with considerably different specific activities.[53] The activity of the H-form of ZSM-5 in the stoichiometric decomposition of NO is low.

The situation regarding the reduction of NO by hydrocarbons is more complex: this reaction also takes place on the H-forms of zeolites.[56] However the introduction of copper into H-ZSM-5 has a significant positive effect in lowering the conversion temperature to ~250 °C.[55,57]

The reaction mechanisms and the structure of the active complex were not investigated in detail in the papers quoted above but it was assumed that Cu^+ ions are involved in the catalytic decomposition process. However the effect of SO_x on the decomposition of NO on Cu-H-ZSM-5 has been studied.[58,59] Use of the EXAFS and XANES methods showed that the Cu^{2+} cations in H-ZSM-5 have more ionic character than in CuO.[59] Treatment with SO_x, which causes deactivation of the catalyst, is accompanied by changes in the local structure of the Cu^{2+} and formation of $CuSO_4$-type species.

All the above results were obtained using ion-exchange specimens of Cu-H-ZSM-5 but our recent results indicate that a system with the same catalytic properties, which are of interest for environmental protection, can also be obtained using solid state reactions. This is not surprising because detailed studies of Cu^{2+}/H-ZSM-5 show that there are no differences between the properties of the cations introduced by these two methods.[11–18]

2. Complete oxidation of alkanes

We have studied the burning of low concentrations of CH_4 at 500 °C on H-ZSM-5 containing a number of transition metal ions.[60–64]

In the oxidation of CH_4 and C_2H_6 by oxygen up to 550 °C pure H-ZSM-5 has a negligibly small catalytic activity but the stabilisation of cations in this inert matrix leads to the appearance of activity. This system is very suitable for comparing the specific activities of different ions and also of the same ions with different coordinations.

Coated chromium-containing systems (chromosilicates, chromo-aluminosilicates) are known to be active catalysts for complete oxidation. A study of aspects of the oxidising properties of the well characterised Cr/H-ZSM-5 system is therefore clearly of interest.

Results on the oxidation of CH_4 at 500 °C [60–62] are shown in Fig. 13. The specific activity of the chromium in the zeolite system is very high, much higher than that of chromium on amorphous substrates. Note that if, instead of relating the activity to the whole of the chromium, it is related to the number of isolated Cr^{5+} cations (broken line in Fig. 13) the specific activity is almost constant over a wide range of total chromium concentration in the zeolite (0.5–3.5%). It is therefore likely that the excess chromium which is present on the outer surface in the form of α-Cr_2O_3 crystals, makes no contribution to the activity, which is determined by the number of isolated cations (which are able to change their oxidation state easily). The extremely high activity of these isolated ions is due to their stabilisation in a coordinately unsaturated enviroment, as is found in the H-ZSM-5 zeolite.

The same reaction has been studied on Cu/H-ZSM-5 specimens with a copper content between 0.25 and 2.8 mass% which were obtained by solid state reactions.[60–64] The dependence of the activity of specimens heated at 550 °C on the copper concentration is shown in Fig. 14. The activity increases for 5–10 min and then reaches a stationary value which shows no decrease during treatment at 500 °C for 10 h. Heating in air at 550 °C for 15 h also gives no reduction in catalytic activity, but heating Cu-H-ZSM-5 at 800 °C for 2 h reduces the activity by a factor of 1000.

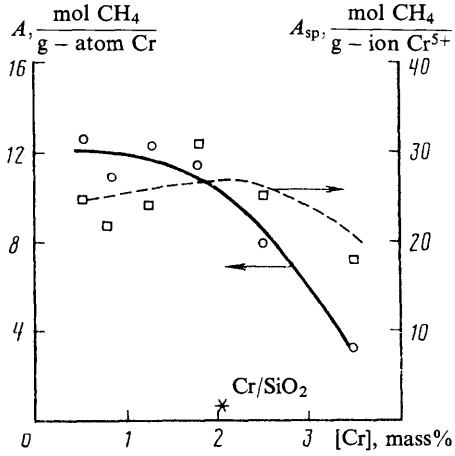


Figure 13. Specific activity of Cr/H-ZSM-5 in the complete oxidation of alkanes.[60]

The relationship shown in Fig. 14 indicates non-uniformity of the active centres. An analysis of catalytic data[63,64] and aspects of the copper distribution which have been thoroughly studied indicate that the high catalytic activity is due mainly to the formation of very coordinately unsaturated (square planar) isolated Cu^{II} ions. In the specimen containing 0.25% copper, which has a low activity, the number of such ions is very small and most of the ions have square pyramidal coordination. Increasing the total copper concentration to 1.0% leads to a significant increase in the concentration of square-planar Cu^{II} ions and there is a good correlation between this and the increase in activity. When the concentration of isolated Cu^{II} ions reaches a maximum (1.5–2.0% Cu) the activity of the catalyst also reaches a limit (see Fig. 14), which remains unchanged when the copper concentration is increased to 2.8 mass%. Therefore an excess of CuO on the outer surface of the zeolite crystals makes no contribution to the catalytic activity of Cu-H-ZSM-5 in the complete oxidation of CH_4.

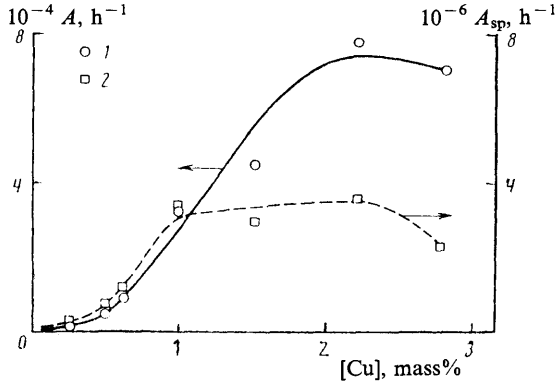


Figure 14. Activity of Cu/H-ZSM-5 specimens in the complete oxidation of CH_4 at 500 °C:[61] *1*, total activity; *2*, activity per 1 g copper.

The deactivation of the catalysts after heating at 800 °C [63,64] may also indicate the role of the coordinately unsaturated, isolated active centre: the number of accessible isolated Cu^{2+} cations is not appreciably reduced by heating at 800 °C but the ligand environment of the Cu^{II} changes considerably. Heating at 800 °C leads to the complete disappearance of the very unsaturated square-planar coordination of Cu^{II} and instead the specimens contain two distinct types of cation with distorted square-pyramidal coordination. Cu^{2+} ions in an HM zeolite or on the surface of SiO_2 (where there is no square-planar copper) have a specific activity that is lower by a factor of 100 than that of Cu^{2+} in H-ZSM-5 which has been heated at 500–550 °C. Such sharp differences in activity also demonstrate clearly the effect of the coordination of the isolated Cu^{2+} ion on its catalytic properties.[63,64]

Systems with a number of other cations (V, Fe, Ni, Co, Mn) have been investigated for comparison with Cu/H-ZSM-5 and Cr/H-ZSM-5.[60-62] The V/H-ZSM-5 system, in which the isolated V^{4+} cations are coordinately unsaturated but incapable of changing their oxidation state, shows a complete absence of catalytic activity in the oxidation of methane. In Fe/H-ZSM-5 specmens micro-crystals of iron oxide on the outer surface of the zeolite make an appreciable contribution to catalysis but the overall activity is not large. However systems containing nickel, cobalt, and manganese ions show significant catalytic activity in the oxidation of methane.

The influence of the local topography of the isolated active centres on the oxidation of C_2H_6 on Cu/H-ZSM-5 has been analysed.[65] The studies were performed on the same catalysts, prepared by solid state reactions, as were used in the work discussed above[63,64] but different conditions were used (low degrees of conversion, temperatures of 270–500 °C). It was shown that the

specific activity of an isolated Cu^{2+} ion in the complete oxidation of C_2H_6 can be varied by a factor of 1000 depending on the coordination of the cation. Cu^{2+} ions with low coordination (square planar) display the highest activity and using a zeolite containing such centres the reaction will proceed at an appreciable rate at 270–300 °C.[65]

VI. Conclusion

HS-zeolites modified by various cations can be used to analyse catalytic processes at the atomic-molecular level because it is possible to produce in them distinct sets of isolated active centres with different topologies. However the standard ion-exchange method cannot be used for the introduction into these matrices of the majority of transition metal ions which are of most interest from a catalytic point of view. The potentialities of this field can be extended by using topochemical methods of introducing cations by means of solid state reactions. The following conclusions can be drawn from a generalisation of the results currently available.

Solid state reactions can be used as a new, environmentally clean method for modifying HS-zeolites with one or more multivalent transition metal cations (Cu^{2+}, Fe^{3+}, V^{4+}, Cr^{5+}, Mo^{5+}, Ni^{2+}, Co^{2+}, Ga^{3+}, Mn^{2+}, Zn^{2+}), the majority of which cannot be introduced into these matrices by other methods.

The ions can be introduced by a solid state reaction because of the presence of free acidic centres in the HS-zeolites. These centres can be regarded as energy traps for migrating cationic species. The potentialities of the method can be extended considerably by using transition metal compounds with different anionic fragments and carrying out the reactions in different gaseous media.

Solid state reactions can be used to replace one highly charged cation by another and also to introduce different cations into the HS-zeolite simultaneously. The different cations occupy the same sites and the processes of their location are competitive and dependent on the conditions used for the solid state reaction.

A distinctive feature of the pentasil matrices is that the isolated cations are stabilised in environments with high coordination unsaturation (low-symmetry crystal fields). A result of this is the very high reactivity of the cations towards various adsorbates.

Pentasil-based systems with distinct isolated centres form unique subjects for physicohemical studies and a proper analysis of the relationship between the local structure and the properties of the isolated transition metal cation. The isolated cationic centres formed in pentasils display an abnormally high and stable catalytic activity in the complete oxidation of alkanes and the decomposition of nitrogen oxides. Therefore, in spite of the low density of active centres produced in the solid state reactions, transition metal cation/pentasil catalysts may be of interest for both theoretical studies and environmental protection.

References

1. D W Breck *Zeolite Molecular Sieves* (Translated into Russian), Mir, Moscow, 1976
2. R M Barrer *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, London, New York, 1978
3. J A Rabo, M L Poutsma, G W Skeels *Proceedings of the 5th International Congress on Catalysis, August 20–26, 1972 Miami Beach, USA*, North Holland Publ. Co.,New York, 1973,p. 1353
4. J A Rabo *Zeolite Chemistry and Catalysis* (Translated into Russian), Mir, Moscow, 1980, Vol. 1, p. 398
5. J A Rabo, P H Kasai *Prog. Solid State Chem.*, 1975, **9** 1
6. A Clearfield, C H Saldarriaga, R C Buckley *Proceedings of the 3rd International Conference on Molecular Sieves, Sept. 3–7, 1973, Zurich, Switzerland*, Recent Progress Reports, 1973, Paper 130, p. 241
7. H G Karge, H K Beyer *Proceedings of the International Sympsium "Zeolite Chemistry and Catalysis", Prague, Czechoslovakia, Sept. 8–13*, 1991, Elsevier, Amsterdam, 1991, p. 43
8. R G Herman, J H Lunsford, H Beyer, et al. *J. Phys. Chem.*, 1975, **79** 2388
9. A A Slinkin, G V Antoshin, M I Loktev, et al. *Kinet. Katal.*, 1978, **19** 754
10. H Beyer, P A Jacobs, J B Uytterhoeven *J. Chem. Soc.*, Faraday Trans. 1, 1976, **72** 674
11. A V Kucherov, A A Slinkin *Kinet. Katal.*, 1986, **27** 671
12. A V Kucherov, A A Slinkin *Zeolites*, 1986, **6** 175
13. A V Kucherov, A A Slinkin, D A Kondrat'ev, et al. *Kinet. Katal.*, 1985, **26** 409
14. A V Kucherov, A A Slinkin, D A Kondratyev, et al. *Zeolites*, 1985, **5** 320
15. M W Anderson, L Kevan *J. Phys. Chem.*, 1987, **91** 4174
16. Y Sendoda, Y Ono *Zeolites*, 1986, **6** 209
17. A A Slinkin A V Kucherov, N D Chuvylkin *J. Chem. Soc., Faraday Trans. 1*, 1989, **85** 3233
18. A A Slinkin, A V Kucherov, D A Chuvylkin, et al. *Kinet. Katal.*, 1990, **31** 698
19. A V Kucherov, A A Slinkin *Kinet. Katal.*, 1989, **30** 497
20. A V Kucherov, A A Slinkin *J. Phys. Chem.*, 1989, **93** 864
21. Lin Zhenyi, Zhang Wangjin, Yu Qin *Proceedings of the 7th International Zeolite Conference, Tokyo, 1986*, Elsevier, Tokyo, Amsterdam, Kodansh, 1986, p. 1091
22. A V Kucherov, A A Slinkin *Kinet. Katal.*, 1985, **26** 1516
23. A V Kucherov, A A Slinkin *Kinet. Katal.*, 1986, **27** 678
24. A V Kucherov, A A Slinkin *Zeolites*, 1987, **7** 38
25. A A Slinkin, A V Kucherov, S S Goryashchenko, et al. *Kinet. Katal.*, 1989, **30** 184
26. A A Slinkin, A V Kucherov, S S Gorjashenko, et al. *Zeolites*, 1990, **10** 111
27. A V Kucherov, A A Slinkin, H K Beyer, G Borbely *Kinet. Katal.*, 1989, **30** 429
28. A V Kucherov, A A Slinkin, H K Beyer, G Borbely *J. Chem. Soc., Faraday Trans. 1*, 1989, **85** 2737
29. J-F Hemidy, F Delavennat, D Cornet *J. Chim. Phys. Phys.-Chim. Biol.*, 1973, **70** 1716
30. J-F Hemidy, D Cornet *J. Chim. Phys. Phys.-Chim. Biol.*, 1974, **71** 739
31. A V Kucherov, A A Slinkin, H K Beyer, G Borbely *Kinet. Katal.*, 1991, **32** 1441
32. A A Slinkin, A V Kucherov, S B Nikishenko *Kinet. Katal.*, 1990, **31** 692
33. A V Kucherov, A A Slinkin *Zeolites*, 1987, **7** 583
34. C E Sass, X Chen, L Kevan *J. Chem. Soc., Faraday Trans.*, 1990, **86** 189
35. V K Sharma, A Wokaun, A Baiker *J. Phys. Chem.*, 1986, **90** 2715
36. C Marchal, J Thoret, M Gruia, et al. *Fluid Catalytic Cracking. 2. Concepts Catalysis Design*, ACS Symposium Series, 1990, p. 452

37. B Wichterlova, S Beran, S Bednarova, et al. *Innovation in Zeolite Material Science*, Elsevier, Amsterdam, 1987, p. 199
38. S Beran, B Wichterlova, H G Karge *J. Chem. Soc., Faraday Trans. 1*, 1990, **86** 3033
39. B Wichterlova, S Beran, L Kubelkova, et al. *Studies Surf. Sci. Catal.*, Elsevier, Amsterdam, 1989, Vol. 46, p. 347
40. N N Tikhomirova, I V Nikolaeva *Zh. Fiz. Khim.*, 1981, **55**(9) 2224 [English translation in *Russ. J. Phys. Chem.*, 1981(9)]
41. N N Tikhomirova, I V Nikolaeva *Zh. Fiz. Khim.*, 1981, **55**(10) 2449 [English translation in *Russ. J. Phys. Chem.*, 1981(10)]
42. A V Kucherov, A A Slinkin *Kinet. Katal.*, 1987, **28** 1199
43. A V Kucherov, A A Slinkin *Zeolites*, 1988, **8** 110
44. Y Yang, X Guo, M Deng, et al. *Proceedings of the International Symposium "Zeolites as Catalysts, Sorbents and Detergent Builders—Application and Innovations" Wurzburg, FRG, Sept. 4–8, 1988*, Elsevier, Amsterdam, Studies Surf. Sci. Catal., 1989, Vol. 46, p. 849
45. G L Price, V Kanazirev *J. Catal.*, 1990, **126** 267
46. P Meriaudeau, C Naccache *Catalyst Deactivation*, Elsevier, Amsterdam, Studies Surf. Sci. Catal., 1991, p. 767
47. J F Joly, H Ajot, E Merlen, et al. *Appl. Catal., A*, 1991, **79** 249
48. A V Kucherov, A A Slinkin *Kinet. Katal.*, 1986, **27** 909
49. A V Kucherov, A A Slinkin *Zeolites*, 1987, **7** 43
50. M Iwamoto, S Yokoo, K Sakai, S Kagawa *J. Chem. Soc., Faraday Trans. 1*, 1981, **77** 1629
51. M Iwamoto, H Furukawa, S Kagawa *New Development in Zeolite Science and Technology*, Kadansha, Tokyo, 1986, p. 943
52. M Iwamoto, H Furukawa, Y Mine, et al. *J. Chem. Soc., Chem. Commun.*, 1986, 1272
53. M Iwamoto, H Yahiro, Y Mine, S Kagawa *Chem. Lett.*, 1989, 213
54. Y Li, W K Hall *J. Phys. Chem.*, 1990, **94** 6145
55. S Sato, Y Yu-u, H Yahiro, et al., *Appl. Catal.*, 1991, **70** L1
56. H Hamada, Y Kintaichi, M Sasaki, et al. *Appl. Catal.*, 1990, **64** L1
57. M Iwamoto, H Yahiro, S Shundo, et al. *Shokubai (Catalyst)*, 1990, **32** 430
58. M Iwamoto, H Yahiro, S Shundo, et al. *Appl. Catalysis*, 1991, **69** L15
59. H Hamada, N Matsubayashi, H Shimada, et al. *Catal. Lett.*, 1990, **5** 189
60. A A Slinkin, A V Kucherov, S S Goryashchenko, K I Slovetskaya *Primenenie Tseolitov v Katalize: Tesizy Dokladov 4 Vsesoyuz. Konf.* (Abstracts of Papers for the Fourth All-Union Conference 'Applications of Zeolites in Catalysis'), Nauka, Moscow, 1989, p. 191
61. A A Slinkin, A V Kucherov, S S Gorjashenko, et al. *Proceedings of the 8th Soviet-French Seminar on Catalysis, Novosibirsk*, 1990, p. 24
62. A A Slinkin, A V Kucherov, S S Gorjashenko, et al. *Proceedings of the 9th Soviet-Japanese Seminar on Catalysis, Novosibirsk*, 1990, p. 224
63. A V Kucherov, A A Slinkin, S S Gorjashenko, K I Sloverskaja *J. Catal.*, 1989, **118** 459
64. S S Goryashchenko, K I Slovetskaya, A V Kucherov, A A Slinkin *Kinet. Katal.*, 1989, **30** 249
65. A V Kucherov, T N Kucherova, A A Slinkin *Catal. Lett.*, 1991, **10** 289

Received 31st March 1992

Translated from *Uspekhi Khimii* 61 1720–1747 (1992) U.D.C. 541.11/123.7.03+546.39–74+669.253

Thermodynamics of formation reactions and hydrometallurgical application of metal–ammonia complexes in aqueous solutions

V E Mironov, G L Pashkov, T V Stupko
Institute of Chemistry and Chemico-Metallurgical Processes, Siberian Branch, Russian Academy of Sciences

ABSTRACT. Critically selected activity coefficients of individual ions stepwise stability constants, and enthalpy and entropy changes during formation of metal–ammonia complexes in aqueous salt solutions are summarised and analysed. Special attention is paid to the specifics of ammonia complexation in solutions with high ammonia concentrations ($\geqslant 1$ mol dm^{-3}), which are of interest in hydrometallurgy. Certain problems and prospects for use of metal–ammonia complexation in hydrometallurgy are discussed. The bibliography includes 154 references.

Contents

I. Introduction 946
II. Aqueous salt solutions of NH_3 946
III. Formation of metal–ammonia complexes in highly concentrated aqueous ammonia 948
IV. Thermodynamic functions of metal–ammonia complexation 951
V. Outer-sphere metal–ammonia complexes 952
VI. Problems and prospects of ammonia hydrometallurgy 953
VII. Conclusion 954

I. Introduction

The theoretical principles of ammonia hydrometallurgy have been formulated by investigating aqueous equilibria:

$$M(H_2O)_N^{z+} + nNH_3 \rightleftharpoons M(NH_3)_n(H_2O)_{N-n}^{z+} + nH_2O, \quad (1)$$

where $n = 1, 2, \ldots N$, and N is the limiting coordination number of M^{z+}. These investigations were performed and summarised in the doctoral dissertation of J Bjerrum, the second printing of which appeared in Russian.[1]

The studies of Caron[2,3] enabled industry to utilise the most common method of ammonia hydrometallurgy. The Nicaro plant in Cuba was the first to implement this technology (Ref. 4, p. 129).

However metal–ammonia complexation in aqueous salt solutions has not yet been sufficiently studied.[5] Thus, the unique capabilities of ammonia hydrometallurgy such as the selectivity, mildly aggressive solutions, reagent recycling and ecological benignity[4,6,7] are not fully appreciated.

The lack of thermodynamic data for the formation of Fe^{II}– and Mn^{II}–NH_3 complexes represented a large gap in studying equilibria of type (1).[8–12] Ammonia complexation in sulphate and carbonate solutions,[5] in which most processes of ammonia hydrometallurgy are carried out has not been studied. The position of equilibrium (1) at temperatures greater than 45 °C is almost completely unknown. Reliable stability constants and other thermodynamic functions of Pd^{II}, Tl^{I}, Pb^{II}, Cr^{II}, Li and alkaline-earth complexes with NH_3 are not available.[8–12] The possibility of ammonia–ammonium complexation was not considered in examining equilibria of type (1).[13,14]

Thermodynamic parameters for the reaction of individual cations and anions with NH_3 in aqueous salt solutions have been calculated[15] only assuming that the activity coefficients of ammonium and chloride are constant. However, this assumption is incorrect in concentrated aqueous ammonia.[13]

Protonation constants of NH_3 in aqueous ammonium carbonate and sulphate solutions have not yet been determined.[8–12,14] These are the most important salts in ammonia hydrometallurgy.

The present review is written with the intent of reducing the aforementioned and a number of other wide gaps in the chemistry of aqueous salt solutions of NH_3. The review is based on studies by us and our co-workers that were published in 1986–1991.

The applied part of the review involves current problems of ammonia hydrometallurgy and prospects for broader utilisation of this chemical technology in the future development of hydrometallurgy.

II. Aqueous salt solutions of NH_3

The dissolution of NH_3 in water is a two-step process described by the following equilibria

$$NH_3(gas) \rightleftarrows NH_3(l)$$

$$NH_3(l)H_2O(l) \rightleftarrows NH_4^+(l) + OH^-(l). \quad (2)$$

The quantitative characteristics of these reactions are Henry's constant (K_H, usually in mol kg^{-1} atm^{-1}) and the base dissociation constant (K_B^0) of NH_3. These constants are defined by the expressions

$$K_H = m_{NH_3}\gamma_{NH_3} / P_{NH_3}, \quad (3)$$

$$K_B^0 = m_{NH_4^+}\gamma_{NH_4^+} m_{OH^-}\gamma_{OH^-} / (m_{NH_3}\gamma_{NH_3} a_{H_2O}), \quad (4)$$

in which m_i are the molalities of the i-th components, P_{NH_3} is the partial pressure of NH_3, γ_i are the molal activity coefficients and a_{H_2O} is the activity of water (usually on a mole fraction scale).

Recently the Pitzer equation[16,17] was recommended for a quantitative description of the solubility data of NH_3 in water and multicomponent aqueous salt solutions. This equation enables the activity coefficients and osmotic coefficients of NH_3 and salts in its aqueous solutions to be rather accurately calculated.

It has been demonstrated[18,19] that Henry's constant as defined by Eqn. (3) varies with temperature according to the expression

$$\ln K_H = a + bT^{-1} + cT, \quad (5)$$

where a, b and c are constants equal to -8.09694, 3917.507 and -0.00314[18] or -8.097, 3917.5 and -0.00314,[19] respectively, at $T = 273-313$ K.

The influence of temperature in the range 273–313 K on K_B^0 as defined by Eqn. (4) gives the equation[18]

$$\ln K_B^0 = 16.9732 + 4411.025 / T - 0.0440T. \quad (6)$$

The molal activity coefficients of NH_3 in solutions with insignificant concentration of ions is expressed as[18]

$$\gamma_{NH_3} = \exp(2m_{NH_3}\lambda_{NH_3,NH_3} + 3m^2_{NH_3}\mu_{NH_3,NH_3,NH_3}), \quad (7)$$

where λ_{NH_3,NH_3} and μ_{NH_3,NH_3,NH_3} are the coefficients of paired and tripled interaction of NH_3. The tripled interaction coefficients in the temperature range 273–313 K contribute little to γ_{NH_3} as defined by Eqn. (7) up to aqueous ammonia concentrations of 20–25 mol kg^{-1} H_2O. The paired interaction coefficients of NH_3 (Table 1) vary with temperature according to the equation

$$\lambda_{NH_3,NH_3} = 0.033161 - 21.12816 / T + 4665.1461 / T^2.$$

The molal activity coefficients of individual ions for $M_{\nu+}X_{\nu-}$ in aqueous salt solutions of NH_3 have been calculated[18,20] using the expressions

$$\nu \ln \gamma_{\pm} = A + 2m_{NH_3}\left(\nu_+\lambda_{NH_3,M^{\nu-}} + \nu_-\lambda_{NH_3,X^{\nu+}}\right) + 3m^2_{NH_3}\left(\nu_+\mu_{NH_3,NH_3,M^{\nu-}} + \nu_-\mu_{NH_3,NH_3,X^{\nu+}}\right) + bm_{NH_3}m_{M_{\nu+}X_{\nu-}}\left(\nu^2_+\mu_{NH_3,M^{\nu-},M^{\nu+}} + 2\nu_+\nu_-\mu_{NH_3,M^{\nu-},X^{\nu+}} + \nu^2_-\mu_{NH_3,X^{\nu+},X^{\nu-}}\right), \quad (8)$$

where A are $M^{\nu+}-X^{\nu-}$ interionic interaction terms defined by the Pitzer equation.[16,17] Experimental data for the average ionic molal activity coefficients ($\gamma_{\pm}$) of salts in aqueous ammonia provided a basis for calculations using Eqn. (8). These primarily yielded coefficients of paired and tripled interactions of ions with NH_3. These coefficients were used to calculate γ_+ and γ_-. The molal activity coefficients of the ions, like the calculation of the coefficients of paired and tripled interactions (Table 1), were calculated[18,20] using the unconventional thermodynamic assumption that in aqueous ammonia

$$\gamma_{NH_4^+} = \gamma_{Cl^-} = 1 \text{ (Refs. 15, 18)}. \quad (9)$$

or

$$\gamma_{Cs^+} = \gamma_{I^-} = 1 \text{ (Ref.20)} \quad (10)$$

Table 1. Critically selected parameters for reaction of NH_3 with ions in aqueous salt (in mol kg^{-1} H_2O) solutions at 25 °C.[18,20]

Ion (i)	$\lambda_{NH_3,i}$		Ion (i)	$\lambda_{NH_3,i}$	
	calc.*1	calc.*2		calc.*1	calc.*2
Mg^{2+}	−0.21	−0.26*3	ClO_3^-	−0.004	0.055
Ca^{2+}	−0.081	−0.13*3	ClO_4^-	−0.056	−0.003
Sr^{2+}	−0.041	−0.090*3	NO_2^-	−0.003 (0,000437)	0.10
Ba^{2+}	−0.021	−0.076*3	NO_3^-	−0.01	0.040*3
Li^+	−0.038	−0.090*3	CNS^-	−0.017	0.034
Na^+	0.0175 (−0.000311)	−0.030	S^{2-}	0.174	0.22
K^+	0.054 (−0.000321)	−0.003	SO_3^{2-}	0.158	0.20
Rb^+	—	0	SO_4^{2-}	0.140	0.19
Cs^+	—	0	CO_3^{2-}	0.180 0.000625)	0.23
NH_4^+	0.0 (−0.00075)	−0.049	$C_2O_4^{2-}$	0.12	0.18
F^-	0.091	0.14	$HCOO^-$	0.048	0.10
Cl^-	0.0	0.048	CH_3COO^-	0.036	0.090
Br^-	−0.022	0.030	OH^-	0.103	0.15
I^-	−0.051	0	NH_3	0.01472	−0.035

*1Calculated assuming $\gamma_{NH_4^+} = \gamma_{Cl^-} \approx 1$.[15] Coefficients of tripled interaction, i.e. $\mu_{NH_3,NH_3,i}$, are shown in parentheses.
*2Calculated assuming $\gamma_{Cs^+} = \gamma_{I^-} = 1$.[20]
*3The contribution of $\mu_{NH_3,NH_3,i}$ is noticeable at $c_{NH_3} > 8-15$ m; however, the accurate value of $\mu_{NH_3,NH_3,i}$ was not calculated.

Table 2. Logarithms of molar activity coefficients (y) of ammonium cations and chloride anions in aqueous ammonia mixtures of ammonium perchlorate and chloride (1.0 mol dm^{-3}) at 25.0 °C.[13,21]

c_{NH_3}, mol dm^{-3}	lg y of the ions	
	NH_4^+	Cl^-
2.0	−0.10	0.10
4.0	−0.22	0.23
6.0	−0.33	0.36
8.0	−0.46	0.40
10.0	−0.56	0.52

Note. It was assumed that $\lg y_{KClO_4} = \lg y_{K^+} = \lg y_{ClO_4^-}$ (Ref.13).

Table 1 summarises such calculations that are based on Eqn. (8) as paired interaction coefficients of ions with NH_3. The numerical data of Table 1 indicate that the unconventional thermodynamic assumptions (9) and (10) produce different paired interaction

coefficients of NH_3 with the ions. However, if the two assumptions mentioned above are used, these coefficients differ by practically identical amounts of 0.05–0.06.

However, assumption (9) is not valid for concentrated aqueous ammonia[13] since ammonium and ammonia form the $NH_4NH_3^+$ compelex with a stability constant of 8.0 ± 0.5 (taking into account the water activity in mol dm^{-3}) in aqueous solutions with ionic strength 1.0 at 25.0 °C.[21] Chloride in these same solutions salts out NH_3, as indicated by the data in Table 2. Therefore, adding NH_4Cl to aqueous ammonia has no affect on the activity of dissolved NH_3 as was proposed on the basis of assumption (9).

The molar activity coefficients (y) have been calculated for a large number of individual ions[13,22] for aqueous ammonia with an ionic strength of 1.0 held constant with NH_4ClO_4 at 25.0 °C. The calculations were performed using the unconventional thermodynamic assumption that

$$y_{KClO_4} = y_{K^+} = y_{ClO_4^-} = 1. \quad (11)$$

Assumption (11) for solutions with $[NH_3]$ less than 12.0 mol dm^{-3} has been confirmed to be valid by various methods.[23–27] It was found[22] that, depending on the molar $(NH_3]$ (c_{NH_3}), these activity coefficients vary with high correlation coefficients (ρ) according to the equation

$$\lg y_i = Ac_{NH_3} + B, \quad (12)$$

where A and B are constants with the values given in Table 3. It is noteworthy that B for all ions (Table 3) is statistically equal to zero within error limits. Thus, log $y_i \to 0$ as $c_{NH_3} \to 0$ according to Eqn. (12).

Table 3. The constants A and B in Eqn. (12).[13,22]

Ions	$A \pm 3\sigma$	$B \pm 3\sigma$	ρ
Cl^-	0.065 ± 0.008	- 0.03 ± 0.05	0.999
Br^-	0.057 ± 0.008	- 0.05 ± 0.05	0.992
NO_3^-	0.047 ± 0.008	- 0.03 ± 0.05	0.986
BrO_4^-	0.091 ± 0.006	- 0.05 ± 0.04	0.998
IO_4^-	0.153 ± 0.003	- 0.02 ± 0.02	0.999
SO_4^{2-}	0.28 ± 0.05	- 0.2 ± 0.3	0.994
$C_2O_4^-$	0.24 ± 0.07	- 0.05 ± 0.4	0.982
CO_3^{2-}	0.24 ± 0.05	- 0.2 ± 0.3	0.992
Tl^+	- 0.100 ± 0.007	0.06 ± 0.04	0.998

The equilibrium below has been studied in a series of careful pH titrations[14,28–30]

$$H^+(solv) + NH_3(solv) \underset{}{\overset{K}{\rightleftharpoons}} NH_4^+(solv), \quad (13)$$

in aqueous solutions with ionic strengths (I) held constant by various monotypic salts (MA_z) and their mixtures (MA_z + BX) at 25.0 °C. It was found in these studies that the equilibrium constants (K) for Eqn. (13) in MA_z salt solutions obey the following linear relationships with a correlation coefficient greater than 0.999:

$$\lg K = \lg K^\circ + bI, \quad (14)$$

where K° are the constants standardised using solutions with zero ionic strength and b are constants (Table 4). It should be especially emphasised that data standardised to ammonium sulphate and carbonate solutions also obey Eqn. (14). These are the most common salts of ammonia hydrometallurgy for which the equilibrium constants of Eqn. (13) have not yet been determined.[14] The validity of Eqn. (14) has also been confirmed with correlation coefficients of 0.99 by other investigators.[31,32] However, these studies did not involve all salts (Table 4) and covered a narrower range of ionic strengths. The results of these studies[31,32] were recently the subject of a thorough mathematical analysis.[14]

Table 4. Equilibrium constants (13) of Eqn. (14) at 25.0 °C.[14]

Background salt	$\lg K^\circ$	b	Range of I	Number of experimental K
$LiNO_3$	9.228 ± 0.006	0.168 ± 0.005	0.1 ± 6.0	14
$NaNO_3$	9.229 ± 0.004	0.192 ± 0.001	0.1 ± 6.0	14
KNO_3	9.199 ± 0.004	0.192 ± 0.002	0.1 ± 3.5	9
$LiClO_4$	9.245 ± 0.003	0.210 ± 0.001	0.1 ± 4.0	10
$NaClO_4$	9.221 ± 0.004	0.250 ± 0.001	0.1 ± 5.5	13
NH_4ClO_4	9.226 ± 0.004	0.141 ± 0.004	0.1 ± 1.5	5
NH_4NO_3	9.230 ± 0.002	0.141 ± 0.001	0.1 ± 6.0	14
$(NH_4)_2SO_4$	9.38 ± 0.01	0.138 ± 0.003	0.3 ± 6.0	5
$(NH_4)_2CO_3$	9.31 ± 0.01	0.131 ± 0.001	0.3 ± 6.0	5

The equilibrium constants of Eqn. (13) in $MA_z \to BX$ salt mixtures with constant ionic strengths lie on the line described by the following equation with a correlation coefficient greater than 0.99

$$\lg K_{(MA_z \to BX)} = \lg K_{(MA_z)} + \lambda_{BX} c_{BX}. \quad (15)$$

where $K_{(MA_z \to BX)}$ and $K_{(MA_z)}$ are constants in the mixed and monotypic salt solutions, c_{BX} are the molar concentrations of BX salts and λ_{BX} are constants (Table 5).[14,30] It is interesting that the constants λ_{BX} can be calculated from the constants b (Tables 4 and 5) in Eqn. (14). Thus, λ_{BX} can be divided into ionic components, the addivity of which can be used to predict $K_{(MA_z \to BX)}$ in mixed solutions of still unstudied salts.

An analysis of the ionic components of λ_{BX} indicates (Table 5) that the cationic components are less than the anionic ones for the salts included in Tables 4 and 5. This is due to the fact that the reagents of equilibrium (13) are cations, the particular behaviour of which depends more on the nature of the anions than on that of the cations.

Table 5. Equilibrium constants (13) of Eqn. (15) at 25.0 °C.[14]

Background salt	Ionic strengths	No. of K	λ_{BX}	
			from Eqn. (15)	from b values
$LiNO_3 \rightarrow NaClO_4$	2.0; 5.0	16	0.083 ± 0.007	0.083 ± 0.005
$Li(NO_3 \rightarrow ClO_4)$	2.0; 4.0	14	0.030 ± 0.005	0.043 ± 0.006
$Na(NO_3 \rightarrow ClO_4)$	2.0; 3.0; 5.0	23	0.052 ± 0.005	0.057 ± 0.005
$(Li \rightarrow Na)NO_3$	2.0; 4.0; 6.0	27	0.028 ± 0.003	0.026 ± 0.004
$(Li \rightarrow NH_4)NO_3$	2.0; 4.0; 6.0	27	−0.024 ± 0.003	−0.023 ± 0.004
$(Li \rightarrow Na)ClO_4$	2.0; 4.0	14	0.033 ± 0.006	0.040 ± 0.007

The additivity of the ionic components of λ_{BX} is not unexpected. The influence of a large number of alkali and alkaline-earth salts on the vapour pressure of NH_3 has been represented and analysed[33] as activity parameters of the individual ions. These parameters were used to predict the analogous functions of unstudied ions. Empirical laws were used for the prediction for example

$$\Delta P = a + bz / r^2, \tag{17}$$

where ΔP are the relative NH_3 vapour-pressure changes caused by ions of charge z and radius r and a and b are constants, or

$$\Delta P = 0.20\Delta G_{A^-} - 49.5, \tag{18}$$

where ΔG_{A^-} is the free energy of hydration of the anions (in J mol^{-1}).

It is interesting that the prediction was made using Eqn. (18)[33] and later experimentally confirmed[13] that cations of the type $Co(en)CO_3^+$ (en = ethylenediamine) salt out NH_3 whereas large anions such as picrate, HgI_3^-, etc. bind NH_3 in aqueous salt solutions.

The ionic components are used to calculate Sechenov constants, which characterise the behaviour of NH_3 in aqueous solutions of alkali metal salts.[34] It is true that the calculated constants did not always agree with those found experimentally. However, the following equation

$$K_s = 0.053z / r_{A^{z-}} - 0.22,$$

where $r_{A^{z-}}$ is the crystallographic radius of A^{z-} (in nm), rather well gives the NH_3 salting-out constants (K_s) by the anions.[13]

Judging from the previous studies,[30,35,36] NH_3 is protonated according to Eqn. (13) owing to a negative enthalpy component of the Gibbs free energy with a small entropy decrease (Table 6). The enthalpy and entropy components become more negative as the ionic strength of the studied solutions increases. Changing from Li to Na salts slightly decreases the entropic barrier. This barrier for both Li and Na sats increases in the order $ClO_4^- < NO_3^- < Cl^-$. However, these effects are small considering that the determination errors of the examined entropy changes ($\pm\sigma$) are ±1 J mol^{-1} K^{-1}.

Footnote: No Eqn. (16) in Russian text.

Table 6. Enthalpy and entropy changes of NH_3 protonation in aqueous salt solutions at 25.0 °C.[30,35,36]

c_{salt}, mol dm^{-3}	Solution					
	LiCl	$LiNO_3$	$LiClO_4$	NaCl	$NaNO_3$	$NaClO_4$
	$(-\Delta H \pm 0.3)$ kJ mol^{-1}					
0.50	53.0	53.7	53.1	53.0	53.2	53.2
1.00	53.8	54.0	54.0	54.0	54.2	54.3
2.00	55.6	56.7	56.2	55.9	56.2	56.4
3.00	57.2	58.4	58.5	57.8	58.3	58.9
4.00	59.0	60.4	—	59.8	60.2	60.7
5.00	60.9	62.5	—	61.8	62.2	—
	$(-\Delta S \pm 1.0)$ J mol^{-1} K^{-1}					
0.50	1.2	2.1	−0.3	0.5	−0.3	−0.3
1.00	2.0	1.7	0	1.2	1.0	0.7
2.00	7.9	7.1	3.3	4.6	4.0	3.3
3.00	10.0	9.7	6.1	8.3	7.4	5.4
4.00	14.3	13.1	—	11.4	10.4	7.4
5.00	16.2	16.8	—	14.7	13.4	—

Table 7. Molar activity coefficients of NH_3 in 2.0 mol dm^{-3} aqueous ammonia solutions of NH_4NO_3 at 25.0 °C.[37]

c_{NH_3}, mol dm^{-3}	$y^*_{NH_3}$	c_{NH_3}, mol dm^{-3}	$y^*_{NH_3}$
1.0	1.02 ± 0.01 (1.01)	10.0	1.90 ± 0.02 (1.89)
2.0	1.07 ± 0.01 (1.06)	12.0	2.25 ± 0.03 (2.24)
4.0	1.23 ± 0.01 (1.23)	14.0	2.89 ± 0.04 —
6.0	1.39 ± 0.02 (1.40)	16.0	3.55 ± 0.05 —
8.0	1.62 ± 0.02 (1.62)	18.0	4.20 ± 0.05 (4.18)

*Values of y obtained from extraction of NH_3 into $CHCl_3$ are given in parentheses.

Many properties of aqueous salt solutions of NH_3 are determined by their activity coefficients. The coefficients markedly increase in solution with $[NH_3] > 1$ mol dm^{-3}.[1,13,14,37,38] The molar NH_3 activity coefficients (up to 18 mol dm^{-3}) at 25.0 °C in aqueous NH_4NO_3 (2.0 mol dm^{-3}) that were recently measured[37] by an electrochemical method using a glass electrode and by extraction into $CHCl_3$ are presented in Table 7. This salt solution is most frequently used to study metal–ammonia complexation equilibria. These activity coefficients have been used in many of our studies[14,37,39–51] to investigate the processes expressed by Eqn. (1) in aqueous solutions with a high $[NH_3]$.

Careful measurements of the NH_3 vapour pressure (P_{NH_3}) over an aqueous $NaClO_4$ solution (1.0 mol dm^{-3}) containing less than 12 *M* NH_3 at 25.0 °C led to the equation[38]

$$P_{NH_3} = 1.58 + 12.4c_{NH_3} - 1.66c_{NH_3}^2 + \\ + 0.937c_{NH_3}^3 - 0.119c_{NH_3}^4 + 0.00529c_{NH_3}^5.$$

Up to $[NH_3]$ = 2 mol dm^{-3}, this function was practically linear and gave a Henry's constant of 12.4. Taking this into account, the NH_3 activity in all studied solutions is correctly described by

$$a_{NH_3} = P_{NH_3} / 12.4.$$

The vapour pressure of NH_3 over the whole concentration range (0–100%) of its aqueous solutions has been measured over a wide temperature range (32–345 °C).[52] The activity coefficients of NH_3 that were standardised to its pure state (i.e. liquid NH_3) were determined under these conditions.

The dependences of the standard solvation enthalpies of NH_3 on the charge density of the cations and anions in aqueous calcium, alkali metal, tetramethyl- and tetraethylammonium chloride solutions and in sodium halide, nitrate and sulphate solutions have been analysed.[53] These functions are nonlinear for the anions and cations owing to the considerable differences in the hydration mechanism of the various ions and in the size of the noncoulombic contributions (covalent, hydrophobic and hydrogen bonds) to the interaction energy of the ions and molecules in the examined solutions.

III. Formation of metal–ammonia complexes in highly concentrated aqueous ammonia

The formation of metal–ammonia complexes in aqueous solutions according to Eqn. (1) involves the metal ions, NH_3 molecules, $M(NH_3)_n(H_2O)_{N-n}^{z+}$ and water molecules. Modern experimental methods for studying equilibria of type (1) in order to determine *n* and the overall stability constants (β_n) of the complexes formed are based on measurements of various properties of $M(H_2O)_N^{z+}$, NH_3 and $M(NH_3)_n(H_2O)_{N-n}^{z+}$ (the metal ion, ligand and complex methods, respectively).[54] Potentiometry with electrodes reversible toward $M(H_2O)_N^{z+}$, polarography and the solubility of salts containing M^{z+} are the most common varieties of the metal-ion methods. Extraction (NH_3),NH_3 vapour-pressure determination over solutions and pH titrations are varieties of ligand methods. Electronic spectroscopy, NMR, thermochemistry and extraction of $M(NH_3)_n^{z+}$ are examples of complex methods.

Ligand methods have provided the most information[8–11] on the composition and stability constants of $M(NH_3)_n^{z+}$. Among these methods, pH titrations have most frequently been used. The equilibrium $[NH_3]$ in aqueous solutions with low total metal concentrations ($c_{M^{z+}}$) and various $[NH_3]$ (c_{NH_3}) are usually measured against a background of practically constant high ($\geqslant$0.1 mol dm^{-3}) concentrations of ammonium salts. These measurements were used to calculate the formation functions ($\bar{n}$).[1] Calculations of the latter yielded the equation

$$\bar{n} = (c_{NH_3} - [NH_3]) / c_{M^{z+}}. \qquad (19)$$

However, Eqn. (19) is incorrect[55] for aqueous salt solutions with $[NH_3]$ > 1.0 mol dm^{-3}. Even Bjerrum demonstrated[1] that $\bar{n}$ calculated for $M(NH_3)_n^{z+}$ using Eqn. (19) are reduced in solutions with high $[NH_3]$. This reduction of $\bar{n}$ is mainly due to the salting-out action of NH_3 on the reagents of equilibrium (1), to the use of experimental NH_3 activities (a_{NH_3}) and not its equilibrium concentrations and to a number of less important factors.[13] The effect of all aforementioned factors can formally be ascribed to the variability of the activity coefficients for the reagents of equilibrium (1) in solutions with $[NH_3]$ > 1.0 mol dm^{-3}. Therefore, equilibrium constants of Eqn. (1) even for aqueous solutions with high and constant concentrations of ammonium salts but with $[NH_3]$ > 1.0 mol dm^{-3} should be represented only in terms of activity, i.e. by the expression

$$\beta_n = \frac{\left[M(NH_3)_n(H_2O)_{N-n}^{z+}\right] y_{M(NH_3)_n(H_2O)_{N-n}^{z+}} a_{H_2O}^n}{\left[M(H_2O)_N^{z+}\right] y_{M(H_2O)_N^{z+}} [NH_3]^n y_{NH_3}^n}, \qquad (20)$$

where y are the molar activity coefficients and a_{H_2O} is the water activity (usually expressed in mole fractions).

The complex concentrations from Eqn. (20) are defined by the equation

$$\left[M(NH_3)_n(H_2O)_{N-n}^{z+}\right] = \beta_n \left[M(H_2O)_N^{z+}\right] [NH_3]^n y_{NH_3}^n a_{H_2O}^{-n}, \qquad (21)$$

if it is assumed that the ratio of $M(H_2O)_N^{z+}$ and $M(NH_3)_n.(H_2O)_{N-n}^{z+}$ activity coefficients is equal to unity and does not change with increasing $[NH_3]$. To a first approximation this assumption is valid since the charges of these ions are identical and their sizes are very similar.[56]

The following equation is obtained by combining Eqns. (19) and (21) and making simple transformations

$$\sum_n (\bar{n} - n)\beta_n [NH_3]^n y_{NH_3}^n a_{H_2O}^{-n} = 0, \qquad (22)$$

and can be used to find $\bar{n}$ and β_n. However, $\bar{n}$ should be corrected for the variable activity of the molecular–salt solution after their determination in solutions with $[NH_3]$ > 1.0 mol dm^{-3} [55] in order accurately to calculate *n* and β_n using Eqn. (22). Bjerrum attempted to determine the size of this effect in terms of corrections ($\Delta\bar{n}$) to the $\bar{n}$ functions. However, the scatter of $\Delta\bar{n}$ in solutions with $[NH_3]$ = 7–10 mol dm^{-3}, according to his data (Ref. 1, p. 149), reached 300%. The reasons for such a scatter were recently discussed.[13,14,37] The neglect of the formation of Ba–NH_3 complexes,[13] the existence of $Ag(NH_3)_3^+$ [47] and the nature of the anion in determining $\Delta\bar{n}$ [20] produced such a scatter.

The quantities $\Delta\bar{n}$ for 1–10 mol dm^{-3} (Refs. 13, 57, 58) and even 1–20 mol dm^{-3} (Refs. 14, 37, 43) for NH_3 solutions of ammonium perchlorate, chloride or nitrate with constant ionic strengths of 1.0 and 2.0 have recently been determined in a series of studies. The most accurate $\Delta\bar{n}$ were determined for Zn^{II}–NH_3 complexes.[37] The Zn^{II} cation is completely converted to the tetrahedral coordinatively saturated $Zn(NH_3)_4^{2+}$ complex even in 0.5 M aqueous ammonia.[1] Increasing $[NH_3]$ further up to 20 mol dm^{-3} causes $\bar{n}$ to decrease from 4.0 to 1.2–1.5.[14,43] Use of the expression

$$\Delta\bar{n} = 4 - \bar{n} \qquad (23)$$

for $Zn(NH_3)_n^{2+}$ in solutions with $[NH_3]$ = 1–20 mol dm^{-3} yielded $\Delta\bar{n}$ over the widest range of $[NH_3]$ (Table 8). Analogous $\Delta\bar{n}$ were obtained during a study of the formation in concentrated aqueous ammonia salt solutions of NH_3 complexes of Ag^I and Cu^{II} [taking

into account formation of $Ag(NH_3)_3^+$ and $Cu(NH_3)_5^{2+}$].[37,43] It is noteworthy that the $\Delta\bar{n}$ found by us (Table 8) are very close to those obtained by Bjerrum using the behaviour of $Cu^{II}-NH_3$ complexes.

Table 8. Average corrections ($\Delta\bar{n}$) to the Bjerrum function for $M(NH_3)_n^{z+}$ in aqueous NH_4NO_3 (2.0 mol dm^{-3}) with high [NH_3] at 25.0 °C.[43]

$-pNH_3^*$	$\Delta\bar{n}$	$-pNH_3^*$	$\Delta\bar{n}$	$-pNH_3^*$	$\Delta\bar{n}$
0	0.05	0.75	0.77	1.50	1.70
0.25	0.22	1.00	1.06	1.75	2.12
0.50	0.50	1.25	1.38	2.00	2.50

Note. Data for the ammonia complexes of Zn^{II}, Cu^{II}, and Ag^I were averaged.
*$pNH_3 = -\log([NH_3]\gamma_{NH_3}/\alpha_{H_2O})$, where a_{H_2O} is in mole fraction and [NH_3] is in mol dm^{-3}.

The averaged $\Delta\bar{n}$ (Table 8) were used to calculate the corrected ($\bar{n}_{corr}$) values of the Bjerrum function.[13,37,47,59] The latter were calculated using

$$\bar{n}_{corr} = \bar{n} + \Delta\bar{n}. \quad (24)$$

The Bjerrum functions corrected by $\Delta\bar{n}$ were substituted into Eqn. (22) during a study of the formation of $Li-NH_3$ complexes (Table 9)[47,51] and Mg−, Ca− and $Cd-NH_3$ complexes (Table 10)[14,37] in addition to those of Tl^I (Refs. 13, 54) and alkaline earths (Table 11)[59] in solutions with $c_{NH_3} \leqslant 18$ mol dm^{-3}. These studies were carried out using a pH-titration ligand method[14,37,47,54] or NH_3 extraction into $CHCl_3$.[13,47,51,59] Some of these complexes were also studied by a thermochemical method,[47,51,60] i.e. by one of the complex methods. The composition and stability constants were calculated using

$$\Delta\bar{H} = \sum_{n=0}^{N} \Delta H_n \alpha_n, \quad (25)$$

where $\Delta\bar{H}$ are the enthalpy changes from Eqn. (1), ΔH_n are the enthalpy changes on formation of $M(NH_3)_n^{z+}$ and α_n are the mole fractions of the complexes, i.e.

$$\alpha_n = \beta_n [M^{z+}] a_{NH_3}^n a_{H_2O}^{-n} / c_{M^{z+}}.$$

Table 9. Logarithms of stepwise stability constants (log K_n) of NH_3 complexes of Li in aqueous NH_4NO_3 (2.0 mol dm^{-3}) at 25.0 °C.[47]

Study method	lg K_n at n			
	1	2	3	4
pH titration	0.28 ± 0.05	0.76 ± 0.09	1.1 ± 0.1	1.5 ± 0.2
Extraction	0.32 ± 0.08	0.8 ± 0.2	1.2 ± 0.3	1.6 ± 0.4
Thermochemistry	0.3 ± 0.1	0.7 ± 0.2	1.2 ± 0.3	1.5 ± 0.5

Table 10. Logarithms of stepwise stability constants (log K_n) of NH_3 complexes of Mg, Ca and Cd in aqueous NH_4NO_3 (2.0 mol dm^{-3}) at 25.0 °C.[14,37]

M^{2+}	lg K_n at n					
	1	2	3	4	5	6
Mg^{2+}	0.25 ± 0.01	−0.13 ± 0.01	−0.40 ± 0.02	0.66 ± 0.02	0.92 ± 0.03	−1.40 ± 0.09
Ca^{2+}	−0.23 ± 0.02	0.61 ± 0.02	−0.87 ± 0.04	−1.02 ± 0.08	−1.49 ± 0.08	−1.80 ± 0.12
Cd^{2+*}	2.68 ± 0.01	2.20 ± 0.01	1.47 ± 0.01	0.95 ± 0.02	−0.30 ± 0.03	−1.7 ± 0.1
	(2.69 ± 0.01)	(2.16 ± 0.02)	(1.49 ± 0.03)	(0.96 ± 0.04)	(−0.28 ± 0.18)	—

*Log K_n obtained from thermochemical data[60] are given in parentheses.

Table 11. Logarithms of stepwise stability constants of NH_3 complexes of alkaline earths in aqueous NH_4ClO_4 (1 mol dm^{-3}) at 25.0 °C.[59]

Cation	I, mol dm^{-3}	lg K_n at n			
		1	2	3	4
Ca^{II}	0	−0.13 ± 0.02	0.26 ± 0.03	0.52 ± 0.03	0.77 ± 0.05
	0.50	−0.05 ± 0.02	0.33 ± 0.03	0.60 ± 0.4	0.85 ± 0.04
	1.0	0.03 ± 0.02	0.42 ± 0.03	0.69 ± 0.04	0.93 ± 0.05
	1.5	0.12 ± 0.02	0.49 ± 0.03	0.76 ± 0.04	1.0 ± 0.05
	2.0*	0.19	0.58	0.84	1.09
Sr^{II}	0	0.04 ± 0.03	0.42 ± 0.04	0.70 ± 0.04	—
	0.50	0.12 ± 0.02	0.50 ± 0.04	0.77 ± 0.04	—
	1.0	0.19 ± 0.03	0.58 ± 0.04	0.85 ± 0.03	—
	1.5	0.27 ± 0.03	0.65 ± 0.05	0.93 ± 0.03	—
Ba^{II}	0	0.11 ± 0.03	0.50 ± 0.05	0.76 ± 0.05	—
	0.50	0.20 ± 0.04	0.58 ± 0.05	0.85 ± 0.05	—
	1.0	0.27 ± 0.03	0.66 ± 0.04	0.92 ± 0.04	—
	1.5	0.36 ± 0.03	0.74 ± 0.05	1.00 ± 0.05	—

*From Eqn. (26).

The ligand method with a correction for $\Delta\bar{n}$ and the complex method (thermochemistry) without corrections for the solvent effect gave identical stability constants for the NH_3 complexes of Li (Table 9), Cd (Table 10) and Tl^I (Table 10).[54] This fact and results from a number of other investigations[13] indicate that the solvent effect for $M(NH_3)_n^{z+}$, like for complexes of anions,[54,61] are decreased on going from a metal method to a ligand method and a complex method.

It should be emphasised that the correct stepwise stability constants for a number of weak ammonia complexes that are formed in highly concentrated NH_3 solutions are summarised for the first time in Tables 9−11. It is interesting that all stepwise stability constants of Ca−, Sr− and $Ba-NH_3$ complexes (Table 11)

decrease with increasing ionic strength (I) using NH_4ClO_4 according to

$$\lg K_n = \lg K_n^0 + AI, \quad (26)$$

where K_n^0 are the constants at $I = 0$ and A is a constant equal to 0.16.[37,59]

The stability constants of $Ca(NH_3)_n^{2+}$ with $n = 1-4$ that are calculated using Eqn. (26) agree with those found for 2.0 M ammonium nitrate (Table 10) and perchlorate (Table 11). Even before the stability of NH_3 complexes of alkaline earths was studied,[37,59] it had been demonstrated[13] that Eqn. (26) is valid for $Mg-NH_3$ complexes in 0–2.0 M aqueous NH_4NO_3.

Table 12. Constants A and B of Eqns. (26) and (30) for aqueous NH_4NO_3 (I, mol dm^{-3}).

M^{2+}	A	Range of I, mol dm^{-3}	B	Temperature range, °C	Refs.
Ag^+	-0.010	0.5—5.0	0.017	22—30	[1]
Tl^+	-0.065	0.1—4.0	0.004	15—45	[13]
Mg^{2+}	-0.16	0.5—2.0	—	25	[13]
Ca^{2+}	-0.16	0.5—1.5*1	—	25	[59]
Sr^{2+}	-0.16	0.5—1.5*1	—	25	[59]
Ba^{2+}	-0.16	0.5—1.5*1	—	25	[59]
Zn^{2+}	0.095	0.5—5.0	0.008	22—30	[1]
Cd^{2+}	0.070	0.5—5.0	0.008	22—30	[1]
Cu^{2+}	0.080	0.5—5.0	0.013	22—30	[1]
Cu^{2+}	0.080	1.0—6.0	0.013	10—40	[62]
Cu^{2+}	0.080	1.0—6.0	0.027	6.0—9.8	[62]
Fe^{2+}	0.060	2.0—6.0	0.045	15—55	[64]
Mn^{2+}	0.060	1.0—5.0	0.031	10—40	[63]
Ni^{2+}	0.061	0.5—5.0	0.0075	22—30	[1]
Ni^{2+}	—	5.0*2	0.0080	5—50	[72]
Ni^{2+}	—	5.0*2	0.0170	75—125	[72]
Cu^{2+}	0.080	1.0—4.0*3	0.014	5—50	[74]
Cu^{2+}	0.080	1.0—4.0*3	0.031	75—125	[74]
Zn^{2+}	0.10	1.0—4.0*3	0.075	5—50	[74]
Zn^{2+}	0.10	1.0—4.0*3	0.22	75—125	[74]
Cd^{2+}	0.072	1.0—4.0*3	0.078	5—50	[74]
Cd^{2+}	0.072	1.0—4.00*3	0.19	75—125	[74]

*1Values of I in NH_4ClO_4 solutions are given.
*2The same in 5.0 mol kg^{-1} H_2O NH_4NO_3 solutions.
*3Values of I in mol kg^{-1} H_2O in $(NH_4)_2SO_4$ solutions.

It is important that Eqn. (26) is consistent with decreased stability of the alkaline-earth–ammonia complexes as the ionic strength increases whereas this phenomenon is not observed for NH_3 complexes of other metals[1,28,62–64] with the exception of Tl^{I},[22] Pb^{II} (Ref. 65) and Ag^{I},[1] for which Eqn. (26) is applicable with negative A (Table 12).

The influence of $[NH_3]$ on the equilibrium constant for the hydrolysis (K_h) of hexaamminecobalt(III) has been studied.[66–68] It follows the equation

$$Co(NH_3)_6^{3+} + H_2O \rightleftharpoons Co(NH_3)_5OH^{2+} + NH_4^+. \quad (27)$$

The ammonia molecule does not explicitly appear in Eqn. (27). However, it has been established[66–68] that K_h in 1.0 M NH_4NO_3 decreases with increasing $[NH_3]$ ($c_{NH_3} = 2-14$ mol dm^{-3}) at 25.0 °C according to

$$-\lg K_h = 1.32 + 0.070\,(c_{NH_3} - 2.0), \quad (28)$$

which is valid with a correlation coefficient of 0.996. This equation indicates that NH_3 has little influence on equilibrium (27) at $c_{NH_3} \leqslant 2.0$ mol dm^{-3}. However, it decreases the hydrolysis of hexaamminecobalt(III) at $c_{NH_3} > 2.0$ mol dm^{-3}. This fact is important for ammonia hydrometallurgy[4,6] where hexaamminecobalt(III) is salted out by NH_3 from aqueous solutions in order to separate Ni and Cu.

Equation (28) was quantitatively explained[66] by analysing the effect of $[NH_3]$ on the molar activity coefficients of $Co(NH_3)_6^{3+}$, $Co(NH_3)_5OH^{2+}$ and NH_4^+. The dependence of $\log(y_{Co(NH_3)_5OH^{2+}} \cdot y_{NH_4^+}/y_{Co(NH_3)_6^{3+}})$ on C_{NH_3} within error limits agrees with the change of K_h from Eqn. (28).

Changing the concentration of background NH_4NO_3 from 0.25 to 6.0 mol dm^{-3} decreases $\log K_h$ from –1.18 to –2.54 (Table 13).[67] Changing NH_4NO_3 to the sulphate has no noticeable effect on $\log K_h$. Changing the temperature has a substantial effect on equilibrium (27) (Table 13).

Table 13. Effect of ionic strength, nature of background salt and temperature on equilibrium (27).[67]

Background salt	Ionic strength	T, °C	$-\lg K_n$	Background salt	Ionic strength	T, °C	$-\lg K_n$
NH_4NO_3	0.25	25.0	1.18	$(NH_4)_2SO_4$	1.0	25.0	1.33
	0.50	25.0	1.25		2.0	25.0	1.65
	1.0	25.0	1.35		3.0	25.0	1.89
	2.0	25.0	1.69		4.0	25.0	2.50
	3.0	25.0	1.91		1.0	15.0	1.70
	4.0	25.0	2.12		1.0	35.0	0.98
	5.0	25.0	2.33	NH_4NO_3	1.0	15.0	1.68
	6.0	25.0	2.54		1.0	35.0	1.00

It is noteworthy that the effect of NH_3 defined by Eqn. (28) is practically identical for all conditions given in Table 13.[67]

Table 14. Stepwise thermodynamic functions for formation of NH_3 complexes $M(NH_3)_n(H_2O)^{2+}_{N-n}$ in aqueous NH_4NO_3 (2.0 mol dm^{-3}) at 25.0 °C.[51,70]

M^{z+}	n	lg K_n	$-\Delta G_n$, kJ mol^{-1}	$-\Delta H_n$, kJ mol^{-1}	$-\Delta S_n$, J mol^{-1} K^{-1}
Mn^{II}	1	0.96	5.48—0.06	5.2—0.2	−0.6 · 0.9
	2	0.52	2.26—0.06	4.8—0.3	8.5—1.2
	3	0.25	1.43—0.11	5.2—0.5	13—2
	4	−0.02	−0.11—0.06	5.0—0.7	17—3
	5	−0.30	−1.71—0.16	4.8—0.8	22—3
	6	(−0.7)*	(−4.0)*	(5.0)*	(30)*
Fe^{II}	1	1.53	8.73 ± 0.10	8.1 ± 0.2	−2 ± 1
	2	0.98	5.58 ± 0.10	7.9 ± 0.5	8 ± 2
	3	0.56	3.2 ± 0.2	8.0 ± 0.7	16 ± 3
	4	0.19	1.1 ± 0.2	7.5 ± 0.8	22 ± 3
	5	−0.31	−1.8 ± 0.3	7 ± 1	30 ± 4
	6	(−0.7)*	(−4.0)*	(8.0)*	(40)*
Co^{II}	1	2.06 ± 0.02	12.3 ± 0.1	11.8 ± 0.2	−2 ± 1
	2	1.65 ± 0.02	9.4 ± 0.1	12.0 ± 0.2	9 ± 1
	3	1.10 ± 0.03	6.27 ± 0.2	11.9 ± 0.4	19 ± 2
	4	0.75 ± 0.05	4.28 ± 0.3	12.3 ± 0.6	27 ± 3
	5	0.22 ± 0.05	1.25 ± 0.3	11.8 ± 0.9	35 ± 4
	6	−0.6 ± 0.1	−3.4 ± 0.6	11 ± 2	48 ± 9
Ni^{II}	1	2.81 ± 0.02	16.0 ± 0.1	15.9 ± 0.2	−0,3 ± 1,0
	2	2.27 ± 0.02	12.8 ± 0.1	15.0 ± 0.4	7 ± 2
	3	1.77 ± 0.02	10.1 ± 0.1	16.0 ± 0.5	20 ± 2
	4	1.27 ± 0.02	7.25 ± 0.1	15.5 ± 0.5	28 ± 2
	5	0.71 ± 0.03	4.05 ± 0.2	17.4 ± 0.7	41 ± 3
	6	0.15 ± 0.04	0.86 ± 0.2	17 ±2	60 ± 7
Cu^{II}	1	4.24 ± 0.02	24.2 ± 0.1	23.9 ± 0.2	−1 ± 1
	2	3.59 ± 0.02	20.4 ± 0.1	23.6 ± 0.2	17 ± 1
	3	2.97 ± 0.02	17.0 ± 0.2	22.8 ± 0.3	20 ± 2
	4	2.20 ± 0.15	12.5 ± 0.2	22.5 ± 0.3	33 ± 2
	5	−0.6 ± 0.1	−3.4 ± 0.6	16 ±1	42 ± 9
Zn^{II}	1	2.4 ± 0.1	13.7 ± 0.6	12 ± 2	−6 ± 9
	2	2.5 ± 0.1	14.3 ± 0.6	13 ± 3	−4 ± 12
	3	2.6 ± 0.2	15 ± 1	16 ± 3	3 ± 13
	4	2.3 ± 0.2	13 ± 1	20 ± 3	24 ± 13
Cd^{II}	1	2.72 ± 0.02	15.5 ± 0.1	14.6 ± 0.2	−3 ± 1
	2	2.18 ± 0.02	12.4 ± 0.1	14.0 ± 0.2	5 ± 1
	3	1,42 ± 0,02	8.1 ± 0,1	13.9 ± 0.4	19 ± 2
	4	0.96 ± 0.03	5.48 ± 0.2	14.5 ± 0.4	34 ± 2
	5	−0.36 ± 0.3	−2.05 ± 0.2	14.0 ± 0.9	54 ± 4
	6	−1.61 ± 0.6	−9.2 ± 3.0	18 ± 3	91 ± 20
Cu^{I}	1	5.78 ± 0.04	33.0 ± 0.2	34 ± 1	3 ± 4
	2	4.80 ± 0.04	27.4 ± 0.2	35 ± 1	26 ± 4
	3	−1.3 ± 0.2	−7.4 ± 1.1	3 ± 2	35 ± 10
Ag^{I}	1	3.3 ± 0.1	18.8 ± 0.6	22 ± 2	11 ± 9
	2	3.90 ± 0.01	22.4 ± 0.06	35 ± 1	42 ± 5
	3	−1.48 ± 0.15	−8.5 ± 0.9	2 ± 2	35 ± 10
Li^{I}	1	−0.28 ± 0.05	−1.6 ± 0.3	1,0 ± 0.3	9 ± 2
	2	−0.76 ± 0.09	−4.2 ± 0.5	1.1 ± 0.4	18 ± 3
	3	−1.1 ± 0.1	−6,3 ± 0.6	0.9 ± 0.5	24 ± 4
	4	−1.5 ± 0.2	−8,4 ± 1.0	1,2 ± 0.6	32 ± 5
Hg^{II}	1	8.75 ± 0.09	50.0 ± 0.5	51 ± 2	−3 ± 8
	2	8.47 ± 0.05	48.4 ± 0.3	52 ± 1	12 ± 4
	3	1,0 ± 0.1	5.7 ± 0.6	8 ± 1	8 ± 5
	4	0.8 ± 0.1	4.6 ± 0.6	8 ± 1	11 ± 5

*Extrapolated values.

IV. Thermodynamic functions of metal—ammonia complexation

Much handbook data is available for the composition and stability constants of metal—ammonia complexes in aqueous solutions.[8–12] A significant part of this information in addition to data for the enthalpy and entropy changes on formation of $M(NH_3)_n(H_2O)^{z+}_{N-n}$ is contained in tables of critically selected, i.e. recommended values.[10,11] However, many mistakes were found through a comparison of these tables. For example, the critical values for an unknown reason include the incorrect stability constant of the Tl^{I} monoammine complex (Ref. 10, p. 41), which varies with increasing $[NH_3]$ in 2.0 mol dm^{-3} aqueous NH_4NO_3 (Ref. 1, p. 183). Approximate stability constants of Li,[51] Mg and Ca[37] ammonia complexes are found in these same tables.[10] The enthalpy and entropy changes for formation of $Mg(NH_3)_n^{2+}$ that are included in the critical tables are also inaccurate.[10]

Unfortunately, it is difficult to select reliable information for the thermodynamics of complexation in solutions even by analysing in detail recent original results[69] since the experimental and mathematical details are not given in many publications.

The most correct, in our opinion, recent stepwise thermodynamic functions for formation of ammonia complexes of various metals are collected in Table 14. Several of these values appear in the critical tables[10] and have additionally been verified or first determined in our new studies.[14,28,43–51,70]

Requirements set for recommended, preliminary, dubious and incorrect complex stability constants in addition to enthalpy and entropy changes during their formation are clearly formulated in the literature.[71] However, these requirements are not fulfilled and are sometimes meaningless for some systems. For example, accurate enthalpy changes during complexation cannot be determined by two different methods, as previously recommended.[71] The correct values of these functions can only be calculated from thermochemical data. This condition is also partially valid for determining the entropy changes during complexation. It is sometimes meaningless to use two methods to determine the stepwise stability constants if the errors in one of the methods are much less than those of all others. The reasons listed above and several others produced the already noted glaring mistakes in selecting the recommended thermodynamic functions of ammonia complexes.[10] In our opinion, the number of such mistakes was held to the minimal possible in Table 14. Almost all (except Pd^{2+} and Au^{3+}) cations that stepwise form labile and comparatively stable ($\log K_1 \geqslant 1.0$) ammonia complexes are included in Table 14. All these complexes are formed through Eqn. (1) owing to the negative enthalpy component of the Gibbs free energy with (in the first coordination step) or without an entropy barrier.

The stepwise enthalpy changes of $M(NH_3)_n^{z+}$ (Table 14) do not depend on n. The enthalpies for adding a fifth NH_3 to Cu^{II}, a third and fourth to Hg^{II}, and a third to Ag^{I} and Cu^{I} are exceptions. The quantity ΔH_n for $M(NH_3)_n^{z+}$ is considered to be constant for the characteristic coordination number, which is four for Cu^{II} and two for Hg^{II}, Cu^{I} and Ag^{I}.

The entropy changes of almost all stepwise changes (within experimental uncertainty) for dications (Table 14) (except Zn) are well described by

$$\Delta S_n = \Delta S_1 + a(n-1), \qquad (29)$$

where a is a constant in the range 7—11 and ΔS_n is in J mol^{-1} K^{-1}. The constant a increases in the order $Mn^{2+} < Fe^{2+} < Co \approx Ni < Cu \approx Cd$, being 7, 9, 10 and 11, respectively. The entropy barrier

increases (Table 14) as n in $M(NH_3)_n^{2+}$ increases. The quantity $\log K_n$ decreases smoothly as n increases for all complexes listed in Table 14 (except the Zn compounds). This decrease for most systems is close to the statistical one[1] taking into account that $N = 6$.

The cation Zn^{II} exhibits an anomalous ability to complex NH_3. The stepwise stability constants for it within error limits are identical for $n = 1-4$ (Table 14). For this reason, it is practically impossible accurately to determine all of its stepwise thermodynamic functions.

Evidence has appeared[60] that addition of the fifth NH_3 to Cd^{II}, in contrast with the first four molecules, occurs with a much more negative entropy change. However, this assertion has not been verified.

Recently, the formation of ammonia complexes of Cu,[46,62] Ni^{I},[72] Co^{II}(Ref. 73) and Zn and Cd[48,74] in aqueous solutions at temperatures from 5 to 100–125 °C has been studied. Semiquantitative data[75,76] have been obtained for the stability of the ammonia complexes of Ag^{I} up to 160 °C and for Ni up to 180 °C. These polythermal investigations of NH_3 complexation were standardised to 2.0 mol dm^{-3},[46,62,75,76] 2.0 mol kg^{-1} H_2O (Ref. 48) or 5.0 mol kg^{-1} (Refs. 72, 73) aqueous NH_4NO_3. Ammonia complexes of Zn, Cd and Cu^{II} (Ref. 74) were only studied in 0.33, 0.66, 1.0 and 1.33 mol kg^{-1} H_2O solutions of $(NH_4)_2SO_4$, i.e. at constant ionic strengths of 1.0, 2.0, 3.0 and 4.0 at temperatures of 5–125 °C.

In the temperature range 5–125 °C, it was found that the dependence of $\log K_n$ on T^{-1} is nonlinear for the ammonia complexes of Cu^{II},[62] Ni^{II},[72] Co^{II} (Ref. 73) and Zn and Cd.[48] Therefore, the enthalpy changes during NH_3 complexation are variable in this temperature range. The enthalpy and entropy changes for formation of ammonia complexes of Co^{II} and Ni^{II} in aqueous salt solutions at 100 °C are given in Table 15. The experimental errors of the thermodynamic functions (Table 15) are large since these quantities were obtained from the temperature dependence of the stability constants.[77] However, a comparison of the numerical data (Tables 14 and 15) unambiguously indicates that a temperature increase causes the enthalpy component of the Gibbs energy for the NH_3 complexes of Co^{II} and Ni^{II} to become more negative. The entropy becomes more negative with increasing temperature than the enthalpy. Hence, a temperature increase decreases the stepwise stability constants of $M(NH_3)_n^{z+}$ and causes n to decrease. The conclusions about the effect of heat on the formation of ammonia complexes of Cu^{II},[46,62] Ni^{II} (Ref. 72) and Co^{II} (Ref. 73) were validated using ammonia complexes of Zn and Cd in ammonium nitrate[48] and sulphate[74] solutions as examples.

An equation of the type

$$\lg K_n = \lg K_n^0 + Al + B(T - 298), \qquad (30)$$

where K_n and K_n^0 are stepwise stability constants of $M(NH_3)_n^{z+}$ in solutions with ionic strengths I and at $I = 0$, T is the temperature and A and B are constants used in many studies (Table 12) to characterise the effect of the ammonium salt concentrations and the solution temperature on equilibrium (1). The value of A was usually constant up to $I \leqslant 6$. The constant B did not vary in the range 20–50 °C. The constants A and B for complexes of various metals are summarised in Table 12. An analysis of these constants indicates that changing from ammonium nitrate to perchlorate or sulphate or from a molar to a molal concentration scale has little effect on their values. In all systems for which data appear in Table 12, temperature increases substantially increase B.

Table 15. Enthalpy (ΔH_n, kJ mol^{-1}) and entropy (ΔS_n, J mol^{-1} K^{-1}) changes for stepwise formation of $M(NH_3)_n^{2+}$ in 5.0 mol kg^{-1} H_2O NH_4NO_3 solutions at 100 °C.[72,73]

n	$-\Delta H_n$ for M^{2+}		ΔS_n at M^{2+}	
	Co	Ni	Co	Ni
1	26 ± 3	51 ± 8	41 ± 8	100 ± 21
2	22 ± 4	40 ± 10	38 ± 11	78 ± 27
3	20 ± 4	48 ± 8	42 ± 11	110 ± 21
4	25 ± 6	40 ± 10	63 ± 16	97 ± 27
5	26 ± 6	38 ± 10	64 ± 16	—
Aver.	24 ± 3	44 ± 8		

V. Outer-sphere metal–ammonia complexes

Larsson[78–80] first studied the formation of outer-sphere ammonia complexes in aqueous solutions using Co^{III} complexes as examples

$$[Co(NH_3)_6](H_2O)_Q^{3+} + qNH_3 \rightleftharpoons [Co(NH_3)_6](NH_3)_q(H_2O)_{Q-q} + qH_2O, \qquad (31)$$

where $q = 1, 2...Q$ and Q is the limiting coordination number of the second sphere of Co^{III}. The increase of solubility of hexaamminecobalt(III) in 1.0 M aqueous NH_4ClO_4 containing 0–3.5 M NH_3 was used to demonstrate the formation of outer-sphere ammonia complexes with $q = 1$ and 2. The overall stability constants of these complexes at 20 °C are 0.24 ± 0.05 ($q = 1$) and 0.05 ($q = 2$). Only K_1, equal to 0.3 ± 0.2 for an aqueous solution with $I = 0.1$, was determined using electronic spectroscopy.[79]

Equilibria of the type (31) have often been studied using hexaammine, anionopentaammine, *tris*-ethylenediamine, and 2,2′-bipyridyl complexes of Co^{III} and Cr^{III} as examples.[80–85] However, all these investigations were carried out in dilute (usually $\leqslant 1.0$ M) NH_3 solutions. Hydrolysis of the anionopentaammine complexes was not considered. The small outer-sphere interactions enabled formation constants to be calculated only for the monoammine complexes. These often had large uncertainties that have already been discussed in detail.[13]

Wide-ranging studies[13,58,86–91] of the formation of outer-sphere ammonia complexes of Co^{III}, Cr^{III} and Pt^{IV} in solutions with $[NH_3]$ reaching 10–12 mol dm^{-3} have recently been completed. The solubility of the complexes, pH titration, electronic spectroscopy and NMR were used in the investigations. A part of the new data for the logarithms of the stepwise stability constants of the outer-sphere ammonia complexes are summarised in Table 16.

The numerical data (Table 16) indicate that the experimental data obtained by the various experimental methods (solubility, pH titration, electronic spectroscopy and NMR) that differ in principle give practically identical stepwise stability constants for the outer-sphere ammonia complexes of Co^{III}, Cr^{III} and Pt^{IV}. Unfortunately, complexes of this type with other metals have not yet been quantitatively studied. In our opinion, the lack of data on the outer-sphere coordination of NH_3 by Rh^{III}, Ir^{III}, Ir^{IV}, Ru^{II}, Ru^{III} and Os^{III} in aqueous solutions of various inner-sphere complexes of these cations represents a particular gap.

It can be seen from the stepwise stability constants (Table 16) that changing from hexaammine to *tris*-ethylenediamine Co^{III} and Cr^{III} complexes slightly decreases the stability of the outer-sphere ammonia complexes. An analogous effect is observed on replacing Co^{III} by Cr^{III}. These differences in the stepwise stability constants

Table 16. Logarithms of stepwise stability constants (K_q) of outer-sphere NH_3 complexes in aqueous solutions with constant ionic strength (I) at 25.0 °C.[91]

Inner sphere	lg K_q^{*1} at q				I set by salt	Determination method*2
	1	2	3	4		
$Co(NH_3)_6^{3+}$	0.95 ± 0.04	0.59 ± 0.05	0.28 ± 0.06	0.02 ± 0.01	1.0 NH_4ClO_4	S
	1.52 ± 0.06	1.13 ± 0.05	0.82 ± 0.04	0.66 ± 0.10	2.0 NH_4NO_3	S
$Co(en)_3^{3+}$	1.46 ± 0.04	1.00 ± 0.06	0.64 ± 0.06	0.28 ± 0.09	2.0 NH_4Cl	pH
	0.90 ± 0.05	0.50 ± 0.07	0.2 ± 0.1	—	1.0 NH_4Cl	SP
	1.4 ± 0.1	1.0 ± 0.1	0.6 ± 0.2	0.3 ± 0.02	2.0 NH_4Cl	$NMR^{59}Co$
	1.2 ± 0.1	0.8 ± 0.1	0.4 ± 0.1	—	2.0 NH_4Cl	$NMR^{59}Co$*3
$Cr(NH_3)_6^{3+}$	0.8 ± 0.1	0.5 ± 0.1	0.2 ± 0.1	—	1.0 NH_4ClO_4	S
	0.9 ± 0.1	0.5 ± 0.1	0.3 ± 0.2	—	1.0 NH_4ClO_4	SP
	1.3 ± 0.1	1.0 ± 0.2	0.6 ± 0.2	—	2.0 NH_4Cl	SP
$Cr(en)_3^{3+}$	0.7 ± 0.1	0.4 ± 0.1	0.1 ± 0.1	—	1.0 NH_4ClO_4	SP
	0.6 ± 0.1	0.4 ± 0.2	0.1 ± 0.1	—	1.0 NH_4Cl	pH
	1.2 ± 0.2	0.9 ± 0.2	0.5 ± 0.2	—	2.0 NH_4Cl	SP
$Pt(NH_3)_5NH_2^{3+}$	1.2 ± 0.1	0.9 ± 0.2	—	—	1.0 NH_4NO_3	S
$Pt(NH_3)_5NH_2^{3+}$	1.1 ± 0.1	0.8 ± 0.1	—	—	1.0 NH_4NO_3	pH
$Pt(en)_2(enH)^{3+}$	1.0 ± 0.1	0.6 ± 0.2	—	—	1.0 NH_4NO_3	S
	0.9 ± 0.2	0.6 ± 0.2	—	—	1.0 NH_4NO_3	SP
	0.95 ± 0.09	0.52 ± 0.15	—	—	1.0 NH_4NO_3	pH

*1 For Co^{III} and Cr^{III} complexes taking into account $[H_2O]$ in equilibria (31), log K_q are given on a molar scale; for Pt complexes, in mole fractions.

*2 S, solubility; pH, pH titration; SP, spectrophotometry; $NMR^{59}Co$, ^{59}Co chemical shift in NMR spectra.

*3 Ignoring the dependence of the ^{59}Co chemical shift in $Co(en)_3(H_2O)_Q^{3+}$ on $[NH_3]$.

are probably due to a change of the size of the coordination spheres, i.e. the inner spheres. Increasing the crystallographic radii of the inner spheres apparently decreases the stability of the outer-sphere ammonia complexes.

It should be especially emphasised that neither hexaammine- nor *tris*(ethylenediamine)Pt^{IV} in aqueous solutions is capable of forming outer-sphere ammonia complexes. Adding NH_3 to aqueous solutions of these compounds leads firstly to deprotonisation of one of the inner-sphere NH_3 or the ethylenediamine.[86,87] Only the triply charged $Pt(NH_3)_5NH_2^{3+}$ and $Pt(en)_2(enH)^{3+}$ that result from the deprotonisation from mono- and probably diammine outer-sphere complexes. Tri- and tetraammine outer-sphere complexes of Pt^{IV} in aqueous solutions have not been detected, in contrast with Co^{III}.

The cation $Pt(NH_3)_5NH_2^{3+}$ binds NH_3 more strongly than $Pt(en)_2(enH)^{3+}$.[91] It should be emphasised that log K_q for outer-sphere $Pt^{IV}-NH_3$ complexes are greater than those of outer-sphere complexes of Co^{III} and Cr^{III}. It should also be emphasised that log K_q (Table 16) for the last ones were calculated taking into account the molar concentration of H_2O and not the mole fractions as for the other complexes examined in the present review and in the bulk of the handbooks.[8–12]

Therefore, the stability data for outer-sphere ammonia complexes given in Table 16 decrease as a function of the nature of the metal in the order $Pt^{IV} > Co^{III} > Cr^{III}$. It is possible that the asymmetry of the inner sphere is responsible for the higher strength of the outer-sphere ammonia complexes of $Pt(NH_3)_5NH_2^{3+}$ and $Pt(en)_2(enH)^{3+}$. However, we think that this assertion needs more thorough verification.

Existing data for the enthalpy and entropy changes during formation of outer-sphere ammonia complexes and for the influence of ionic strength on log K_q are extremely contradictory. Judging from the new data,[13,87] Eqn. (26), in which A is 0.54 (I = 0.1–1.0) and −0.10 (I = 0.5–6.0), is valid for monoammine complexes of hexaamminecobalt(III) and $Pt(en)_2(enH)^{3+}$. Such ionic strengths are maintained by ammonium perchlorate and nitrate.

VI. Problems and prospects of ammonia hydrometallurgy

The thermodynamics of formation and dissociation of metal–ammonia complexes in aqueous solutions determines the specifics of most industrial processes of ammonia hydrometallurgy, i.e. the leaching, purification, separation and isolation of metals.

Few cations can form labile and comparatively stable (log $K_1 \geqslant 1.0$) ammonia complexes in aqueous solutions.[92] These include such cations as Zn^{II}, Cu^{I}, Cu^{II}, Ni^{II}, Co^{II}, Fe^{II}, Mn^{II}, Cd^{II}, Ag^{I}, Pd^{II} and Hg^{II} (see Table 14). The elements forming these cations occupy a triangle in the expanded periodic table. The corners are occupied by Mn, Cu and Hg. The elements inside this triangle are leached into aqueous salt solutions of ammonia.

Ammonia hydrometallurgy is presently used to produce a large part of the Ni and Co. This is considered to be the most feasible method of treating oxidised Ni ores.[93,94] Such ores contain ~85% of the world reserves of Ni.[95] Ammonia hydrometallurgy has been used to prepare Cu,[96–99] Mn,[100] Zn[101] and Ag.[102,103]

One of the most important advantages of ammonia hydrometallurgy is the high selectivity of extracting Cu, Ni, Co, Zn and Cd over Fe and gangue. Iron extracts into ammonia–ammonium solutions only after reductive leaching as $Fe(NH_3)_n^{2+}$.[14] Under oxidative conditions, which are usually present for ammonia leaching, this cation decomposes into insoluble $Fe_2O_3 \cdot xH_2O$.

However, the ease and completeness of separating precious metals from iron by ammonia leaching entails low (50–70%) Co extraction. This is observed during processing of both sulphide[104] and oxidised[105] ores and secondary raw materials. It was found[106] that Co during ammonia leaching is first dissolved and then sorbed on Fe^{III} hydroxide.

The ammonia complexes of Ni^{II} and Co^{II} exhibit the same capability to be sorbed on Fe^{III} hydroxide. However, the losses of Co due to this are much greater than those of Ni. The principal reason for these differences involves the oxidation of sorbed Co^{II} to Co^{III} and conversion to $Co(NH_3)_5OH^{2+}$ and $Co(NH_3)_6^{3+}$. These are sorbed much more strongly than ammonia complexes of Co^{II}.

Studies of Co sorption[107–111] led to development of a feasible method for releasing Co sorbed by Fe^{III} hydroxide.[112] This method significantly increases Co leaching in ammonia–carbonate solutions, i.e. solves one of the most important problems of ammonia hydrometallurgy.

Contradictory data have been obtained for the optimal ratio of $[NH_3]$ and $[CO_2]$ and the process temperatures for autoclave winning of ores and secondary materials containing Cu, Co and Ni.[93,112–116] Changing the type of starting material probably has the largest effect on optimising these factors. However, careful investigations and computer analysis of the data[112] enabled this problem of ammonia hydrometallurgy to be solved for arsenide–arsenate ores of Cu, Co and Ni by increasing the dissolution of these metals.

Distillation of NH_3 and Co^2,[3,112,117,118] precipitation of the sulphides,[3,93,96] extraction,[7,119–122] sorption[123–126] and electrolysis[3,93,127] have been used to separate and isolate metals from ammonia solutions. For the last 20 years, the capabilities of ammonia hydrometallurgy have sharply increased owing to the incorporation of extraction methods involving new types of specific extractants for Cu, Ni, Co[121] and Ag[128] in addition to the combination of extraction with electrolysis.[120] The latter can produce high-quality Cu, Co and Ni powders if the ammonia complexes are used.[129]

In our country, the ammonia–carbonate scheme was successfully used to process high-magnesium oxidised ores of the Buruktalsk deposit.[95] This same scheme was used to process arsenide–arsenate polymetallic ores at the Tuvakobalt plant,[115,130] where a collective carbonate concentrate containing Cu, Co and Ni was produced. The Tuvakobalt plant is the only installation in our country at which ammonia hydrometallurgy is used on an industrial scale. The poor knowledge of the formation and decomposition processes of $M(NH_3)_n^{z+}$ have prevented all the capabilities of ammonia hydrometallurgy from being used. Our studies and those of our co-workers[13,14,51,62,64,72,73,112,131–138] that have been carried out in the last few years have certainly contributed to a deeper understanding of the chemistry of ammonia hydrometallurgy and have led to operating procedures at the Tuvakobalt plant that are new in principle.

It has been demonstrated[14] that As^V can be separated from Co in ammonia–carbonate solutions using the Fe found in the ore. Thus, the leaching can at first be carried out in a reducing and then in an oxidising solvent. The complex $Fe(NH_3)_n^{2+}$ forms in the reducing solvent. This converts to Fe^{III} in the oxidising solvent. The Fe^{III} then completely precipitates the arsenate. This original and simple method for highly purifying Co from As has not yet been implemented. Furthermore, a method for preparing analytically-pure grade hexaamminecobalt(III) oxalate from the distilled liquid of the Tuvakobalt plant has been found.[13] Synthesis methods of various Co salts and As compounds[112,135,136] have been developed on the basis of process solutions of this plant. The ability to prepare reactive salts of Co, Ni and Cu from the ammonia complexes by avoiding isolation of the free metals has been demonstrated. This represents the great promise of ammonia hydrometallurgy.

The combination of ammonia–carbonate distillation with sulphide precipitation of metals opened the way to produce selective Cu, Ni and Co concentrates instead of their mixture at the Tuvakobalt plant.[112] Thus, Co is practically completely separated from As, i.e. one of the important problems of hydrometallurgy was serendipitously solved.

VII. Conclusion

Stability constants and other thermodynamic functions of the ammonia complexes of many metals in aqueous solutions are experimentally difficult or impossible to determine owing to the relatively weak affinity of the cations for ligands containing nitrogen and to their comparatively high propensity to hydrolyse.[92] However, these cations form complexes suitable for studies in aqueous solutions with a number of other ligands containing nitrogen (N–L) and oxygen (O–L). Glycolate, glycinate, hydroxyacetate, iminodiacetate, maleate, asparaginate, [(2-hydroxyethyl)imino]diacetate, [(2-aminoethyl)imino]diacetate, dihydroxyethylenediacetate and ethylenediamine-*N*,*N*′-diacetate are some of the O–L and N–L ligands for which stability constants have been determined.[8–12] Formation constants of many unstudied monoammine complexes (Table 17) were calculated[92] on the basis of linear dependences of the differences of the logarithms of the first stability constants of complexes with N–L and O–L ligands on the logarithms of the stability constants of the monoammine complexes (assuming the same structure for the compared complexes). The quantities $\log K_1$ for certain of these complexes have recently been experimentally determined.[59,63–65] The calculated and experimentally determined $\log K_1$ (Table 17) are in good agreement. The predicted stability constants of the monoammine complexes are interesting for ammonia hydrometallurgy, for modelling the acid–base behaviour of metals in aqueous solutions,[139] and for a deeper understanding of the chelate[140] and macrocyclic[141] effects.

An analysis of a large body of critically selected stepwise stability constants of the ammonia complexes of Mg, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II} and Cu^{II} in aqueous solutions with ionic strengths 0–6.0 (using ammonium nitrate or sulphate) in the range 5–55 °C and in a number of systems up to 125 °C yielded the empircal equation[14]

$$\lg K_n^0 = (0.751 - 0.0611n)E_2 + 0.597n - 10.468 + aI - b(T - 298), \quad (32)$$

in which $n = 1-6$ (for Cu^{2+} $n = 1-4$) and E_2 are the second ionisation potentials of the analysed metals. This equation enables the stepwise stability constants to be calculated under any of the aforementioned conditions using the constants a and b from Table 12. Reliable information on the mole fraction of $M(NH_3)_n^{z+}$ can be obtained from stability constants calculated using Eqn. (32) under conditions encountered in processes of ammonia hydrometallurgy.[4,6,93]

It is thought (Ref. 121, p. 7) that ammonia processing of ores (at least those containing Cu, Co and Ni) will soon become one of

Table 17. Predicted ($\log K_1^{II}$)[92] and experimental ($\log K_1^0$) stability constants of $M(NH_3)^{z+}$ in aqueous solutions at 25 °C.

M^{z+}	$\lg K_1^n$	$\lg K_1^0$	M^{z+}	$\lg K_1^n$
Ba^{2+}	−0.15	−0.11±0.03 (Ref.59)	Ga^{3+}	4.1
Cr^{2+}	1.51*	–	In^{3+}	4.0
Mn^{2+}	0.8	0.84±0.01 (Ref.63)	La^{3+}	0.2
Fe^{2+}	1.4	1.40±0.02 (Ref.64)	Lu^{3+}	0.7
Fe^{3+}	3.8	–	Sc^{3+}	0.7
Pb^{2+}	1.6	1.66±0.03 (Ref.65)	Y^{3+}	0.4
Bi^{3+}	5.0	–	UO_2^{2+}	2.0

* $\log K_1^{II}$ are calculated using Eqn. (32).[14]

the most important methods of hydrometallurgy. In our opinion, such thinking is hardly justified. However, the appearance of many studies[143–151] with novel approaches attests to the promise of ammonia hydrometallurgy for solving problems connected with processing of secondary raw materials and oxidised ores. Unfortunately, the unique capabilities of ammonia hydrometallurgy are not fully utilised although 60% of Ni is obtained using ammonia solutions in hydrometallurgy.[143]

Construction of "M^{z+} activity–pH" graphs, where M^{z+} is Co, Ni, Cu,[152] Mn[153] and Fe,[154] enabled the mechanism of many processes of ammonia hydrometallurgy in aqueous salt solutions to be unravelled and a number of improvements to be made in them. The separation of metals through the production of two phases in solutions of ammonium sulphate and carbonate after their saturation with NH_3, i.e. in effect "extraction without an extractant",[150] the leaching of metals by NH_3 in sulphite–carbonate solutions,[149] the widespread use of Caron processes[144] in combination with extraction[121,148] and the application of autoclaves[143] may become very fruitful directions for future development of ammonia hydrometallurgy.

References

1. J Bjerrum *Metal Ammine Formation in Aqueous Solution. Theory of the Reversible Step Reactions* (Russian translation), Izd. Inostr. Lit., Moscow, 1961, 308 pp
2. M H Caron *J. Met.*, 1950, **188**(1) 67
3. M H Caron *J. Met.*, 1950, **188**(1) 91
4. V I Smirnov, I F Khudyakov, V I Deev *Izvlechenie Kobalta iz Mednykh i Nikelevykh Rud i Kontsentratov* (Extraction of Cobalt from Copper and Nickel Ores and Concentrates), Metallurgiya, Moscow, 1970, 256 pp
5. V M Valyashko, K G Kravchuk *Termodinamicheskie Svoistva Rastvorov pri Ekstremal'nykh Usloviyakh* (Thermodynamic Properties of Solutions Under Extreme Conditions) (Edited by G A Krestov, et al.), Ivanovo Chemical Technology Institute, Ivanovo, 1986, p. 3
6. V F Borbat, I Yu Leshch *Novye Protsessy v Metallurgii Nikelya i Kobal'ta* (New Processes in Nickel and Cobalt Metallurgy), Metallurgiya, Moscow, 1976, 360 pp
7. G M Ritcey, A W Ashbrook *Process Metallurgy, Vol. 1; Solvent Extraction: Principles and Applications to Process Metallurgy, Part 2* (Russian translation), Metallurgiya, Moscow, 1983, 480 pp
8. L G Sillen, A E Martell *Stability Constants of Metal-ion Complexes*, Chemical Society, London, 1964, p. 754
9. E Högfeldt *Stability Constants of Metal-ion Complexes*, Pergamon Press, Oxford, New York, Toronto, et al., 1982, 330 pp
10. R M Smith, A E Martell *Critical Stability Constants. Inorganic Complexes*, Plenum Press, New York, London, 1976, Vol. 4, p. 257
11. R M Smith, A E Martell *Critical Stability Constants. 1st Supplement*, Plenum Press, New York, London, 1982, Vol. 5, p. 604
12. R M Smith, A E Martell *Critical Stability Constants. Vol. 6. Sec. Suppl.*, Plenum Publ. Corp., 1989, p. 662
13. T V Stupko, Candidate's Dissertation in Chemical Sciences, Inst. Chem. Nonaqueous Solutions, USSR Acad. Sci., Ivanovo, 1990, 151 pp
14. L K Novikov, Candidate's Dissertation in Chemical Sciences, Kranoyarsk, Inst. Chem. Chem.-Metall. Processes, Siberian Branch, USSR Acad. Sci., 1991, 109 pp
15. H L Silcock (Editor) *Solubilities of Inorganic and Organic Compounds*, Pergamon Press, 1979, Vol. 3, Part 3
16. K S Pitzer *Activity Coefficient in Electrolyte Solutions* (Edited by R M Pytkowicz), CRC Press, Boca Raton, Florida, 1979, Vol. 1, p. 209
17. K S Pitzer *Rev. Mineral*, 1987, **17** 97
18. S L Clegg, P Brimblecombe *J. Phys. Chem.*, 1989, **93** 7237
19. T V Stupko, I D Isaev, G L Pashkov, V E Mironov *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamike i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1991, p. 183
20. T V Stupko, L K Novikov, G L Pashkov, V E Mironov *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamike i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1991, p. 282
21. T V Stupko, I D Isaev, G L Pashkov, V E Mironov *Zh. Neorg. Khim.*, 1990, **35**(12) 3086 [English translation in *Russ. J. Inorg. Chem.*, 1990(12)]
22. T V Stupko, I D Isaev, G L Pashkov, V E Mironov *O Solyakh Talliya(I) v Vodnykh Rastvorakh Ammiaka* [On Thallium(I) Salts in Aqueous Ammonia], Moscow, 1991, 10 pp; Manuscript deposited VINITI, 19th April, 1991, No. 1703–B91
23. T V Stupko, I D Isaev, V E Mironov *Koord. Khim.*, 1989, **13** 1467
24. T V Stupko, I D Isaev, V E Mironov *Zh. Neorg. Khim.*, 1989, **34**(7) 1765 [English translation in *Russ. J. Inorg. Chem.*, 1989(7)]
25. T V Stupko, I D Isaev, V E Mironov *Koord. Khim.*, 1990, **16** 555
26. V E Mironov, I D Isaev *Tezisy Dokladov XII Vses. Chugaevskoe Soveshch. po Khimii Kompleksnykh Soedinenii* (Abstracts of Papers of the Twelfth Chugaevskii Conference on the Chemistry of Complex Compounds),Krasnoyarsk,1987, p. 9
27. E N Kozlova, I D Isaev, G L Pashkov, V E Mironov *Vliyanie Ammiaka na Rastvorimost Solei Geksaamminkobal'ta(III) i Perkhloratov Kaliya, Rubidiya i Tseziya v Vodnykh Rastvorakh* [Effect of Ammonia on the Solubility of Hexaamminecobalt(III) Salts and Potassium, Rubidium and Caesium Perchlorates in Aqueous Solutions], Moscow, 1991, 6 pp; Manuscript deposited VINITI, 19th April, 1991, No. 1701–B91
28. L K Novikov, I D Isaev, G L Pashkov, V E Mironov *Konstanty Ustoichivosti Ammiachnykh Kompleksov Margantsa(II), Zheleza(II), Kobal'ta(II), Nikelya(II) i Palladiya(II) v Vodnykh Rastvorakh* (Stability Constants of Ammonia Complexes of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II} and Pd^{II} in Aqueous Solutions), Moscow, 1990, 25 pp; Manuscript deposited VINITI, 1st August, 1990, No. 4352–B90
29. L K Novikov, T V Stupko, et al. *Zh. Prikl. Khim.*, 1991, **64** 771
30. V E Mironov, G L Pashkov, T V Stupko, et al. *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamike i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1991, p. 295
31. M Maeda, G Nakagawa, C Biederman *J.Phys. Chem.*, 1983, **87**

32. K Szabo, I Nagupal, I Fabian *Talanta*, 1983, **30** 801
33. I D Isaev, T V Stupko, M A Shat'ko, V E Mironov *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1989, **32**(6) 22
34. M Maeda, O Hisada, K Ito *Denki Kagaku*, 1987, **55** 778
35. M Maeda *J. Phys. Chem.*, 1986, **90** 1134
36. M Maeda, M Hayashi, S Ikeda, et al. *Bull. Chem. Soc. Jpn.*, 1987, **60** 2047
37. T G Padar, L K Novikov, et al. *Zh. Neorg. Khim.*, 1991, **36**(6) 1514 [English translation in *Russ. J. Inorg. Chem.*, 1991(6)]
38. O Horvath, K L Stevenson *Inorg. Chem.*, 1989, **28** 2548
39. L K Novikov, S V Drozdov, et al. *Zh. Prikl. Khim.*, 1991, **64** 904
40. L K Novikov, T V Stupko, et al. *Zh. Neorg. Khim.*, 1991, **36**(4) 983 [English translation in *Russ. J. Inorg. Chem.*, 1991(4)]
41. I D Isaev, L K Novikov, T V Stupko, et al. *Tezisy Dokladov I Vses. Konf. "Zhidkofaznye Materialy"* (Abstracts of Papers of the First All-Union Conference "Liquid-Phase Materials"), Ivanovo, 1990, p. 51
42. I D Isaev, S V Tverdokhlebov, V E Mironov, et al. *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamkie i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1991, p. 290
43. V E Mironov, G L Pashkov, T G Padar, et al. *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamkie i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1991, p. 288
44. V E Mironov, G L Pashkov, T V Stupko, et al. *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamkie i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1991, p. 297
45. V G Troyanova, T V Stupko, S V Drozdov, et al. *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamkie i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1991, p. 289
46. S V Tverdokhlebov V G Troyanova, T V Stupko, et al. *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamkie i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1991, p. 279
47. V E Mironov, G L Pashkov, T V Stupko *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamkie i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1991, p. 298
48. S V Drozdov, L K Novikov, G L Pashkov, V E Mironov *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamkie i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1991, p. 293
49. L K Novikov, T G Padar, T V Stupko, et al. *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamkie i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1991, p. 283
50. L K Novikov, T G Padar, T V Stupko, et al. *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamkie i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1991, p. 283
51. V E Mironov, G L Pashkov, T V Stupko, et al. *Termodynamika Obrazovaniya Ammiachnykh Kompleksov Litiya, Medi(I), Serebra(I) i Rtuti(II) v Vodnykh Rastvorakh* (Thermodynamics of Formation of Ammonia Complexes of Li, Cu^{I}, Ag^{I} and Hg^{II} in Aqueous Solutions), Moscow, 1991, 10 pp; Manuscript deposited VINITI, 18th April, 1991, No. 1667–B91
52. S N Rizvi, R A Heidmann *J. Chem. Eng. Data*, 1987, **32** 183
53. V N Prorokov, G G Arutyunyan, G A Krestov *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1989, **32**(10) 58
54. V E Mironov, V A Fedorov, I D Isaev *Usp. Khim.*, 1991, **60**(6) 1128 [English translation in *Russ. Chem. Rev.*, 1991(6)]
55. V E Mironov, I D Isaev, G L Pashkov *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamkie i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1991, p. 17
56. H Optaki *Advances in Solution Chemistry*, Pleunum Press, New York, London, 1980, p. 67
57. T V Stupko, I D Isaev, V E Mironov *Zh. Neorg. Khim.*, 1989, **34**(9) 2441 [English translation in *Russ. J. Inorg. Chem.*, 1989(9)]
58. T V Stupko, I D Isaev, V E Mironov *Obrazovanie Ammiakatov Tris-(etilendiamin)kobal'ta(III) v Vodnykh Rastvorakh* [Formation of Ammonia Complexes of *Tris*(ethylenediamine)-cobalt(III) in Aqueous Solutions], Cherkassy, 1986, 12 pp; Manuscript deposited ONIITEKhIM, 16th April, 1986, No. 489-khp-Dep.
59. T G Padar, T V Stupko, I D Isaev, et al. *Zh. Neorg. Khim.*, 1990, **35**(6) 1626 [English translation in *Russ. J. Inorg. Chem.*, 1990(6)]
60. V Yu Frolov, Author's Abstract of a Candidate's Dissertation in Chemical Sciences, Ivanovo Chemical Technology Institute, Ivanovo, 1988, 14 pp
61. G P Gordienko, Candidate's Dissertation in Chemical Sciences, Sib. Technol. Inst., Krasnoyarsk, 1985, 166 pp
62. I D Isaev, S V Tverdokhlebov, et al. *Zh. Neorg. Khim.*, 1990, **35**(8) 2034 [English translation in *Russ. J. Inorg. Chem.*, 1990(8)]
63. I D Isaev, S V Tverdokhlebov, L K Novikov, et al. *Zh. Neorg. Khim.*, 1990, **35**(8) 2043 [English translation in *Russ. J. Inorg. Chem.*, 1990(8)]
64. I D Isaev, S V Tverdokhlebov, L K Novikov, et al. *Zh. Neorg. Khim.*, 1990, **35**(8) 2039 [English translation in *Russ. J. Inorg. Chem.*, 1990(8)]
65. I D Isaev, T V Stupko, E N Kozlova, et al. *Vzaimodeistvie Svintsa(II) s Ammiakom v Vodnykh Rastvorakh Nitrata Ammoniya* (Reaction of Pb^{II} with Ammonia in Aqueous Ammonium Nitrate), Moscow, 1991, 10 pp; Manuscript deposited VINITI, 19th April, 1991, No. 1705–B91
66. I D Isaev, S V Tverdokhlebov, et al. *Zh. Neorg. Khim.*, 1990, **35**(11) 2855 [English translation in *Russ. J. Inorg. Chem.*, 1990(11)]
67. I D Isaev, S V Tverdokhlebov, V E Mironov, et al. *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamkie i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1991, p. 290

68. I D Isaev, S V Tverdokhlebov, T V Stupko, et al. *Tezisy Dokladov XVII Vses. Chugaevskoe Soveshch. po Khimii Kompleksnykh Soedinenii* (Abstracts of Papers of the Seventeenth All-Union Chugaevskii Conference on the Chemistry of Complex Compounds), Minsk, 1990, p. 176
69. V E Mironov, I D Isaev *Konstanty Ustoichivosti Vneshnesfernykh Kompleksov Metallov v Rastvorakh* (Stability Constants of Outer-sphere Metal Complexes in Solutions), Izd. Krasnoyar. Univ., Krasnoyarsk, 1983, 366 pp.
70. V E Mironov, G L Pashkov, V G Troyanova, et al. *Termodinamika Obrazovaniya Ammiachnykh Kompleksov Margantsa(II), Zheleza(II), Kobal'ta(II), Nikelya(II), Medi(II), Tsinka(II) i Kadmiya(II) v Vodnykh Rastvorakh* (Thermodynamics of Formation of Ammonia Complexes of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} in Aqueous Solutions), Moscow, 1991, 9 pp; Manuscript deposited VINITI, 18th April, 1991, No. 1608–B91
71. *Rekomendatsii Mezhdunarodnogo Soyuza Chistoi i Prikladnoi Khimii* (Critical Reviews of the Stability of the Stability Constants of Metal Complexes, Recommendations of the International Union of Pure and Applied Chemistry) *Zh. Fiz. Khim.*, 1976, **50**(10) 2723 [English translation in *Russ. J. Phys. Chem.*, 1976(10)]
72. I D Isaev, S V Tverdokhlebov, et al. *Zh. Prikl. Khim.*, 1990, **60** 2177
73. I D Isaev, S V Tverdokhlebov, et al. *Zh. Neorg. Khim.*, 1990, **35**(12) 3149 [English translation in *Russ. J. Inorg. Chem.*, 1990(12)]
74. V E Mironov, G L Pashkov, S V Drozdov, et al. *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamkie i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1991, p. 291
75. B Kozlowcka, F Letowski, J Niemiec *Rocz. Chem.*, 1969, **43** 1597
76. F Letowski *Rocz. Chem.*, 1970, **44** 1665
77. K B Yatsimirskii *Zh. Neorg. Khim.*, 1957, **2**(3) 491 [English translation in *Russ. J. Inorg. Chem.*, 1957(3)]
78. R Larsson *Acta Chem. Scand.*, 1957, **11** 1405
79. R Larsson *Acta Chem. Scand.*, 1958, **12** 708
80. V E Mironov, I D Isaev *Vvedenie v Khimiyu Vneshnesfernykh Kompleksnykh Soedinenii Metallov v Rastvorakh* (Introduction to the Chemsitry of Outer-sphere Metal Complexes in Solutions), Izd. Krasnoyar. Univ., Krasnoyarsk, 1986, 312 pp
81. V E Mironov, A K Pyartman *Usp. Khim.*, 1983, **52**(9) 1468 [English translation in *Russ. Chem. Rev.*, 1983(9)]
82. V E Mironov, T E Shnurova, Yu B Solov'ev, N K Blagovestov *Zh. Neorg. Khim.*, 1982, **27**(2) 215 [English translation in *Russ. J. Inorg. Chem.*, 1982(2)]
83. V E Mironov, T E Shnurova, N K Blagovestov, Yu B Solov'ev *Zh. Neorg. Khim.*, 1982, **27**(2) 213 [English translation in *Russ. J. Inorg. Chem.*, 1982(2)]
84. I D Isaev, T V Stupko, et al. *Zh. Neorg. Khim.*, 1984, **29**(4) 690 [English translation in *Russ. J. Inorg. Chem.*, 1984(4)]
85. N P Kolobov, V E Mironov, K N Lyubomirova, A K Pyartman *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1981, **24** 803
86. I M Khon, Candidate's Dissertation in Chemical Sciences, Sib. Technol. Inst., Krasnoyarsk, 1987, 198 pp
87. I M Khon, I D Isaev, V E Mironov *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1987, **30**(4) 123
88. T V Stupko, I D Isaev, V E Mironov *Vzaimodeistvie Ammiaka s Geksaamminkobal'tom v Vodnykh Rastvorakh* (Reaction of Ammonia with Hexaamminecobalt in Aqueous Solutions), Cherkassy, 1986, 12 pp; Manuscript deposited ONIITEKhIM, No. 488-khp-86
89. T V Stupko, I D Isaev, G L Pashkov, V E Mironov *Tezisy Dokladov IV Vses. Soveshch. "Problemy Sol'vatatsii i Kompleksoobrazovaniya v Rastvorakh"* (Abstracts of Papers of the Fourth All-Union Conf. "Problems of Solvation and Complex Formation in Solutions"), Ivnaovo, 1989, p. 88
90. T V Stupko, I D Isaev, V E Mironov *Koord. Khim.*, 1990, **16** 555
91. V E Mironov, G L Pashkov, T V Stupko, et al. *Stupenchatye Konstanty Ustoichivosti Ammiachnykh Kompleksov Kobal'ta(II), Khroma(III) i Platiy(IV)* (Stepwise Stability Constants of Ammonia Complexes of Co^{II}, Cr^{III} and Pt^{IV}), Moscow, 1991, 8 pp; Manuscript deposited VINITI, 19th April, 1991, No. 1702–B91
92. F Mulla, F Marsicano, B S Nakani, R D Hancock *Inorg. Chem.*, 1985, **24** 3076
93. I V Khudyakov, A I Tikhonov, V I Deev, S S Naboichenko *Metallurgiya Medi, Nikelya i Kobal'ta* (Metallurgy of Copper, Nickel and Cobalt), Metallurgiya, Moscow, 1977, Vol. 2, 264 pp
94. V V Mechev, G P Gigantov, E N Mazurchuk, et al. *Gidrometallurgiya v Protsessakh Proizvodstva Tyazhelykh Tsvetnykh Metallov* (Hydrometallurgy in Production Processes of Heavy Nonferrous Metals), TsNIIEITsM, Moscow, 1985, No. 3, 48 pp
95. G F Rezvanov, M V Klement'ev, N F Ivnaov *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1985, No. 3(4) 14
96. S S Naboichenko, V I Smirnov *Gidrometallurgiya Medi* (Copper Hydrometallurgy), Metallurgiya, Moscow, 1974, 272 pp
97. M C Kuhn, N Arbiter, H Kling *Can. Min. Metall. Bull.*, February 1974, 62
98. D M Agers *1st Annual Meeting Canadian Hydrometallurgist, Can. Min. Metall. Bull.*, Proc. Ottawa: Mines Branch, 1971, p. 34
99. D Pearson *Reclam. Ind. Rev.*, July 1972, 10
100. S S Pyzhov, A D Besser, S N Makarova *Polychenie Tsvetnykh Metallov iz Glubokovodnykh Konkretsii za Rubezhom* (Production of Nonferrous Metals from Foreign Deep-sea Deposits), TsNIIEITsM, Moscow, 1985, No. 2, 66 pp
101. S S Naboichenko *Avtoklavnaya Pererabotka Medno–Tsinkovykh Kontsentratov* (Autoclave Processing of Copper–Zinc Concentrates), Metallurgiya, Moscow, 1989, 113 pp
102. I N Maslenitskii, P V Chugaev *Metallurgiya Blagorodnykh Metallov* (Metallurgy of Noble Metals), Metallurgiya, Moscow, 1972, 367 pp
103. I I Smirnov, G N Shivrin, S V Greiver, L V Ivanov *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, 1982, (4) 61
104. R Stuffer, S Lindsay *Can. Min. Metall. Bull.*, 1967, (6) 669
105. G I Kraskovskii, I Yu Leshch *Nauchnye Trudy* (Scientific Works), Gipronikel, Leningrad, 1969, Vols. 39–40, p. 43
106. S I Sobol *Byull. Tsvetn. Metall.*, 1963, (11) 26
107. K Osseo-Asare *Hydrometallurgical Process Fundamentals* (Edited by R G Bautista), Plenum Press, New York, London, 1984, p. 227

108. K Osseo-Asare *Ammonia Hydrometallurgy Thermodynamics of Dissolution and Adsorption Phenomena in Oxide Systems*, Univ. California, Berkeley, 1975
109. K Osseo-Asare, D W Fuerstenau *Int. J. Miner. Process.*, 1980, **8** 117
110. K Osseo-Asare, D W Fuerstenau *Int. J. Miner. Process.*, 1979, **5** 85
111. J E De Graaf *Hydrometallurgy*, 1980, **5** 255
112. V G Troyanova, Candidate's Dissertation in Technical Sciences, KITsM, Krasnoyarsk, 1992
113. V N Moiseeva, N S Barinov, L A Balitskii, L V Silina *Izvlechenie Tsennykh Metallov iz Otrabotannykh Geterogennykh Katalizatorov* (Extraction of Previous Metals from Spent Heterogeneous Catalysts), Informational Review, TsNIITEneftekhim, Seriya Neftekhimiya i Neftepererabotka, 1988, No. 5, 60 pp
114. F A Fopwand, V N Mackiv *J. Met.*, 1955, **7** 457
115. G F Rezvanov, Yu I Kaletnikov, et al. *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, 1984, (9) 32
116. J E De Graaf, *Hydrometallurgy*, 1979, **5** 47
117. G N Shivrin, I I Smirnov, L V Ivnaova, I V Il'chak *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, 1984, (1) 50
118. G I Kraskovskii, Yu N Leshch, L M Frumina, Ya M Shneerson *Tsvetn. Met. (Moscow)*, 1970, (3) 32
119. V I Bukin, A M Reznik, S V Vasil'echeniko, N A Frant *Sovremennoe Sostoyanie i Perspektivy Ispol'zovaniya Protsessov Ekstraktsii pri Ammiachnoi Pererabotke Nikel-Kobal'tsoderzhashchego Syr'ya* (Current State and Prospects of Using Extraction Processes for Ammonia Processing of Nickel–Cobalt-containing Ores), TsNIIEITsM, Moscow, 1983, 58 pp
120. V Kumar, R K Jana, B D Pandey, et al. *Trans. Indian Inst. Met.*, 1987, **40** 64
121. F I Shekiliev, Candidate's Dissertation in Chemical Sciences, Inst. Inorg. Phys. Chem., Baku, 1986, 175 pp
122. K Kh Kunyasheva, M D Navtanovich *Primenenie Ekstraktsionnykh Protsessov v Gidrometallurgii Kobal'ta* (Application of Extraction Processes in Cobalt Hydrometallurgy), TsNIIEITsM, Moscow, 1982, 46 pp
123. L E Slobtsev, N D Ekhanina *Tsvetn. Met. (Moscow)*, 1979, (5) 23
124. L E Slobtsev *Tsvetn. Met. (Moscow)*, 1983, (11) 11
125. V F Borbat, I Yu Leshch *Primenenie Geterogennogo Ionnogo Obmena v Metallurgii* (Application of Heterogeneous Ion Exchange in Metallurgy), TsNIIEITsM, Moscow, 1979, 44 pp
126. USSR P. No. 616312; *Byull. Izobret.*, 1978, (27)
127. V D Kheifets, T V Gran *Elektrolyz Nikelya* (Electrolysis of Nickel), Metallurgiya, Moscow, 1975, 333 pp
128. E I Lys'kova, Candidate's Dissertation in Chemical Sciences, Lomonosov Inst. Fine Chem. Technol., Moscow, 1985, 118 pp
129. E P Tkachenko, N F Ivnaova *Avtogennye i Avtoklavnye Protsessy v Medno–Nikelevom Proizvodstve* (Autogenic and Autoclave Processes in Copper–Nickel Production), Gipronikel, Leningrad, 1987, p. 115
130. G N Dobrokhotov *Sovremennye Problemy Tsvetnoi Metallurgii* (Current Problems of Nonferrous Metallurgy), Plekhanov Leningr. Technol. Inst., Leningrad, 1975, p. 68
131. I D Isaev, V D Matveev, T V Stupko, A I Gidalevich *Tezisy Dokladov XVI Vses. Chugaevskoe Soveshch. po Khimii Kompleksnykh Soedinenii* (Abstracts of Papers of the Sixteenth All-Union Chugaevskii Conf. on the Chemistry of Complex Compounds), Krasnoyarsk, 1987, p. 92
132. USSR P. No. 1580820; *Byull. Izobret.*, 1991
133. L K Novikov, L I Kiprin, I D Isaev, et al. *Zh. Prikl. Khim.*, 1990, **63** 799
134. I D Isaev, V G Troyanova, V P Saprunov, et al. *Tezisy Dokladov Region. Konf. Sibiri i Dal'nego Vostoka "Perspektivy Razvitiya Malotonazhnoi Khimii "* (Abstracts of Papers of the Regional Conf. of Siberia and the Far East "Prospects of Development of Low-tonnage Chemistry"), Krasnoyarsk, 1989, p. 16
135. I D Isaev, A V Gidalevich, I V Statsenko, et al. *Tezisy Dokladov Region. Konf. Sibiri i Dal'nego Vostoka "Perspektivy Razvitiya Malotonazhnoi Khimii "* (Abstracts of Papers of the Regional Conf. of Siberia and the Far East "Prospects of Development of Low-tonnage Chemistry"), Krasnoyarsk, 1989, p. 17
136. I D Isaev, V G Troyanova, V P Saprunov, et al. *Tezisy Dokladov Region. Konf. Sibiri i Dal'nego Vostoka "Perspektivy Razvitiya Malotonazhnoi Khimii'* (Abstracts of Papers of the Regional Conf. of Siberia and the Far East "Prospects of Development of Low-tonnage Chemistry"), Krasnoyarsk, 1989, p. 18
137. I D Isaev, G L Pashkov, et al. *Zh. Neorg. Khim.*, 1990, **35**(10) 2688 [English translation in *Russ. J. Inorg. Chem.*, 1990(10)]
138. I D Isaev, D G Pashkov, S V Drozdov, et al. *Tezisy Dokladov XIII Vses. Konf. po Khimii, Termodinamkie i Kalorimetrii* (Abstracts of Papers of the Thirteenth All-Union Conference on Chemistry, Thermodynamics and Calorimetry), Krasnoyarsk, 1990, p. 277
139. R D Hancock, F Marsiano *Inorg. Chem.*, 1980, **19** 2709
140. R D Hancock, F Marsicano *J. Chem. Soc. Dalton Trans.*, 1976, 1096
141. V J Thom, J C A Boeyens, G J McDougall, R D Hancock *J. Am. Chem. Soc.*, 1984, **106** 3198
142. A M Sukhotin (Editor) *Spravochnik po Elektrokhimii* (Handbook of Electrochemistry), Khimiya, Leningrad, 1981, 488 pp
143. V P Saprunov *Tsvetn. Met. (Moscow)*, 1988, (12) 13
144. J M Van Put, W de Bruijin, W P C Duyvesteyn *Prod. and Process. Fine Part: Proc. Intern. Symp. Montreal*, New York, 1988, p. 691
145. R K Jana, D D Akerkar *Hydrometallurgy*, 1989, **22** 363
146. USSR P. No. 1486534; *Byull. Izobret.*, 1989, (22)
147. USSR P. No. 1581762; *Byull. Izobret.*, 1990, (28)
148. G L Paskov, I D Isaev, V E Mironov *Intern. Solv. Estr. Conf. Kyoto*, 1990, 213
149. Naganori Rokukawa *J. Min. Mater. Proc. Inst. Jpn.*, 1990, **106** 205
150. T V Stupko, V M Leont'ev, I D Isaev, et al. *Tezisy Dokladov I Vses. Konf. "Zhidkofaznye Materialy"* (Abstracts of Papers of the First All-Union Conf. "Liquid-phase Materials"), Ivanovo, 1990, p. 182
151. C Kailash Nathsarma, V R Bhaskara Sarma Pervla *Erzmetall.*, 1989, **42** 259
152. K Osseo-Asara, D W Fuerstenau *Fundamental Aspects Hydrometallurgical Processes. Al. C.H. Symposium Series.* 74(173) (Edited by T M Chapman, et al.) Institution of Mining Metallurgy, 1978, p. 1
153. K Osseo-Asara *Trans. Inst. Min. Metall. Sect. C*, 1981, **90** 152
154. K Osseo-Asara *Trans. Inst. Min. Metall. Sect. C*, 1981, **90** 159

Received 22nd October 1991

Translated from *Uspekhi Khimii* **61** 1748–1775 (1992) U.D.C. 541.11

Conductometry of electrolyte solutions

L P Safonova, A M Kolker
Institute of Chemistry of Nonaqueous Solutions, Russian Academy of Sciences, Ivanovo

ABSTRACT. A review is given of the theories of the electrical conductance of electrolyte solutions of different ionic strengths and concentations, and of the models of ion association. An analysis is made of the methods for mathematical processing of experimental conductometric data. An account is provided of various theories describing the dependence of the limiting value of the ionic electrical conductance on the properties of the solute and solvent

The bibliography contains 115 references.

Contents

I. Introduction 959
II. Dependence of the electrical conductance on concentration 959
III. Limiting molar ionic electrical conductance 966
IV. Parameters of ion association 970

Introduction

Conductometry, i.e. measurement of the electrical conductivity, is used widely in fundamental investigations of electrolyte solutions and in tackling many applied problems. It is one of the simplest and yet most accurate methods for the investigation and analysis of substances. It makes it possible to carry out studies over a wide range of temperatures, pressures, and electrolyte solutions (from strongly dilute to melts), and this can be done using practically any solvent. The fact that the electrical conductance of electrolyte solutions can be measured with a high degree of precision at low concentrations makes it possible to apply quite rigorous theories and model representations which can give information on the state of particles in a solution, their effective size, mobility, and association. Combination of the conductometric method with determination of the transport (transference) numbers makes it possible to find the transport characteristics of individual ions without making any assumptions.

Many monographs and reviews have been published on the conductometric method.[1–9] However, the majority of them concentrate on the theory and practice of the determination of the resistance of electrolyte solutions and less prominence is given to theoretical interpretations of the results obtained. The present review therefore stresses a theoretical description of the dependence of the electrical conductance of an electrolyte solution on the concentration, temperature, pressure, and properties of the solvent, and also the problems encountered in mathematical processing of the experimental results, particularly selection of a suitable algorithm needed to find the parameters of interest.

II. Dependence of the electrical conductance on concentration

The existing theory of electrolyte solutions is incapable of describing, from a unified point of view, the concentration dependence of the electrical conductance of an electrolyte solution throughout the full range of compositions. There are different approaches to the interpretation of the electrical conductance of strong and weak electrolytes.

1. Dilute solutions of strong electrolytes

The theoretical problems of interpretation of the concentration dependence of the electrical conductance of dilute electrolyte solutions were considered by Onsager. The Onsager theory is based on the hypothesis that the limiting velocity v of an ion is determined by the action of three forces: 1) an external force eE; 2) average interionic forces F_r responsible for what is known as the relaxation effect; 3) forces of electrophoretic drag F_e which arise because the motion of a central ion does not occur in an immobile medium but in a medium moving in the opposite direction to this ion:

$$v = v_e + u_0(eE + F_r),$$

where v_e is the velocity of an ion under the action of the electrophoretic forces F_e; u_0 is the mobility of an ion at infinite dilution

$$u_0 = \frac{v_0}{E} = \lambda^0/zeF,$$

F is the Faraday; z is the charge of the ion.

The forces exerting the drag on an ion can be defined in terms of the distribution functions f and the pair interaction potentials U. Therefore, the theoretical problem of the electrical conductance reduces to estimating these quantities. The pair distribution functions f_{ij} and f_{ji} can be calculated by solving the continuity equation

$$-\frac{\partial}{\partial t} f_{ji} = \nabla_P f_{ij} \vec{V}_{ij} + \nabla_0 f_{ji} \vec{V}_{ji} = -\frac{\partial}{\partial t} f_{ji},$$

where $\vec{V}_{ij}$ and $\vec{V}_{ij}$ are the velocities of two particles; ∇_P and ∇_Q are the nabla operators acting in the vicinity of the points P and Q.

The continuity equation given in Ref. 10 contains the distribution functions for two, three, and four particles. A similar equation was obtained by Ebeling[11,12] directly from the Liouville equation.[13] This makes it possible to find the relationship between the Onsager approach to the problem of the electrical conductance from the point of view of diffusion and using an approach based on statistical physics.

When weak electric fields are applied to a system (as in measurements of the electrical conductance) the velocity of a charged particle can be regarded as directly proportional to the electric field E. This assumption makes it possible to solve the continuity equation by introducing the following approximations:

$$f_{ij} = f_{ij}^0 + f_{ij}',$$

$$\psi_i = \overset{0}{\psi_i} + \psi_i,$$

where ψ_i is the potential of the mean force; f^0 and ψ^0 are quantities corresponding to the equilibrium state; f' and ψ' are the contributions due to the presence of an external electric field. The relationship between the pair distribution function and the mean-force potential can be described by the Poisson–Boltzmann equation. The selection of U_{ij} and f_{ij}^0, and of the appropriate boundary conditions, for solving the continuity equation, together with the different degrees of precision of this solution are the reasons for the multiplicity of equations proposed for the concentration dependence of the molar electrical conductance, such as the equations proposed by Pitts,[14] Fuoss, Onsager and Skinner,[15] Fuoss and Hsia,[16] Quint and Viallard,[17] Chen,[18] etc.

In their most general form all the equations describing the electrical conductance on the basis of the Debye–Hückel–Onsager theory can be represented as follows:

$$\lambda = \lambda^0\left(1 + \frac{\Delta X}{X}\right) + \Delta\lambda_e, \qquad (1)$$

where $\Delta X/X$ and $\Delta\lambda_e$ represent, respectively, the relaxation and electrophoretic contributions to the electrical conductivity. We can find the interpretation of $\Delta X/X$ and $\Delta\lambda_e$ in the original papers.

One primitive model considers the behaviour of a solid charged unpolarisable sphere of radius a_j in a continuum whose permittivity ε and viscosity η are the same as in the bulk of the solvent. When equations based on this primitive model are used, it is assumed initially that an electrolyte is fully dissociated and association is considered only at the second stage using the law of mass action. Dielectric saturation is ignored and the bulk value of ε is used right up to $r = a_{ij} = R$ (which is the distance of closest approach of the ions).

Expanding $\Delta X/X$ and $\Delta\lambda_e$ as a series in terms of the concentration, we can reduce Eqn. (1) to

$$\lambda = \lambda^0 - Sc^{1/2} + Ec\ln c + I_1 c + I_2 c^{3/2} + \ldots, \qquad (2)$$

where $S = \alpha^0\lambda^0 + \beta^0$, (2a)

$$E' = E_1'\lambda^0 - hE_2', \qquad (2b)$$

$$I_1 = \sigma_1\lambda^0 + \sigma_2, \qquad (2c)$$

$$I_2 = \sigma_3\lambda^0 + \sigma_4. \qquad (2d)$$

The coefficients S and E' can be calculated from the following relationships:

$$\alpha^0 = \frac{kab}{3\sqrt{c}}\frac{1/2}{1+1/\sqrt{2}} = \frac{kab}{3\sqrt{c}}0.29282 = 8.2042\cdot10^5(\varepsilon T)^{-3/2}, \qquad (3a)$$

$$\beta^0 = \frac{Fe|z|}{3\pi\eta C}\frac{k}{\sqrt{c}} = 82.4907\eta^{-1}(\varepsilon T)^{-1/2}, \qquad (3b)$$

$$E_1' = \frac{\beta^2k^2}{24c} = 2.9437\cdot10^{12}(\varepsilon T)^{-3}, \qquad (3c)$$

$$E_2' = \frac{\beta k\beta^0}{16\sqrt{c}} = 43.3244\eta^{-1}(\varepsilon T)^{-2}, \qquad (3d)$$

$$\beta = ab = (ze)^2/\varepsilon kT = 1.6712\cdot10^{-3}(\varepsilon T)^{-1}, \qquad (3e)$$

$$\frac{k}{\sqrt{c}} = \left[\frac{8\pi N(ze)^2}{1000\varepsilon Tk}\right]^{1/2} = 5.02956\cdot10^9(\varepsilon T)^{-1/2}, \qquad (3f)$$

$$\sigma_1 = 2E_1'\Delta_1,\ \sigma_2 = 2E_2'\Delta_2,\ \sigma_3 = -ZE_1'\Delta_3,\ \sigma_4 = -ZE_4'\Delta_4,\ Z = \frac{k\beta}{\sqrt{c}}.$$

The expressions for $\Delta_1 - \Delta_4$ and the values of h obtained using various theories are as follows:

Pitt (Ref.14)

$$\Delta_1 = \frac{2}{b} + 1.7718 + \ln Z,$$

$$\Delta_2 = \frac{8}{b} + 0.01387 - \ln Z,$$

$$\Delta_3 = \frac{5.1716}{b} + 6.2928,$$

$$\Delta_4 = \frac{16}{\beta_0 b} + 1.25248,$$

$h = 1$;

Quint–Viallard (Ref.17)

$$\Delta_1 = \frac{2}{b} + \frac{2}{b^2} - \frac{1}{b^3} + 0.9074 + \ln Z,$$

$$\Delta_2 = \frac{1}{b^2} + \frac{35}{6b} - 1.6764 - 2\ln Z,$$

$$\Delta_3 = \frac{3.8048}{b^2} + \frac{4.4296}{b} + 1.6094,$$

$$\Delta_4 = \frac{34}{3b} - 3.7844,$$

$h = 2$;

Fuoss–Hsia (Ref.16)

$$\Delta_1 = \frac{2}{b} + \frac{2}{b^2} - \frac{1}{b^3} + 0.9074 + \ln Z,$$

$$\Delta_2 = \frac{22}{3b} + 0.01422 - \ln Z,$$

$$\Delta_3 = \frac{3.8284}{b^2} + \frac{4.4748}{b} + 0.6094,$$

$$\Delta_4 = \frac{4}{3b^2} + \frac{16.3906}{b} + 2.6883 - 1.2922b + \frac{\beta_0}{Z\lambda^0}\left(\frac{4}{3} - 2.2194\right),$$

$h = 1$;

Fuoss–Justice–Chen (Ref.19)

$$\Delta_1 = \frac{2}{b} + \frac{2}{b^2} - \frac{1}{b^3} + 0.9074 + \ln Z,$$

$$\Delta_2 = \frac{1}{b^2} + \frac{35}{3b} - 1.0344 - 2\ln Z,$$

$$\Delta_3 = \frac{3.8284}{b^2} + \frac{4.4748}{b} + 0.6094,$$

$$\Delta_4 = \frac{34}{3b} - \frac{2}{b^2} - 1.3693,$$

$h = 2$.

The role of the ion–ion interactions increases on increase in the concentration and on reduction in the permittivity. This leads to association of ions, which lowers the electrical conductance of electrolyte solutions. Then Eqns. (1) and (2) assume the following form if we allow for the degree of dissociation of an electrolyte α:

$$\lambda = \alpha\left[\lambda^0\left(1 + \frac{\Delta X}{X}\right) + \lambda_e\right], \qquad (4)$$

$$\lambda = \alpha\left[\lambda^0 - S(\alpha c)^{1/2} + E'\alpha c\ln(\alpha c) + I_1\alpha c + I_2(\alpha c)^{3/2} + \ldots\right]. \qquad (5)$$

However, investigators are interested more in finding not the degree of dissociation of an electrolyte but the association constant:

$$K_a = \frac{(1-\alpha)\gamma_a}{\alpha^2 c\gamma_\pm^2}, \qquad (6)$$

where γ_a is the activity coefficient of ion pairs (usually assumed to be unity): $\gamma_\pm$ is the mean-ion activity coefficient, which is usually calculated employing the Debye–Hückel theory

$$\gamma_\pm = \exp\left(-\frac{qk}{1+kR}\right), \tag{7}$$

where $q = \beta/2$.

It should be pointed out that when Eqns. (4) and (5) are used the coefficient should be interpreted bearing in mind that $c_i = \alpha c$. Fuoss[20] showed that when the series of parameters λ^0, K_a, and R are used, the values of the electrical conductance calculated from Eqn. (1) are always less than those obtained using the exact expression (2), and they agree satisfactorily with one another only up to $kR \approx 0.2$.

Justice[21] suggested making the parameter I_2 in Eqn. (5) a fitting variable and thus allowing for all the inaccuracies associated with calculation of the exponential integral. It should be pointed out that the validity of Eqns. (4) and (5) is limied to the maximum electrolyte concentration corresponding to the condition $kq \approx 0.5$.

Fuoss[22] and Lee and Wheaton[23–25] proposed equations describing the electrical conductivity on the basis of a more realistic physical picture than the primitive model described above. In the model of Lee and Wheaton it is assumed that an ion is surrounded by three different regions: in the first ($a_j < r < R_j'$, where a_j is the crystallographic radius of an ion) the solvent molecules are oriented in the electric field of an ion and the dielectric saturation effect applies; in the second region ($R_j' < r < R_j$, where R_j is the radius of the Gurney co-sphere of an ion[26]) the structure of the solvent is still modified by the field of the ion and the permittivity is not equal to the bulk value; in the third region ($r > R_j$) the properties of the solvent are the same as in the bulk.

In this way Lee and Wheaton allow for the dielectric saturation effects and also include the concept of ion association right from the beginning. This leads to the following equation

$$\lambda = \alpha\left\{\lambda_0\left[1 + C_1\beta k + C_2(\beta k)^2 + C_3(\beta k)^3\right] - \frac{\rho k}{1+t}\left[1 + C_4\beta k + C_5(\beta k)^2 + \frac{t}{12}\right]\right\}, \tag{8}$$

$$C_1 = \frac{\left(1-1/\sqrt{2}\right)\left[1\left(1+1/\sqrt{2}\right)t/2\right]}{3k_0k_3},$$

$$C_2 = -\frac{1}{24k_0k_3}\left[\frac{2\left[Tr\left(2+1/\sqrt{2}\right)t + 1/2\right]}{k_0} + \frac{H_1(t)}{k_3}\right],$$

$$H_1(t) = \left\{-1.91421356 - 1.35355t - 0.198t^2 - 3k_3Tr\left[\left(1+1/\sqrt{2}\right)t\right] + 4k_3k_2Tr(t) - k_1k_2Tr\left(t/\sqrt{2}\right)\right\},$$

$$C_3 = \frac{\left(3+1/\sqrt{2}\right)Tr\left[\left(3+1/\sqrt{2}\right)t\right]}{36k_0k_3\left(1+1/\sqrt{2}\right)},$$

$$C_4 = -\left\{H_2(t)/2 + \frac{\left[1+\left(1+1/\sqrt{2}\right)t/2\right]}{6k_0k_3\left(1+1/\sqrt{2}\right)}\right\},$$

$$H_2(t) = \left\{-Tr(t)/2 + \frac{3Tr\left[\left(1+1/\sqrt{2}\right)t\right]}{4k_3} + 0.436886 - 0.3085t\right\},$$

$$t = kR,\ \rho R = \beta_0(\alpha c)^{1/2},$$
$$k_0 = 1 + t,\ k_1 = 1 + t + t^2/2,\ k_2 = 1 + t/\sqrt{2},\ k_3 = 1 + t/\sqrt{2} + t^2/4.$$

In Ref. 27 the coefficients $C_1 - C_5$ are represented as a series in terms of t and $\ln t$, which is accurate to within 0.01% in the range $0.005 < t < 0.7$:

$$C_1 = -0.09753 + 0.08185t - 0.044144t^2 + 0.01114t^3,$$
$$C_2 = 0.11798 - 0.18737t + 0.09052t^2 - 0.02393t^3 + 0.08358\ln t,$$
$$C_3 = -0.19454 + 0.39764t - 0.37557t^2 + 0.25118t^3 - 0.07843t^4 - 0.10296\ln t,$$
$$C_4 = -0.04724 + 0.06445t - 0.07419t^2 + 0.01784t^3 + 0.12428\ln t + 0.09863t\ln t,$$
$$C_5 = 0.84185 - 0.90051t + 0.07809t^2 - 0.05333t^3 + 0.50097\ln t + 0.45252t\ln t.$$

In Refs. 22 and 28 Fuoss proposed an equation describing formation of ion pairs separated by solvent and those in direct contact:

$$M^+ + A^- \underline{K}_1 (M^+ \ldots A^-) \underline{K}_2 M^+A^-.$$

If α_1 is the fraction of free ions and α_2 is the fraction of contact ion pairs, the equation describing the electrical conductivity becomes

$$\lambda = [1 - \alpha_2(1-\alpha_1)]\left[\lambda^0\left(1 + \frac{\Delta X}{X}\right) + \Delta\lambda_e\right]. \tag{9}$$

Formation of ion pairs separated by solvent is described by the expression

$$K_1 = \frac{(1-\alpha_1)(1-\alpha_2)}{c\alpha_1^2\gamma_\pm^2},$$

whereas the formation of contact pairs from solvent-separated ones is given by

$$K_2 = \frac{\alpha_2}{(1-\alpha_2)}.$$

The association constant is

$$K_a = K_1(1 + K_2).$$

According to Fuoss, all the short-range effects can be represented by a single parameter LK_2 which can be calculated from

$$K_2 = \exp\left[\frac{\Delta E_s}{kT}\right],$$

where ΔE_s is the difference between the energies of the ions in the states $r = R$ and $r = a$.

An analysis of the experimental results using Eqn. (9) reduces to solution of the equaiton $\lambda = \lambda(c, \lambda^0, R, E_s)$. The value of K_1 is calculated on condition that R is known using the Fuoss equation for the association constant [Eqn. (28)].

Ebeling and his colleagues[29–31] used nonequilibrium thermodynamics and statistical physics in combination with the mean-sphere approximation and the law of mass action to propose the following equation for the electrical conductance:

$$\lambda = a\lambda^0[1 + S^{Rel}(t, b) + S^{Int}(t, b) + S^{Ext}(t, b)], \tag{10}$$

where

$$S^{Rel}(t,b)=\frac{1}{6\sqrt{2}tb}\left[2-2b+\sqrt{2}tb-t^2\right]-\frac{\exp(-\sqrt{2}t)}{6\sqrt{2}tb}\left[2-2b+\right.$$

$$\left.+\ 2\sqrt{2}t-\sqrt{2}tb+t^2\right]+\frac{1}{3(1+\Gamma R)^2}\left[\left(1+\frac{t}{\sqrt{2}}-b\right)\exp\left(\frac{2-\sqrt{2}t}{2}t\right)\right.$$

$$\left.-1-t+b\right]-\frac{t^2}{12b}\left(\frac{1}{3}+b\right)(1+t-b)\exp(-t),$$

$$\frac{S^{Int}(t,b)}{h}=\frac{tb}{2}E_i\left(-\frac{t}{\sqrt{2}}\right)\left[\left(\sqrt{2}-t\right)\exp\left(\frac{t}{\sqrt{2}}\right)-\left(\sqrt{2}+t\right)\exp\left(-\frac{t}{\sqrt{2}}\right)\right]-$$

$$-\frac{\exp(-\sqrt{2}t)}{t}\left[\left(\sqrt{2}+2t+\frac{t^2}{\sqrt{2}}\right)b-2\sqrt{2}-4t-\sqrt{2}t^2\right]+$$

$$+\frac{\sqrt{2}}{t}\left[\left(1-\frac{t^2}{2}\right)b-2+t^2\right]+\frac{2b^2\exp(t)}{(1+\Gamma R)^2}\left[\frac{t^2}{2}E_i\left(-\frac{t^2}{\sqrt{2}}\right)-t^2E_i(-t)+\right.$$

$$\left.+\left(1-\frac{2}{b}+\frac{t}{\sqrt{2}}-\frac{\sqrt{2}t}{b}\right)\exp\left(-\frac{t}{\sqrt{2}}\right)-\left(1-\frac{2}{b}+t\frac{2t}{b}\right)\exp(-t)\right]-t^2\left(\frac{1}{3}+b\right)$$

$$\left[\frac{t^2b}{2}E_i(-t)-\left(1-\frac{b}{2}+t-\frac{tb}{2}\right)\exp(-t)\right],$$

$$S^{Ext}(t,b)=-\frac{8tbh}{(1+\Gamma R)^2},$$

$$\Gamma R=\frac{1}{2}(1+2t)^{1/2}-\frac{1}{2},$$

$$h=\frac{\varepsilon kTN}{3\pi\eta\lambda^0\cdot 9\cdot 10^{11}}=\frac{H}{\lambda^0},\ H=1.226956\cdot 10^{-6}\varepsilon T/\eta;$$

$$E_i(-x)=0.577215665+\ln(-x)+\sum_{n=1}^{\infty}\frac{(-x)^n}{n\cdot n!},\quad b=\frac{\beta}{R}.$$

In calculation of the degree of association in this approach the constant is obtained from the Ebeling equation[32]

$$K_a=8\cdot 10^3\pi R^3N\sum_{m=2}^{\infty}\frac{q^{2m}}{(2m)!(2m-3)},\qquad(11)$$

and the mean ion activity coefficient is found from the mean-sphere approximation

$$\ln\gamma_{\pm}=-\frac{10^3t}{4\pi cNR^3}\left[1+2t-(1+2t)^{1/2}\right].\qquad(12)$$

It should be stressed that all the equations given above describe only the concentration dependences of the electrical conductance of symmetric electrolytes.

The choice of one or another theoretical equation for the calculation λ^0, K_a, and R is quite subjective. The majority of these equations give the same value of λ^0, but the values of K_a agree only to within an order of magnitude. Therefore, a correct analysis of the dependences of the conductometric parameters on the temperature of an electrolyte solution and on the ion radius should involve treatment of all the experimental data on the basis of the same equation.

In obtaining reliable values of λ^0 and K_a it is important not only to select in a reasoned manner a theoretical equation, but also a mathematical approach for its solution.

All the equations given above can be represented in the form

$$\lambda_i=f(c_i,\varepsilon,\eta,T,|z|,\lambda^0,K_a,R),$$

where λ_i is the molar electrical conductance of a symmetric electrolyte with the ion charge z and a molar concentration c_i; ε is the permittivity and η is the viscosity of the solvent at a temperature T; λ^0, K_a, and R are the unknown parameters.

The task then reduces to finding such λ^0, K_a, and R that the values of the electrical conductance calculated on the basis of theoretical equations are as close as possible to the experimental data. We shall bear in mind that an analysis of the experimental data using the above equations for the electrical conductance may be carried out only within a certain range of concentrations. Since these equations are based on the concept of formation of ion pairs, the upper limit to the concentration range is limited by that value at which associates of higher orders can be ignored. An approximate estimate of the upper concentration limit can be obtained (ignoring the degree of dissociation) using the relationship $kq \approx 0.5$,[10] which corresponds to $c_{max} = 1.4 \times 10^{-4}(\varepsilon T)^3$. The lower limit of the concentration is set by the experimental capabilities and it is usually $(0.5-1.0) \times 10^{-4}$ mol/dm^3. Moreover, it is important to stress that the values of upper and lower limits of the concentration range should differ by at least one order of magnitude.

From the mathematical point of view the finding of the unknown parameters (λ^0, K_a, R) reduces to solution of a redundant system of nonlinear equations: a) the concentration dependence of the electrical conductance [Eqns (5), (8), and (10), or others]; b) the law of mass action [Eqn. (6)]; c) the expressions for the mean ion activity coefficient [Eqns. (7) and (12)]. The solution of a system of such equations is then obtained by minimisation of the function

$$\sigma(\lambda)=\sum_{i=1}^{n}\omega_i(\lambda_i^{calc}-\lambda_i^{exp})^2/(n-m-1),\qquad(13)$$

where n is the number of experimental points; m is the number of unknown parameters; ω_i is a weighting coefficient.

The coefficient ω_i is usually assumed to be 1, but since the precision of the experimental data decreases on reduction in the solute concentration, Kay et al.[33] suggested using a weighting coefficient proportional to $c^{1/2}$. A more rigorous way of calculating the weighting coefficient for each point involves using the overall r.m.s. deviation $\omega = 1/\sigma_\lambda$.

The solution of the problem of minimisation of the function $\delta(\lambda)$ is most frequently tackled employing the nonlinear least squares method, which is not difficult when using modern computers.

One should point out however that calculations carried out by the method of least squares require the knowledge of the derivatives with respect to the parameters being sought. Analytic differentiation of such complex dependences as the equations describing the electrical conductance meets with certain difficulties. Therefore, these derivatives are frequently found by numerical differentiation but this increases the computer time. However, the derivatives with respect to λ^0 and K_a can be obtained employing the approximate equation

$$\left(\frac{\partial\lambda}{\partial K_a}\right)=-\frac{\gamma_{\pm}^2c\alpha}{(1+K_a\gamma_{\pm}^2c\alpha)}.$$

If we employ the Lee–Wheaton equation, then

$$\left(\frac{\partial\lambda}{\partial K_a}\right)\simeq\frac{E_s c\alpha}{\left(1+K_a\gamma_\pm^2 c\alpha\right)},$$

where $E_s c\alpha$ corresponds to the expression in the first square brackets of Eqn. (8).

If we use an equation of the (5) type, then

$$\left(\frac{\partial\lambda}{\partial K_a}\right)\simeq\frac{1-\alpha^0(\alpha c)^{1/2}+E_1'(\alpha c)\ln(\alpha c)+\sigma_1\alpha c+\sigma_3(\alpha c)^{3/2}}{\left(1+K_a\gamma_\pm^2 c\alpha\right)}.$$

If we employ Eqn. (1), then

$$\left(\frac{\partial\lambda}{\partial K_a}\right)\simeq\alpha\left(1+\frac{\Delta X}{X}\right).$$

We can in this way obtain derivatives with respect to λ^0 also from Eqn. (10).

In tackling such problems one may encounter cases when the derivatives with respect to K_a and R have opposite signs. Consequently, the search for a minimum may continue indefinitely. Moreover, in the case of some of the theoretical equations for the electrical conductance [Fuoss–Hsia or Fuoss (1975)] the dependence $\sigma(\lambda) = f(R)$ may have two minima in the range of physically reasonable values of R,[10] which in the opinion of these authors is related to the internal inconsistency of the equations themselves. Moreover, in solutions of specific problems it is frequently found that there is a wide range of values of K_a and R which yield practically the same value of $\sigma(\lambda)$. Difficulties are therefore encountered in an analysis of the data for such systems.

Such difficulties can be avoided either by varying R, as suggested by Fuoss[22] [then the values of λ^0, K_a, and R are selected on the basis of an analysis of the dependence $\sigma(\lambda) = f(R)$] or by reducing the problem to one with two parameters by selecting a physically reasonable value of R (it is usually the Bjerrum distance, equal to the sum of the crystallographic radii of ions and the diameter of the solvent molecule). It should be pointed out that many of these shortcomings are avoided also if the problem of minimisation is solved by the direct search method (Powell, deformed polyhedron, Rosenbrock, coordinate descent, and other methods[34]). However, in contrast to the least-squares method, the direct search methods do not yield the standard errors of the required parameters.

In tackling the task of minimisation of the function (13) we need to know the initial approximations in respect of the required parameters. In the case of λ^0 we can find this quantity approximately by: a) graphical extrapolation of the function $\lambda_i = f(c^{1/2})$ to zero concentration; b) from the Walden rule ($\lambda^0\eta_0$ = const); c) from the Fuoss–Kraus[35] or Shedlovsky[36,37] equations. The first approximation for K_a can be selected either from the Ostwald equation (if we specify λ^0 first), which gives

$$K_a=\frac{(\lambda^0)^2(1-\lambda/\lambda^0)}{c\lambda^2},$$

or from the Fuoss–Kraus and Shedlovsky equations. The first approximation for R is frequently taken to be the sum of the crystallographic radii of the ions.

We can find also other approaches to the solution of the electrical conductance equation in the published literature. They are based on a selection of an analytic relationship between K_a and R, so that the task of minimisation can be reduced to a two-parameter problem. However, we must then bear in mind that the selection should be based on the same model which underlies the theoretical equation for the electrical conductance. This approach is employed most frequently in Refs. 12, 29, 30, and 38 when the relationship between K_a and R is of the type given by Eqn. (11). On the other hand, in using the Lee–Wheaton equation the best grounded is the expression for K_a which allows for the short-range effects [Eqn. (32)]. Therefore, the number of the unknown parameters does not decrease and one of them (K_a) is simply replaced with another (U^*).

An approach developed by Justice[21] is also very popular and it involves solving equations of the (5) type. The fitting parameters are then λ^0, K_a, and I_2; the values of I_1 and $\gamma_\pm$ are then calculated on the assumption that R is equal to the Bjerrum distance (q).

The descriptions of the algorithms and the computer programs used in an analysis of conductometric data can be found in a number of original papers.[25,27,39–41]

All the equations given above describe the concentration dependence of the electrical conductance of symmetric electrolytes. In the case of solutions of asymmetric electrolytes (particularly asociated solutions) or mixtures of electrolytes the number of suggested equations is considerably less, although such solutions are encountered more frequently (they include natural water, solutions used in various technologies, etc.). The first attempts to provide a quantitative description of the electrical conductance of asymmetric electrolytes were made by Righellato and Davis,[42] and by Fuoss and Edelson.[43] The equations derived for associated 2–1 (or 1–2) electrolytes are based on the limiting Onsager law and on a number of other assumptions. Subsequently, Quint and Vialliard,[17] Murphy and Cohen,[44] and Chen[18] used the framework of the primitive model to calculate more accurately the contributions of the electrophoretic and relaxation effects to the electrical conductance of solutions of asymmetric and mixed electrolytes. The final equations for the electrical conductance can be found in the original papers. We shall give here the equation of Lee and Wheaton[23,24] obtained on the basis of their new model of a solution containing s types of charged particles:

$$\lambda(j)=\lambda^0(j)\left\{1+z_j\sum_{p=2}^{s}\chi_j^p\sum_{\nu=1}^{s}t_\nu\chi_\nu^p\left[A_\nu^p(t)(\beta k)+B_\nu^p(t)(\beta k)^2+C_\nu^p(t)(\beta k)^3\right]\right\}-$$

$$-\frac{|z_j|\beta^0 c_j^{1/2}}{(1+t)}\left[1+V_j^{(1)}(t)(\beta k)+V_j^{(2)}(t)(\beta k)^2+\Pi_j^{(3)}t/6\right], \qquad (14)$$

$$\lambda=\sum_{j=1}^{s}\left(|z_j|c_j\lambda(j)/c\right).$$

An interpretation of the coefficients in Eqn. (14) can be found in Ref. 24. However, even such a complex equation is only approximate and the expressions for C_ν^p and $V_j^{(2)}$ are incomplete.

The simplest case in which we can apply Eqn. (14) is that of 2–1 electrolytes in which ions are associated in accordance with the scheme

$$K^{2+} + A^- \leftrightarrow KA^+.$$

In the case of such a solution we find that Eqn. (14) contains five unknown parameters: the values of the limiting electrical conductance of three ions, K_a, and R. In the presence of such a

large number of unknown parameters the solution of the above equation becomes multivalued. It was shown in Refs. 27 and 45 how the number of unknown parameters can be reduced to three and in Ref. 41 an algorithm was given for calculation of the parameters of complex associated and asymmetric electrolytes.

We described above the most frequently employed theoretical approaches to the description of the electrical conductance of dilute solutions of weakly associated electrolytes. We must stress again that all these equations give practically the same value of λ^0, whereas the values of K_a are in agreement only to within an order of magnitude. As far as the parameter a (or r) is concerned, we can *a priori* expect its value to depend on the nature of the equation, because it is governed by the selection of the boundary conditions and the mathematical approximations adopted in the treatment. Moreover, we cannot expect the parameter R to have a real physical meaning if we use equations based on the primitive model because the model itself does not describe reality. Therefore, an experimentalist should bear in mind that the conductometric parameters can be compared only if they are obtained on the baiss of the same equation.

Several statistical-mechanical theories have been put forward recently and they make it possible to describe quite rigorously the transport properties of electrolyte solutions right down to the average concentrations.[30,46–49] However, the equations derived using such theories are too complex for practical use.

2. Concentrated electrolyte solutions

There is as yet no theoretically rigorous equation for the description of the electrical conductance of concentrated electrolyte solutions. Therefore, the transport properties of such solutions are being interpreted on the basis of three main approaches: 1) 'generalisation' of equations for dilute solutions by introduction of empirical terms; 2) use of the equations applicable to molten salts; 3) description of the experimental data by purely empirical or semi-empirical equations. Among the first group of equations tl most widely used is the equation of Robinson and Stokes[1], corrected for the viscosity and allowing for the influence of the relaxation effect, as estimated by Falkenhagen et al.:[51]

$$\lambda = \left(\lambda^0 - \frac{\beta^0\sqrt{c}}{1+ka}\right)\left(1 - \frac{\alpha^0 F\sqrt{c}}{1+ka}\right)\frac{\eta_0}{\eta}, \qquad (15)$$

where $F = [\exp(0.2929ka) - 1]/(0.2929ka)$.

Equation (15) describes satisfactorily the electrical conductance of some salts in water up to concentrations of 5–6 mol/litre,[52,53] whereas in the case of other salts there is no satisfactory agreement[54] even at concentrations less than 1 mol/litre. In all probability this equation works well as long as the ratio η/η_0 is small.[55] Otherwise in calculation of the coefficient β^0 [Eqn. (3b)] it is necessary to use the viscosity of a solution with a given concentration. The authors of Ref. 56 suggest extending the validity of Eqn. (15) by calculating the coefficients employing both the viscosity of a solution and its permittivity (so that the quantities β^0, α^0, and k become concentration-dependent). If calculations based on Eqn. (15) give values of the electrical conductance lower than those found experimentally, this is evidence of ion association and can be allowed for by introducing the degree of dissociation α into Eqn. (15):

$$\lambda = \alpha\lambda'(\alpha c),$$

where $\lambda'(\alpha c)$ is given by Eqn. (15) with the actual ion concentration amounting to αc; α can be found by successive approximation or by applying the law of mass action. Equation (10) allows us to describe the concentration dependence of the electrical conductance of strong (concentrated) electrolytes in water right up to a concentration of $\sim$1 M.

Among the second group of equations one should mention particularly the Vogel–Fulcher–Tammann equation describing the temperature dependence of the transport properties of glass-forming liquids and molten salts:

$$x(T) = AT^{-1/2}\exp\left(-\frac{B}{T-T_0}\right),$$

where A and B are constants, and T_0 is the ideal or theoretical vitrification temperature.

If the solubility of an electrolyte is sufficiently high, the isotherms of the composition dependence of the electrical conductance have a maximum whose position and amplitude are governed by the nature of the components of the solution. These dependences are described most frequently employing the empirical equation of Castel and Amis:[57]

$$\frac{\kappa}{\kappa_{max}} = \left(\frac{m}{m_{max}}\right)^2 \exp\left[b(m-m_{max})^2 - \frac{a}{m_{max}}(m-m_{max})\right],$$

where κ_{max} and m_{max} are the values of the electrical conductivity and of the concentration corresponding to an extremum of the dependence $\lambda = f(m)$: a and b are empirical coefficients.

Among the empirical dependences describing the electrical conductivity of electrolyte solutions, we may mention a correlation equation which allows for a whole range of the solvent and salt parameters:[53]

$$\varkappa = A\exp\{aDN(r_+)^2 + bAN/(r_-)^2 + \mu[c/(r_+)^2 + d/(r-)^2] + e/\varepsilon\}/\eta_0 V_m^{1/3}, \qquad (16)$$

where A is the coefficient of proportionality; DN is the donor number; AN is the acceptor number; μ is the dipole moment of the solvent; a, b, c, d, e are empirical coefficients.

In some cases Eqn. (16) simplifies. For example, in the case of 1 M solutions of lithium salts in aprotic solvents we can ignore the solvation of the ions, so that Eqn. (16) becomes[53]

$$\varkappa = A\exp(aDN + b\mu + c/\varepsilon)/\eta_0 V_m^{1/3},$$

where the empirical coefficients are constant for a given salt in all the aprotic solvents.

In Ref. 58 it is assumed that the electrolytic properties of electrolyte solutions are governed by the processes of association in an electrolyte

$$nA \xleftrightarrow{K_1} A_n \xleftrightarrow{K_2} aA_j^{b+} + bB_j^{a-} \qquad (17)$$

and by its interaction with the solvent

$$mA + lS \leftrightarrow A_mS_l \leftrightarrow cA^{d+} + dB^{c-}, \qquad (18)$$

which leads to equations for the iostherms of the electrical conductance of binary liquid electrolyte–solvent systems.

In the case of noninteracting systems, we have

$$\kappa\eta = \kappa_A\eta_A\left(\frac{V_A}{V}\right)^{n/2} X^{n/2}, \qquad (19)$$

where κ_A, η_A, and V_A are the electrical conductivity, viscosity, and molar volume of the electrolyte, respectively; V is the molar volume of the solution; n is the stoichiometric equilibrium coefficient of Eqn. (17); X_A is the molar fraction of the electrolyte.

The electrical conductivity of interacting systems is then

$$\kappa\eta = \kappa_A\eta_A\left(\frac{V_A}{V}\right)^{n/2} X^{n/2} + Q_i\frac{X_A^{m/2}(1-X_A)^{1/2}}{V^{(m+l)/2}}, \qquad (20)$$

where Q_i is a constant governed by the values of the equilibrium constants K_3 and K_4 of Eqn. (18), by the molar volume, and by the conductance of the resultant electrolyte A_mS_l (Q_i is found from experimental data by calculation); m and l are the stoichiometric equilibrium coefficients of Eqn. (18).

Equations (19) and (20) are derived subject to the following assumptions: 1) the mechanism of the flow of the current involves ion migration; 2) the mobility of ions is inversely proportional to the viscosity of the solution; 3) the equilibrium constants in Eqns. (17) and (18) are smaller than 1×10^{-3}; 4) the ratio of the activity coefficients of different particles in a solution varies little with the concentration.

These equations describe satisfactorily the isotherms of the electrical conductance of a wide range of systems formed by alkylammonium salts with solvents of different types in the range of concentrations ranging from molten salts to dilute solutions (the latter with 1–2 mol%).

Moreover, several more empirical and semi-empirical equations have been proposed in the literature for the description of the electrical conductivity of solutions.[59,67] Some of these equations apply only to specific systems.

3. Solutions of weak electrolytes

In the case of weak electrolyte solutions the value of λ falls steeply on increase in the concentration and this is primarily due to a strong aggregation of current-carrying particles. In the case of such systems the ionicity of the medium is low so that the Debye–Hückel–Onsager effects make a relatively small contribution and the electrical conductivity of the solution is then described by simpler equations. The best of these are the Fuoss–Kraus[35] and Shedlovsky[36,37] equations

$$\frac{1}{\lambda S(Z)} = \frac{1}{\lambda^0} + \frac{c\lambda f_A S(Z)}{(\lambda^0)^2}, \qquad (21)$$

where $Z = S\sqrt{\lambda c}/\lambda^0$, S is the limiting Onsager coefficient, described by

$$\frac{1}{S(Z)} = F(Z) = 1 - Z\left\{1 - Z\left[1 - Z(\ldots)^{-1/2}\right]^{-1/2}\right\}^{-1/2}$$

in the Fuoss–Kraus method and by

$$S(Z) = \left\{\frac{Z}{2} + \left[1 + \left(\frac{Z}{2}\right)^2\right]^{1/2}\right\}^2 = 1 + Z + \left(\frac{Z}{2}\right)^2 + \left(\frac{Z}{2}\right)^3 + \ldots$$

in the Shedlovsky method. The coefficients $F(Z)$ and $S(Z)$ can be found in Refs. 68 and 69, respectively. In the first approximation the degree of dissociation α is calculated from $\alpha = \lambda/\lambda^0$. Then, the dependence $1/\lambda S(Z)$ on $c\lambda f_{\pm}^2 S(Z)$ is linear and it can be used to find the values of K_a and λ^0. These values can then be employed as the first approximation for the association constant and the limiting electrical conductance, respectively, which can then be used to calculate a new value of the degree of dissociation from $\alpha = \lambda S(Z)/\lambda^0$. Such a calculation is carried out until the required precision of the degree of dissociation (usually 1×10^{-4}) is achieved by the method of successive approximations.

In the case of very weak electrolytes the slope of the dependence $1/\lambda S(Z) = f[c\lambda f_{\pm}^2 S(Z)]$ is so steep that the extrapolation procedure becomes uncertain and gives rise to large errors in the values of K_a and λ^0. In this case we can estimate λ^0 from the Kohlrausch law on the independence of ion migration and by combining the values of the limiting electrical conductance of strong electrolytes. For example, in the case of a solution of acetic acid in water, we can write down

$$\lambda^0_{CH_3COOH} = \lambda^0_{HCl} + \lambda^0_{CH_3COONa} - \lambda^0_{NaCl}.$$

It should be pointed out that Eqn. (21) is derived on the assumption that ion association produces only ion pairs. However, in solvents with a low permittivity we can expect also attachment of ions to an ion pair, forming ion triplets:

$$MA + M^+ \xleftrightarrow{K_1} M_2A^+,$$

$$MA + A^- \xleftrightarrow{K_2} MA_2^-.$$

These processes are most typical of solutions of electrolytes containing large organic ions.[70,71] It is usual to assume that the equilibrium constants of both processes are equal ($K_1 = K_2 = K_t$). In this case the results are usually analysed employing the Fuoss–Kraus equation[35]

$$\lambda c^{1/2} = \lambda^0 K_a^{-1/2} + \lambda_t^0 K_t K_a^{-1/2} c,$$

where λ_t^0 is the limiting electrical conductance due to ion triplets. We can find the association constant K_t representing the formation of triplets if the values of λ^0 are calculated by the method described above using the electrical conductances of strong electrolytes and λ_t^0 is obtained from the approximate expression $\lambda^0 = 3\lambda_t^0$.

Another approach to find the K_t and λ_t^0 was suggested by Beronius.[72] If we denote the equilibrium concentrations of the M^+ and A^- ions by $\alpha_1 c$ and the corresponding concentrations of M_2A^+ and MA_2^- by $\alpha_2 c$, we find that the electrical conductance is given by

$$\lambda = m(\alpha_1\lambda^0 + \alpha_2\lambda_t^0),$$

where m is a coeffficient allowing for the reduction in the conductance because of the ion–ion interaction and given by

$$m = \left(\lambda^0 - Sc_i^{1/2} + Ec_i \ln c_i + I_1 c_i + I_2 c_i^{3/2}\right)\Big/\lambda^0,$$

m can be calculated using Eqns. (2) and (3); $c_i = c(\alpha_1 + \alpha_2)$. The expressions for the association constants are:

$$K_a = (1 - \lambda_1 - 3\lambda_2)/(c\lambda_1^2 f_{\pm}^2),$$

$$K_t = \lambda_2/[c\lambda_1(1 - \lambda_1 - 3\lambda_2)].$$

However, once again we can calculate λ_t^0 and K_t only if we find first the values of λ^0 and K_a.

A combined method is suggested in Ref. 41 and a description is given there of an algorithm for the processing of conductometric data in the case of complex associated electrolytes; this is done employing the Brickley formalism to describe chemical equilibria in solutions, the modified Newton second-order method for optimisation of the required parameters, and the equation of Lee and Wheaton for the concentration of the dependence of the molar electrical conductance of an electrolyte.

III. Limiting molar ionic electrical conductance

The value of the limiting electrical conductance due to ions can be calculated using λ^0 for the electrolyte in question and the limiting transport (transference) number t^0 for one ion forming a given electrolyte. In the case of our binary electrolyte we have

$$\lambda_+^0 = t_+^0\lambda^0,$$

$$\lambda_-^0 = (1 - t_+^0)\lambda^0.$$

Similar equations can be written down if we know t_-^0.

Determination of the transport numbers of nonaqueous solvents meets with major difficulties because of the frequent use of indirect methods for calculation of λ_{ion}^0 and subject to various assumptions. An analysis of these methods can be found in Refs. 73 and 74. The author of Ref. 73 is of the opinion that a physically more justified method uses the product $\lambda^0\eta_0$ for large tetraalkylammonium ions (beginning from Bu_4N^+) in various organic solvents and at different temperatures. The physical justification is the hypothesis that large tetraalkylammonium ions do not become solvated in organic solvents at any temperature. The following indirect methods of separation into ion components are given in Ref. 73:

$$\left(\lambda_\pm^0\right)_{(CH_3)_2CO} = \left(\lambda_\pm^0\right)_{H_2O}\frac{\eta_{0\,H_2O}}{\eta_{0\,(CH_3)_2CO}},$$

$$\lambda^0_{(Pi^-)}\eta_0 = 0.267,$$

$$\lambda^0_{(Et_4N^+)}\eta_0 = 0.296,$$

$$\lambda^0_{(Bu_4N^+)}\eta_0 = \begin{cases}0.208\\0.206\\0.209,\\0.201\\0.233\end{cases}$$

$$\left[\lambda^0_{(iso-Am_3BuN^+)}\eta_0\right]_{n-PrOH,n-BuOH} = \left[\lambda^0{}_{(iso-Am_3BuN^+)}\eta_0\right]_{EtOH},$$

$$\left[\lambda^0_{(Hept_4N^+)}\eta_0{}_{n-PrOH,n-BuOH}\right. = \left[\lambda^0_{(Hept_4N^+)}\eta_0\right]_{EtOH},$$

$$\lambda^0_{R_4N^+} = ZF^2/6\pi N\eta_0[R_i - (0.0103\varepsilon + r_j)],$$

$\lambda^0_{M^+} = \lambda^0_{A^-}$, where M^+ and A^-: iso-Am_4N^+ and iso-Am_4B^-, Bu_4N^+ and BPh_4F-, Bu_4N^+ and Ph_4B^-, $MeOctN^+$ and $OcldSO_4^-$, and Ph_4B_-, Me_3PhN^+ and $PhSO_3^-$, Bu_4N^+ and Bu_4B^-, Ph_4As^+ and Ph_4B^-;

$$\lambda^0_{Bu_4N^+} = 1.08\lambda^0_{iso\text{-}Am_4N^+},$$

$$\lambda^0_{Ph_4B^-} = 1.01\lambda^0_{iso\text{-}Am_4B^-},$$

An analysis of the transport numbers of ions in a number of solvents was given in Refs. 75–77, but the results reported have been obtained mainly at 289 K. There have been only few studies of the temperature dependences of the transport numbers.[78–80]

The dependence of the limiting ionic electrical conductance on the various factors can be analysed conveniently in the form of an expression for the friction coefficient ξ (kg/s):

$$\xi_i = \frac{Z_i^2F^2}{N_A\lambda_i^0}, \qquad (22)$$

where N_A is the Avogadro number.

Different theories give the following expressions for the friction coefficients† of spherical ions of radius R_i.

Continuum models

1. $\xi = \xi_v = A\pi\eta R_i$.

In the above case only the viscous friction forces are allowed for.[1]

2. $\xi = \xi_v + \Delta\xi$, $\Delta\xi = B\dfrac{(Ze)^2(\varepsilon - \varepsilon_\infty)\tau}{R_i^3\varepsilon(2\varepsilon + 1)}$.

The viscous and dielectric friction forces are now included.[81]

3. $\xi = \xi_V + \Delta\xi$,

$\Delta\xi = \eta_0 R_{x0}\sum_{j=1}^{j=4} a_j(R_{x0})^j$ [values of a; can be found in (Ref.82)],

$R_i^4/R_{x0} \to 0$, $\xi = \xi_T = 15.624\eta R_{x0}^{1/4}$,

$R_i^4/R_{x0} >> 1$, $\Delta\xi = A\pi\eta R_i[A_1(R_{x0}/R_i^4) - A_2(R_{x0}/R_i^4)^2]$,

$R_{x0} = \dfrac{(Ze)^2}{16\pi\eta}\dfrac{\varepsilon - \varepsilon_\infty}{\varepsilon^2}\tau$.

The viscous and dielectric friction forces are included.[83–85]

3.1. $\xi = \xi_V + \Delta\xi + \Delta\xi_{DH}$,

$R_i^4/R_{x0} >> 1$, $\Delta\xi_{DH} = A\pi\eta R_i\left[A_3\dfrac{R_{x0}}{R_i^4}\dfrac{R_{HK}}{R_i^4}\right]$,

$R_{HK} = -\dfrac{\alpha(Ze)^2(\varepsilon - 2\varepsilon_\infty)}{\varepsilon^2(\varepsilon - \varepsilon_\infty)}$.

† The values of the coefficients can be found also in the original papers (the references to these papers alongside the name of the model).

The effects of dielectric saturation are included.[86]

3.2. $\xi=\xi_V+\Delta\xi+\Delta\xi_{BB}$,

$R_i^4/R_{x0} >> 1$, $\Delta\xi_{BB} = A\pi\eta R_i\left[A_4\frac{R_{x0}}{R_i^4}\frac{R_R}{R_i^4}\right]$,

$R_R=R_{x0}\eta/\eta_R$, where η_R – is the 'rotational viscosity'

$R_i^4/R_{x0}\to 0$, $\xi=\xi_T=14.089\eta R_{x0}^{1/4}$ when $R_R\to\infty$,

$\xi=\xi_T=15.624\eta R_{x0}^{1/4}$ when $R_R\to 0$.

The influence of 'rotational' viscosity is allowed for.[87]

3.3. $\xi=\xi_V+\Delta\xi+\Delta\xi_e$,

$R_i^4/R_{x0} >> 1$, $\Delta\xi_e = A\pi\eta R_i\left(\frac{b-c}{R_i^4}\right)$,

$C = A_5\frac{(Ze)^2}{4\pi\varepsilon}\left(\frac{\partial\ln\eta}{\partial P}\right)_T$,

$b = A_6\frac{C}{\beta_T}\left(\frac{\partial\ln\eta}{\partial P}\right)_T$,

The influence of electrostriction is included.[88]

4. $\xi=\xi_V+\Delta\xi$,

$\Delta\xi = A_7\frac{(Ze)^2(\varepsilon-\varepsilon_\infty)}{R_iD\varepsilon^2}$.

The Debye relaxation mechanism is supplemented by a nonlocal translational diffusion of molecules along a gradient of a nonequilibrium polarisation field.[89]

5. $\xi=\xi_V+\Delta\xi$,

$R_i^4/R_{x0} > 1$, $\Delta\xi = A\pi\eta Ry(1-g)$,

$R_i^4/R_{x0} < 1$, $\Delta\xi = x\cdot 15.624\eta R_{x0}^{1/4}$,

$xy = f\left(g, R^4/R_{x0}\right)$,

$0 > g > 1/3$.

The ion is assumed to have a finite polarisability and the polarisation changes abruptly at the surface of an ion. The solvent may have more than one relaxation time.[90]

6. $\xi = 2\pi\eta R_i\left\{\sigma+2+\frac{R_{x0}}{R_i^4}\left[\frac{1}{105}\left(56-69\sigma+59\sigma^2\right)+\left(\frac{\lambda_e}{\lambda_h}-1\right)\sigma(1-\sigma)\right]\right\}$,

$\sigma = R_i/(R_i+3\lambda_h)$.

In the above case the energy dissipation in polar liquids is allowed for. The boundary conditions on the surface of an ion are governed by electrical (λ_e) and hydrodynamic (λ_h) parameters.[91]

Continuum-molecular models

1. $\xi=\xi'_V+\xi_D$,

$\xi'_V = 4\pi\eta_0\sigma\left[1+\Delta\left(\frac{\sigma}{R_i}-1\right)\right]^{-1}$; $\xi_D = \frac{(Z_e^2(\varepsilon-\varepsilon_\infty)}{\varepsilon(2\varepsilon+1)R_i^4}\tau A_D\left[1+3\left(\frac{R_i}{\sigma}\right)_y^4\right]$,

$y = \left[\left(1+2\frac{\varepsilon}{\varepsilon_R}+\left(-\frac{\varepsilon-\varepsilon_\infty}{\varepsilon}\right)\left(\frac{\varepsilon_R}{\varepsilon_R-\varepsilon_\infty}\right)\left(\frac{2\sigma}{A_D}-\frac{3B_0}{A_D}\right)-\frac{2c\sigma}{A_D}+\right.\right.$

$\left.\left.+\frac{2\sigma}{R_i}\left(\frac{3\varepsilon_R+1}{2\varepsilon_R+1}\right)\left(1-\frac{\varepsilon}{\varepsilon_R}\right)\right]/\left[\left(1+\frac{2\varepsilon}{\varepsilon_R}\right)-2\left(\frac{R_i}{\sigma}\right)^3\left(\frac{\varepsilon_R-1}{2\varepsilon_R+1}\right)\left(1-\frac{\varepsilon}{\varepsilon_R}\right)\right.\right.$

$B_0 = \frac{\sigma}{2}\left[1+\Delta\left(\frac{\sigma}{R_i}-1\right)\right]^{-1}$, $\sigma = R_i+2R_s$,

$A_D = \frac{\sigma}{2}\frac{\eta}{\eta_{\text{eff}}}\left[1+\Delta\left(\frac{\sigma}{R_i}-1\right)\right]^{-1}$, $\Delta = \eta\rho_R/\eta_{\text{eff}}\rho(0\leqslant\Delta\leqslant 1)$,

$C = \frac{\sigma}{R_i}\frac{\eta}{\eta_{\text{eff}}}\left[1+\Delta\left(\frac{\sigma}{R_i}-1\right)\right]^{-1}$, $\rho_R, \eta_R, \varepsilon_R, \tau_R$ – for $R<r<\sigma$, ρ, η, ε, τ, – in the bulk,

$\eta_{\text{eff}} = \eta_R+\frac{\tau_R}{6M_s}\rho\left[\left(\frac{\rho_R}{\rho}\right)^2-1\right]\left(\frac{\sigma}{R_i}-1\right)\left(\rho\frac{dV(r)}{dr}\right)_{r=\sigma}$.

If $\varepsilon_R = \varepsilon$, then

$$\xi_D = \frac{1}{2}\frac{(ze)^2(\varepsilon-\varepsilon_\infty)\tau}{\varepsilon(1+2\varepsilon)}\frac{\sigma}{R_i^4}\times$$

$$\times\left\{\frac{(\rho/\rho_R)\Delta+(R_i/\sigma)^4\left[1+4\Delta(4\sigma/R_i-1)-(4\sigma/R_i-3)(\rho/\rho_R)\Delta\right]}{1+\Delta(\sigma/R_i-1)}\right\}.$$

If $\varepsilon_R = \varepsilon$ and $\rho_R = \rho$, we have

$$\xi_D = \frac{1}{2}\frac{(ze)^2(\varepsilon-\varepsilon_\infty)\tau}{\varepsilon(1+2\varepsilon)}\frac{\sigma}{R_i^4}\left\{\frac{\Delta+(R_i/\sigma)^4\left[1+\Delta(12\sigma/R_i-1)\right]}{1+\Delta(\sigma/R_i-1)}\right\}.$$

If $\varepsilon_R = \varepsilon_\infty \approx 1$, then

$$\xi_D = \frac{1}{2}\frac{(ze)^2(\varepsilon-\varepsilon_\infty)\tau}{\varepsilon(1+2\varepsilon)}\frac{1}{\sigma^3}\left[\frac{1+4\Delta(\sigma/R_i-1)}{1+\Delta(\sigma/R_i-1)}\right].$$

The local changes in the properties of the solvent near an ion are allowed for in the above expressions.[92]

2. $\xi = A\pi\eta R+\frac{2}{3}(ze)^2\frac{\varepsilon-\varepsilon_\infty}{\varepsilon^2}\frac{\tau}{R_e^3}$.

The short-range order around an ion is allowed for. The finite size of the solvent molecule is taken into acocunt.[93]

Molecular models[94–96]

1. $\xi=\frac{1}{kT}\int_0^\infty\left\langle F^R(0)F^R(t)\right\rangle dT = \xi^{HH}+\xi^{SH}+\xi^{HS}+\xi^{SS}$,

where S and H are, respectively, the soft and hard forces between an ion and the solvent molecules; ξ^{HH} is due to the hard interaction of particles considered as solid spheres and it is given by $\xi^{HH} = 4\pi\eta R_i$; ξ^{SS} corresponds to the soft interactions and is given by

$$\xi^{SS}=\frac{1}{kT}\left\langle\left(F^S\right)^2\right\rangle\tau_F;$$

$\langle(F^S)^2\rangle$ is the mean-square vibration of the soft component of the force; τ_F is the characteristic decay time; ξ^{HS} and ξ^{SH} are cross terms.

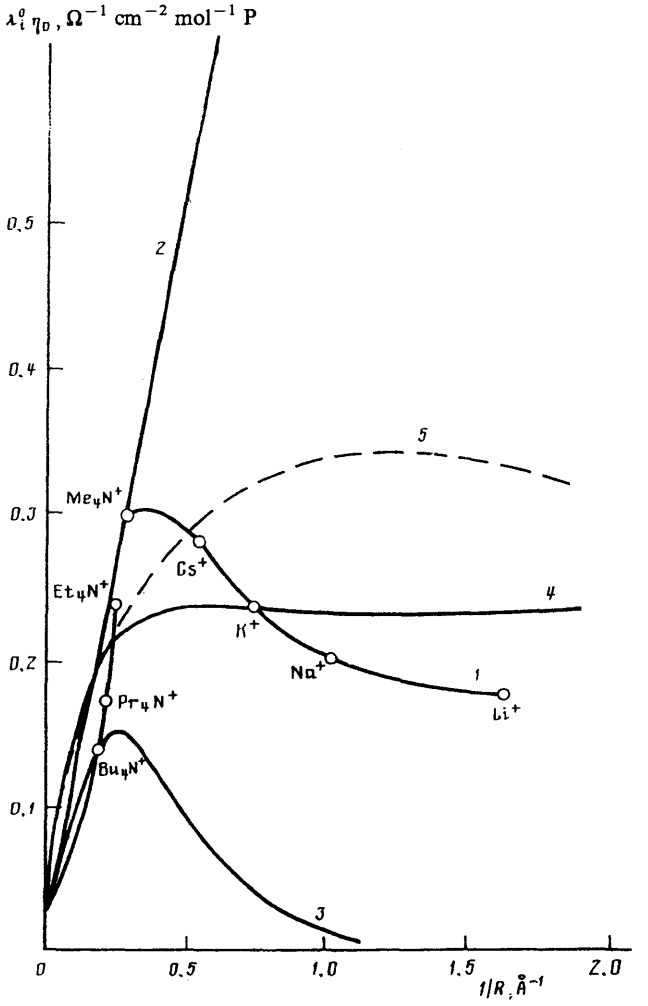


Figure 1. Experimental (*1*) and theoretical (*2*–*5*) dependences of $\lambda_i^0\eta_0$ for methanol on the reciprocal ionic radius at 298.15 K.[85] Theory: *2*, Stokes; *3*, Zwanzig; *4*, Hubbard–Onsager; *5*, Wolynes.

As pointed out in Spiro's review,[4] the Stokes equation 'does not work' until the ionic radius reaches 5.5 Å in water and 10 Å in such solvents as sulpholane. The reason for this is the hydrodynamic model, in which the solvent is regarded as a structure-free continuum. There have been many attempts to develop empirical and theoretical modifications of the Stokes theory among which we should mention the work reported in Refs. 1 and 97. It is assumed in the continuum models that an ion experiences not only the hydrodynamic, but also the dielectric friction. A moving ion orients the solvent dipoles around itself and they return back to a disordered distribution after a certain time (which is the dielectric relaxation time τ). Therefore, an additional electrostatic force acts on an ion.

The continuum models allowing for the dielectric friction have been checked for a large number of electrolytic systems, including protic, aprotic, and mixed solvents.[82,98,99] The results of such calculations are diappointing, particularly in the case of small ions for which the dielectric friction effect in the largest (Fig. 1 shows, by way of example, the experimental and theoretical dependences of λ^0 on $1/R_i$ for methanol). Introduction of dielectric saturation yields an effect which is far too small to improve the results significantly. Moreover, none of the continuum theories can account for the physical nature of the investigated phenomena.

An ideal theory of the ionic electrical conductance should account for the motion of an ion allowing for the ion–solvent interaction, for the structure of the solvent surrounding the ion, and for the motion of the solvent molecules. Wolynes started[94–96] to develop such a molecular approximation. The numerical calculations reported in Ref. 95 were carried out using only the solid-sphere radial distribution functions and the ion-dipole potentials: they showed that the calculated values of the electrical conductance due to small ions were higher than the experimental values, exactly as in the case of the continuum theories (Fig. 1). A theoretical investigation of the dielectric friction coefficient considered from the molecular positions was reported in a recent paper.[100] In principle, such an approach is analogous to that of Wolynes, but there are also some differences.

It should be pointed out that the Walden product is used widely in the interpretation of the electrical conductance data. As assumed in Ref. 101, one of the reasons for the popularity of the product $\lambda^0\eta_0$ is the erroneous view that multiplicaiton of the electrical conductance by the viscosity avoids the problem of the influence of the viscosity on the motion of an ion and makes it possible to consider the influence of other factors. However, this approach should be treated with caution. Since an ion carries a charge, the neglect of the influence of temperature, pressure, and nature of the solvent on the electrostatic interaction of an ion with the solvent may result in an unjustified stress on the structure of the pure solvent. On the other hand, the treatment given in Ref. 102 demonstrates the correctness of the use of the Walden product in diagnostics of structural features of solvents. The relationships governing the changes in the product $\lambda^0\eta_0$ with the properties of the solvent and with the ion size are investigated in Ref. 103.

It is stressed in several papers[82,101] that it is essential to analyse the conductometric data allowing for the residual friction coefficient

$$\Delta\xi = \xi - \xi_V,$$

where ξ is the overall ionic fraction coefficient [deduced from Eqn. (22)]; ξ_V is the Stokes friction coefficient under glide conditions.

In the continuum theories the quantity $\Delta\xi$ reflects mainly the dielectric friction. In the Hubbard–Onsager theory the expression for $\Delta\xi$ includes both dielectric and viscous properties of the solvent, whereas in the theory of Zwanzig only the dielectric properties are

allowed for, because of the separate description of the viscous and dielectric frictions.

The expression for the residual friction coefficient is also in agreement with the formalism of the molecular Wolynes theory. The following assumptions are made in this case: the component of the coefficient of friction due to hard collisions is equated to the Stokes friction coefficient $\xi^{HH} = \xi_V$; the cross terms ξ^{SH} and ξ^{HS} are ignored. We then have $\Delta\xi = \xi^{SS}$. However, it is shown in Refs. 100 and 104 that the neglect of the cross terms is an unjustified simplification.

In the molecular-continuum theory of Chen and Adelman,[92] in contrast to the continuum theories, the dielectric friction contribution is small even in the case of small ions. However, the function Δ introduced there to represent the degree of solvation of an ion is not determined on the basis of microscopic data but is selected to ensure agreement with the experimental conductometry results and is therefore a fitting parameter.

Since the approximation of an ion by a sphere is fairly rough, other geometric approximations have been used to describe the configuration of an ion (ellipsoid, disk, cylinder, etc.). The equations for calculation of Δ is the case of these ion configurations can be found in Spiro's review.[4]

The Hubbard–Onsager theory of dielectic friction and the Onsager–Kirkwood–Fröhlich theory of insulators are used in Ref. 105 to propose a new quantitative characteristic (θ) of the influence of an ion on the dynamic structure of the solvent. The value of θ is calculated using the limiting molar electrical conductance due to ions and it agrees well with the other characteristics of ion solvation (such as the energy of close solvation of ions proposed by Samoilov and denoted by ΔE_i and a coefficient B in the Jones–Dole equation).

One of the quantitative methods for describing the temperature dependence of the electrical conductance is the kinetic approach based on the theory of a transient state. It is shown in Ref. 106 that this theory can be used as the basis of various methods for calculating the thermodynamic characteristics of ion migration. We shall give here only one of the possible variants of such a calculation. If the motion of an ion is regarded as migration across a liquid by a series of jumps from one equilibrium position to another, the distance between which is l, we can write down

$$\lambda_i^0 = \frac{z_i e_i F l^2}{6h} \exp\left(\frac{\Delta G_{\lambda^0}^*}{RT}\right), \tag{23}$$

where h is the Planck constant and $\Delta G_{\lambda^0}^*$ is the free Gibbs energy of activation of electrical conduction.

If we assume that $l = (V_M/N_N)^{1/3}$, then differentiation of Eqn. (23) with respect to temperature and presure yields the following relationships:

$$\left(\frac{\partial \ln \lambda_i^0}{\partial T}\right)_P = \frac{\Delta H_{\lambda^0}^*}{RT^2} + \frac{3}{2}\alpha, \tag{24}$$

$$\left(\frac{\partial \ln \lambda_i^0}{\partial T}\right)_V = \frac{\Delta U_{\lambda^0}^*}{RT^2},$$

$$\left(\frac{\partial \ln \lambda_i^0}{\partial T}\right)_T = \frac{\Delta V_{\lambda^0}^*}{RT} - \frac{2}{3}\beta,$$

where α is the thermal expansion coefficient; β is the isothermal compressibility of the solvent. The first expression in the system (24) is obtained only on the assumption that the entropy of activation of electrical conduction is independent of temperature.

The electrical conductance data can also be used to calculate the number of physicochemical characteristics of solutions and then these characteristics can be useful in tackling many practical problems.[2,4] For example, using the Stokes law, we can determine the radius of a moving solvated ion (Stokes radius):

$$R_s = \frac{zF^2}{6\pi N_A \eta_0 \lambda^0} = \frac{0.82z}{\eta_0 \lambda^0},$$

and then the value of R_s can be used to calculate the solvation number of an ion

$$n_s = \frac{V_c - V_{cv}}{V_s} = \frac{1}{V_s}\frac{4}{3}\pi(R_s^3 - R_{cv}^3),$$

where V_{cv} is the volume of an ion with the crystallographic radius R_{cv} and V_c is the volume of a solvated ion of radius R_s.

It was also suggested in Ref. 97 that the radius of a solvated ion can be calculated using the semi-empirical relationship based on the Stokes law:

$$R_s = \frac{zF^2}{6\pi N_A \eta_0 \lambda^0} + 0.0103\varepsilon + r_y,$$

where $r_y = 0.85$ Å describes dipolar unsassociated solvents and $r_y = 1.13$ Å applies to protic and other associated solvents.

The limiting molar conductance of an individual ion is related to its limiting diffusion coefficient D_i by the Nernst–Einstein equation:

$$D_i = \frac{RT\lambda_i^0}{z_i^2 F^2}.$$

The limiting diffusion coefficient of an electrolyte is

$$D^0 = \frac{RT}{F^2}\frac{z_+|z_-|}{z_+|z_-|}\frac{\lambda_+^0\lambda_-^0}{|z_-|\lambda_+^0 + z_+\lambda_-^0}.$$

The electrical conductance data can be used to calculate the parameters of self-dissociation (autoprotolysis) of water ($K_w = c_H + c_{OH^-}$) and of other pure solvents. Since the ionicity of a medium in a pure solvent is low ($\lambda = \lambda^0$), we can write down

$$\kappa = \frac{\lambda^0 c_{H^+}}{1000} = \frac{\lambda^0 K_w^{1/2}}{1000}. \tag{25}$$

the value of λ^0 is obtained in the same way as in the case of electrolytes, for example, $\lambda_{HOH}^0 = \lambda_{HCL^+}^0 + \lambda_{KOH}^0 - \lambda_{KCl}^0$. By analogy with Eqn. (25), saturated solutions of low-solubility completely dissociated 1–1 electrolytes can be described, in the first approximation, by the expression

$$\varkappa = \frac{\lambda_{sat}^0}{1000} = \frac{{}^0SP^{1/2}}{1000}.$$

If an electrolyte is associated in the solution, then

$$SP^{1/2} = c_{sat} = \frac{1000\varkappa}{\lambda^0} + \left(\frac{\varkappa \times 1000}{\lambda^0}\right)^2 K_a.$$

This makes it possible to calculate the solubility product (SP) of low-solubility salts.

IV. Parameters of ion association

The association constant is introduced into the equations for the electrical conductance of electrolyte solutions using the law of mass action. Therefore, the association constant obtained by solving these equations is an experimental quantity which does not require selection of the ion association model, but depends on the selection of the ionic conductance model. We must mention straight away that the association constant obtained in this way is preferred to the molar scale of concentrations. Therefore, in comparing the ion association processes in different solvents and at different temperatures it is preferable to use the association constant referred to the scale of molar fractions $[K_a(X)]$, which is related to K_a on the molar concentration scale by

$$K_a(X) = \frac{1000\rho}{M_s} K_a.$$

On the other hand, K_a can be calculated using different theories of ion association.

The association constant is related to the distribution function which gives the distribution of ions of opposite change around the central ion. The distribution function is related to the mean-force potential by

$$W^{(s)}(\bar{r}_1 \ldots \bar{r}_s) = -kT \ln f^{(s)}(r_1 \ldots r_s).$$

There are many ways of finding the relevant distribution functions and the mean-force potentials. However, all of them are based on similar assumptions. Firstly, it is postulated that the mean-force potential can be represented as a sum of the long-range (Coulomb) and short-range parts. In fact, such a separation is justified at low concentrations. Secondly, the mean-force potential corresponding to the short-range component is replaced with the pair potential describing this interaction. The second step is again justified by the low concentrations and short distances between ions with opposite signs, when they can be regarded as ion pairs.

In connection with such a separation of the meanforce potential into components, it is usual to solve the problem of the long-range component, since it is the most significant in the formation of an ion pair, and the parameters representing the short-range part are introduced only during the second stage.[22,107,108] There have been recent treatments[23,24,109,110] in which right from the beginning both types of interaction have been allowed for. However, it must be pointed out that it is quite difficult to treat the problem rigorously in view of the mathematical difficulties which are encountered and, therefore, many authors sacrifice the physical and mathematical rigour in order to obtain easily analysable results.

Without going into details of the various theories of ion association, we can point out that for the majority of them an analytic expression for the calculation of the association constant can be represented in the form

$$K_a = \frac{4\pi N_A}{1000} \int_a^R r^2 \exp\left(-\frac{U_\pm}{kT}\right) \omega(r) dr, \qquad (26)$$

where $\omega(r)$ is a weighting function which determines the weight of a paired state of ions as a function of the distance between them. The real potential $U_\pm$ (of Fig. 2*a*) is most frequently represented by the primitive model with an apparent distance a' between the solid spheres (Fig. 2*b*) or a model potential which allows for the long- and short-range components (for example, that shown in Fig. 2*b*),

The equations for calculation of the association constants based on the primitive model allow only for the electrostatic interaction between the ions ($U_\pm/kT = 2q/r$) and they differ in respect of selection of the upper limit of integration and in respect of the expression used for $\omega(r)$. For example, in the Bjerrum theory the value of R is governed by the distance q between the ions at which the energy of the electrostatic interaction is $2kT$. The value is $\omega(r) = 1$ for $a \leqslant r \leqslant q$ and $\omega(r) = 0$ for $r > q$.

The expression for K_a then becomes

$$K_a = \frac{4\pi N_A}{1000} \int_a^q r^2 \exp\left(\frac{2q}{r}\right) dr = \frac{4\pi N}{1000} \left(\frac{|z_+ z_-| e^2}{\varepsilon kT}\right)^3 Q(b), \qquad (27)$$

where

$$Q(b) = \frac{1}{6}\left[e^2 - E_i(2) + E_i(b) - \frac{e^b}{b^3}\left(2 + b + b^2\right)\right].$$

The value of $Q(b)$ is tabulated in Ref. 1 for different values of b.

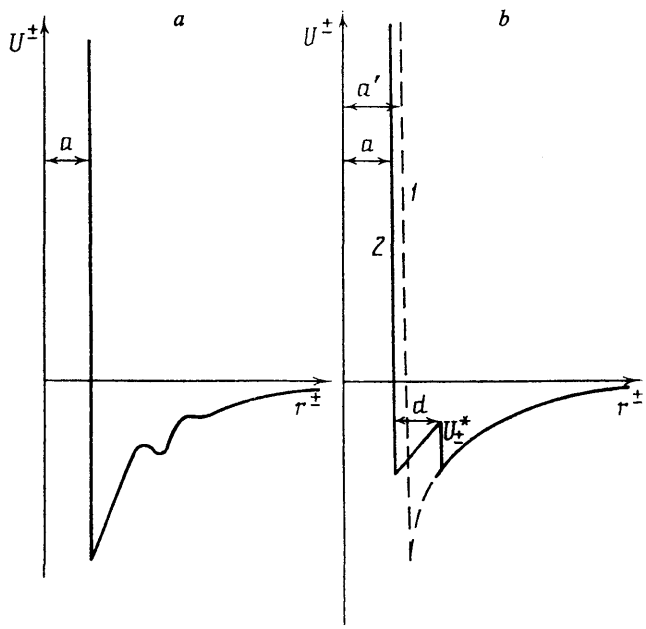


Figure 2. Representation of the cation–anion potential:[10,115] *a*, real potential; *b*, equivalent primitive model with an apparent distance a' between the hard spheres (*1*) and one of the simplest models allowing for the long- and short-range components (*2*).

In the theory of ion association proposed by Fuoss only the contact ion pairs are considered and the value of r is assumed to be $(4/3)a$. Then $\omega(r) = 1$ for $a \leqslant r \leqslant (4/3)a$ and $\omega(r) = 0$ for $r > (4/3)a$. The association constant is then given by

$$K_a = \frac{4\pi N_A a^3}{3000} e^h \cdot \qquad (28)$$

A better justified selection of the weighting function $\omega(r)$, which allows us to obtain an expression for the ion association constant using the primitive model, is made by Ebeling[12,32]

$$\omega(r) = 1 + \exp\left(\frac{2q}{r}\right) - 2\exp\left(\frac{2q}{r}\right) - \left(\frac{2q}{r}\right)^2 \exp\left(\frac{2q}{r}\right).$$

The upper limit of integration [see Eqn. (26)] is ∞. As a result, we obtain Eqn. (10).

However, the most satisfactory description of the process of ion association can be obtained by employing a model potential that allows for the long- and short-range effects. There are various ways of representing the combined potential as a function of the distance:

$$\frac{U_\pm(r)}{kT} = \begin{cases} \infty, & r \leqslant a \\ \dfrac{U_\pm}{kT} = \text{const}, & a \leqslant r \leqslant R' \\ \dfrac{2q}{r}, & R' \leqslant r \leqslant R, \end{cases} \tag{29}$$

$$\frac{U_\pm(r)}{kT} = \begin{cases} \infty, & r \leqslant a \\ \dfrac{2q}{r} + \dfrac{U_\pm^*}{kT}\left(U_\pm^* = \text{const}\right), & a \leqslant r \leqslant R' \\ -\dfrac{2q}{r}. & R' \leqslant r \leqslant R, \end{cases} \tag{30}$$

$$\frac{U_\pm(r)}{kT} = \begin{cases} \infty, & r \leqslant a \\ -\dfrac{2q}{r} + \dfrac{U_\pm^*(r)}{kT}, & a \leqslant r \leqslant R' \\ -\dfrac{2q}{R} & R' \leqslant r \leqslant R. \end{cases} \tag{31}$$

Depending on the assumptions made by the authors, one can find other designations for the quantity $U_\pm^*$: $W_\pm^*$,[110] $d_\pm$,[111] and ν_1.[112] The lower limit of integration a in Eqn. (26) is equal to the 'hard-sphere' contact distance between the ions calculated from the crystallographic radii. The upper integration limit R may be specified in a variety of ways: it may be equated to the Bjerrum distance q: it may be equal to the distance found by solving the electrical conduction equation; it may also be selected using some other approach. The intermediate distance R' is most frequently expressed in the form $R' = a + S$, where S is equal to one or several diameters of the solvent molecule or some fragment of this molecule. The effective diameter of the solvent molecule d_S can be calculated from its molar volume V_S:

$$d_S = \left(\frac{6V_S}{\pi N_A}\right)^{1/3}$$

or from the geometric parameters of the solvent molecules. If in the case of $U_\pm$ we use the model potential of the type given by Eqn. (30), we find that K_a is given by

$$K_a = \frac{4\pi N}{1000}\left[\exp\left(-\frac{U^*}{kT}\right)\int_a^{R'} r^2 \exp\left(\frac{2q}{r}\right)dr + \int_{R'}^{R} r^2 \exp\left(\frac{2q}{r}\right)dr\right]. \tag{32}$$

Then,

$$\exp\left(-\frac{U_\pm^*}{kT}\right) = \frac{K_a - (4\pi a/1000)\int_{R'}^{R} r^2 \exp(2q/r)dr}{(4\pi N/1000)\int_a^{R'} r^2 \exp(2q/r)dr}. \tag{33}$$

Eqn. (33) is frequently written in the form

$$\exp\left(-\frac{U^*}{kT}\right) = \frac{K_a - (4\pi N/1000)\int_{R'}^{R} r^2 \exp(-2q/r)dr}{(4\pi N/1000)\int_a^{R} r^2 \exp(2q/r)dr - (4\pi N/1000)\int_{R'}^{R} r^2 \exp(2q/r)dr} =$$

$$= \frac{K_a - K_a(R')}{K_a(a) - K_a(R')},$$

where $K_a(R')$ and $K_a(a)$ are calculated using either the Bjerrum equation (27) or the Ebeling equation (28).

The selection of a specific form of the functional dependence $U_\pm^*(r)$ [Eqn. (31)] of Refs. 113 and 114 widens the concentration range of the validity of this equation, but it greatly complicates the problem. Therefore, it is not used much in practical applications when an analysis is made of conductometric data.

Knowledge of the ion association constants at different temperatures allows us to calculate all the thermodynamic characteristics of the association process using the following relationships:

$$\Delta G_a^0 = -RT \ln K_a,$$

$$\Delta H_a = \frac{RT^2 d\ln K_a}{dT},$$

$$\Delta S_a = \frac{\Delta H_a^0 - \Delta G_a^0}{T}$$

If the pair interaction potential is given by Eqns. (29)–(31) then ΔG_a can be represented as a combination of the long-range (Coulomb) and short-range contributions.

It follows from our review that conductometry of electrolyte solutions can provide in a fairly reliable way of obtaining some important information on the state and mobility of ions in solvents of different kinds and in a wide range of parameters. This is largely due to a good theoretical basis of this branch of physical chemistry of solutions and the experimental capabilities of the method itself.

References

1. R A Robinson, R H Stokes *Electrolyte Solutions,* 2nd ed. (Translated into Russian), Inostr. Lit., Moscow, 1963, 646 pp
2. M Grilikhes, B K Filanovskii *Kontaktnaya Konduktometriya. Teoriya i Praktika Metoda* (Contact Conductometry: Theory and Practice of the Method), Khimiya, Leningrad, 1980, 176 pp
3. D F Evans, M A Matesich *Techniques of Electrochemistry,* Vol. 2 (Edited by E Yeager, A J Salkind) (Translated into Russian), Mir, Moscow, 1977, Vol. 2, p. 10
4. M Spiro *Physical Methods of Chemistry* (Edited by B W Rossiter, J F Hamilton), Vol. 2: *Electrochemical Methods,* Wiley, New York, 1985, p. 663

5. B A Lopatin *Konduktometriya (Izmerenie Elektroprovodnosti Elektrolitov)* [Conductometry (Measurement of the Electrical Conductance of Electrolytes)], Siberian Division of the Academy of Sciences of the USSR, Novosibirsk, 1964, 280 pp
6. B A Lopatin *Teoreticheskie Osnovy Elektrokhimicheskikh Metodov Analiza* (Theoretical Basis of Electrochemical Analysis Methods), Vysshaya Shkola, Moscow, 1975, 269 pp
7. V M M Lobo *Elektrokhimiya,* 1991, **27** 613
8. S F Ledenkov, V N Afanas'ev, G A Krestov *Termodinamicheskie Svoistva Rastvorov* (Thermodynamic Properties of Solutions), Institute of Chemical Engineering, Ivanovo, 1984, p. 81
9. J Barthel, R Wachter, H-J Gores *Modern Aspects of Electrochemistry,* Vol. 13 (Edited by B E Conway, J O'M Bockris), Plenum Press, New York, 1979, p. 1
10. J-C Justice *Comprehensive Treatise of Electrochemistry* (Edited by B E Conway, J O'M Bockris, E Yeager), Vol. 5: *Thermodynamic and Transport Properties of Aqueous and Molten Electrolytes,* Plenum Press, New York, 1983, p. 233
11. W Ebeling *Wiss. Z. Univ. Rostock Math.-Naturwiss. Reihe* 1965, **14** 271
12. H Falkenhagen, W Ebeling, W D Kraeft *Ionic Interactions: From Dilute Solution to Fused Salts,* Vol. 1 (Edited by S Petrucci), Academic Press, New York, 1971, p. 61
13. G E Uhlenbeck, G W Ford *Lectures in Statistical Mechanics* (Translated into Russian), Mir, Moscow, 1965
14. E Pitts *Proc. R. Soc. (London), A,* 1953, **217** 43
15. R M Fuoss, L Onsager, J E Skinner *J. Phys. Chem.,* 1965, **69** 2581
16. R M Fuoss, K-L Hsia *Proc. Natl. Acad. Sci. USA,* 1967, **57** 1550
17. J Quint, A Viallard *J. Solut. Chem.,* 1978, **7** 533
18. M-S Chen *J. Solut. Chem.,* 1978, **7** 675; 1979, **8** 509
19. J Barthel, S-C Justice, R Wachter *Z. Phys. Chem. (Frankfurt am Main),* 1973, **84** 100–113
20. R M Fuoss, R M Jarret *J. Phys. Chem.,* 1985, **89** 3167
21. J-C Juistice *J. Phys. Chem.,* 1975, **79** 454
22. R M Fuoss *J. Phys. Chem.,* 1975, **79** 525
23. W H Lee, R J Wheaton *J. Chem. Soc., Faraday Trans. 2,* 1978, **74** 743
24. W H Lee, R J Wheaton *J. Chem. Soc., Faraday Trans. 2,* 1978, **74** 1456
25. W H Lee, R J Wheaton *J. Chem. Soc., Faraday Trans. 2,* 1979, **75** 1128
26. R W Gurney *Ionic Processes in Solution,* Dover Publ., New York, 1953
27. A D Pethybridge, S S Taba *J. Chem. Soc., Faraday Trans. 1,* 1980, **76** 368
28. R M Fuoss *Proc. Natl. Acad. Sci. USA,* 1978, **75** 16
29. W Ebeling, J Rose *J. Solut. Chem.,* 1981, **10** 599
30. W Ebeling, M Grigo *J. Solut. Chem.,* 1982, **11** 151
31. R Sändig *Z. Phys. Chem. (Leipzig),* 1984, **265** 663
32. W Ebeling *Z. Phys. Chem. (Leipzig),* 1968, **238** 400
33. R L Kay, B J Hales, G P Cunningham *J. Phys. Chem.,* 1967, **71** 3925
34. D M Himmelblau *Applied Nonlinear Programming* (Translated into Russian), Mir, Moscow, 1975
35. R M Fuoss, C A Kraus *J. Am. Chem. Soc.,* 1933, **55** 2387
36. T Shedlovsky *J. Franklin Inst.,* 1938, **225** 739
37. R M Fuoss, T Shedlovsky *J. Am. Chem. Soc.,* 1949, **271** 1496
38. S Elshazly, M Grigo *Z. Phys. Chem. (Leipzig),* 1984, **265** 417
39. L P Safonova, B K Patsatsiya *Programma Obrabotki Eksperimental'nykh Dannykh po Elektroprovodnosti Razbavlennykh Rastvorov Simmetrichnykh Elektrolitov* (Program for Processing of Experimental Data on the Electrical Conductance of Dilute Solutions of Symmetric Electrolytes), Deposited Paper No. 2081-V-91, VINITI, Ivanovo, 22nd May 1991, 5 pp
40. O N Kalugin, I N V'yunnik *Zh. Obshch. Khim.,* 1989, **59** 1628
41. O N Kalugin, I N V'yunnik *Zh. Obshch. Khim.,* 1989, **59** 1633
42. I K Righellato, C W Davis *Trans. Faraday Soc.,* 1930, **26** 592
43. R M Fuoss, D Edelson *J. Am. Chem. Soc.,* 1951, **73** 269
44. T J Murphy, E G B Cohen *J. Chem. Phys.,* 1970, **53** 2173
45. A D Pethybridge *Z. Phys. Chem. (Frankfurt am Main),* 1982, **133** 143
46. A R Altenberger, H L Friedman *J. Chem. Phys.,* 1983, **78** 4162
47. E C Zhong, H L Friedman *J. Phys. Chem.,* 1988, **92** 1685
48. R Sändig *J. Solut. Chem.,* 1985, **14** 311
49. R Feistel, H Kunstner, R Sändig *Z. Phys. Chem. (Leipzig),* 1985, **266** 656
50. B F Wishov, R H Stokes *J. Am. Chem. Soc.,* 1954, **76** 2065
51. H Falkenhagen, M Leist, G Kelbg *Ann. Phys. (Leipzig),* 1952, **11** 51
52. A N Campbell, W G Paterson *Can. J. Chem.,* 1958, **36** 1004
53. Yu A Karapetyan, V N Eichis *Fiziko-Khimicheskie Svoistva Elektrolitnykh Nevodnykh Rastvorov* (Physicochemical Properties of Nonaqueous Electrolyte Solutions), Khimiya, Moscow, 1989, 256 pp
54. G J Jans, B G Oliver, G P Lakshminarayanan, G E Mayer *J. Phys. Chem.,* 1970, **74** 1285
55. M Della Monica, A Ceglie, A Agostiano *J. Phys. Chem.,* 1984, **88** 2124
56. S S Islam, R L Gupta, K Ismail *J. Chem. Eng. Data,* 1991, **36** 102
57. J F Castel, A S Amis *J. Chem. Eng. Data,* 1972, **17** 55
58. A N Ivashkevich, V P Kostynyuk *Elektrokhimiya* 1987, **23** 887
59. G A Krestov, N P Novoselov, I S Perelygin, et al. *Ionnaya Sol'vatatsiya* (Ion Solvation), Nauka, Moscow, 1987, 320 pp
60. M Nicolas, R Reich *J. Phys. Chem.,* 1979, **83** 749
61. Yu Ya Fialkov, N I Kulinich, V L Chumak *Elektrokhimiya* 1988, **24** 1391
62. V V Serdyuk *Zh. Fiz. Khim.,* 1981, **55**(3) 722 [English translation in *Russ. J. Phys. Chem.,* 1981(3)]
63. I N Maksimova, N N Pravdin, V E Razuvaev, et al. *Rastvory Elektrolitov v Vysoko- i Nizkotemperaturnom Rezhimakh: Fiziko-Khimicheskoe Issledovanie* (Solutions of Electrolytes at High and Low Temperatures: Physicochemical Investigations), Leningrad State University, 1980, 127 pp
64. E M Kuznetsova *Zh. Fiz. Khim.,* 1987, **61**(10) 2788 [English translation in *Russ. J. Phys. Chem.,* 1987(10)]
65. E M Kuznetsova *Zh. Fiz. Khim.,* 1987, **61**(10) 2791 [English translation in *Russ. J. Phys. Chem.,* 1987(10)]
66. Chkhon Su Pak, I N Maksimova *Zh. Prikl. Khim.,* 1986, **59** 2543
67. M M Baldanov, B B Tanganov, M V Mokhosoev *Zh. Fiz. Khim.,* 1991, **65**(2) 362 [English translation in *Russ. J. Phys. Chem.,* 1991(2)]
68. R M Fuoss *J. Am. Chem. Soc.,* 1935, **257** 488
69. H M Doggett *J. Am. Chem. Soc.,* 1951, **73** 4977
70. M Hojo, Y Miyauchi, I Nakatani, T Mizobuchi, Y Imai *Chem. Lett.,* 1990, 1035
71. M Salomon *J. Solut. Chem.,* 1990, **19** 1225

72. P Beronius, L Petaki *Acta Chim. Hung.*, 1980, **103** 17
73. B S Krumgalz *J. Chem. Soc., Faraday Trans. 1*, 1983, **79** 571
74. Yu Ya Fialkov, A N Zhitomirskii *Zh. Fiz. Khim.*, 1987, **61**(2) 390 [English translation in *Russ. J. Phys. Chem.*, 1987(2)]
75. O Popovych, R P T Tomkins *Nonaqueous Solution Chemistry*, Wiley, New York, 1981, 499 pp
76. M Spiro *Physical Chemistry of Organic Solvent Systems* (Edited by A K Covington, T Dickinson), Plenum Press, New York, 1973, p. 615
77. N H El-Hammamy, F M Abd. El-Halim *J. Electrochem. Soc. India*, 1984, **33** 160
78. J Barthel, U Ströder, L Iberl, H Hammer *Ber. Bunsenges. Phys. Chem.*, 1982, **86** 636
79. G P Gunningham, D F Evans, R L Kay *J. Phys. Chem.*, 1966, **70** 3998
80. G A Vidulich, G P Gunningham, R L Kay *J. Solu. Chem.*, 1973, **2** 23
81. R Zwanzig *J. Chem. Phys.*, 1970, **52** 3625
82. K Ibuki, M Nakahara *J. Phys. Chem.*, 1987, **91** 1864
83. J B Hubbard *J. Chem. Phys.*, 1977, **67** 4850
84. J B Hubbard *J. Chem. Phys.*, 1978, **68** 1649
85. D F Evans, T Tominaga, J B Hubbard, P G Wolynes *J. Phys. Chem.*, 1979, **83** 2669
86. P J Stiles, J B Hubbard, R F Kayser *J. Chem. Phys.*, 1982, **77** 6189
87. J B Hubbard, R F Kayser *J. Chem. Phys.*, 1981, **74** 3535
88. P J Stiles, J B Hubbard *Chem. Phys. Lett.*, 1984, **105** 655
89. P J Stiles, J B Hubbard *Chem. Phys.*, 1984, **84** 431
90. B V Felderhof *Mol. Phys.*, 1983, **49** 449
91. E Novak *J. Chem. Phys.*, 1983, **79** 976
92. J H Chen, S A Adelman *J. Chem. Phys.*, 1980, **72** 2819
93. S Hyodo, U Nagashima, T Fujiyama *Bull. Chem. Soc. Jpn.*, 1983, **56** 1041
94. P G Wolynes *J. Chem. Phys.*, 1978, **68** 473
95. P Colonomos, P G Wolynes *J. Chem. Phys.*, 1979, **71** 2644
96. P G Wolynes *Annu. Rev. Phys. Chem.*, 1980, **31** 345
97. D S Gill *Electrochim. Acta*, 1979, **24** 701
98. K Ibuki, M Nakahara *J. Chem. Phys.*, 1986, **84** 2776
99. K Ibuki, M Nakahara *J. Phys. Chem.*, 1987, **91** 4411–4414
100. B Bagchi *J. Chem. Phys.*, 1991, **95** 467
101. M Nakahara, K Ibuki *J. Phys. Chem.*, 1986, **90** 3026
102. I I Vaisman, R B Lyamina, Yu M Kessler, et al. *Zh. Fiz. Khim.*, 1988, **62**(3) 838 [English translation in *Russ. J. Phys. Chem.*, 1988(3)]
103. Yu A Karapetyan, V N Eichis *Zakonomernosti Izmeneniya Velichiny* $\lambda^0\eta$ *v Nevodnykh Sredakh* (Relationships Governing Changes in the Quantity $\lambda^0\eta$ for Nonaqueous Media), Deposited Paper No. 2203-Uk87, UkrNIINTI, Kiev, 28th July 1987, 28 pp
104. M Berkowitz, W Wan *J. Chem. Phys.*, 19987, **86** 376
105. O N Kalugin, I N V'yunnik *Khim. Fiz.*, 1991, **10** 708
106. A N Khitomirskii *Zh. Fiz. Khim.* 1987, **61** 1748
107. J C Justice, M-C Justice *Faraday Discuss. Chem. Soc.*, 1977, (64) 265
108. J Barthel *Ber. Bunsenges. Phys. Chem.*, 1979, **83** 252
109. W Ebeling, R Feisted, R Sändig, *J. Solut. Chem.*, 1979, **8** 53
110. O N Kalugin, I N V'yunnik *Vestn. Khar'k. Univ.*, 1989, 18
111. S Elshazly, M Grigo *Z. Phys. Chem. (Leipzig)*, 1984, **265** 417
112. S Ciccariello *J. Chem. Soc., Faraday Trans.*, 1985, **81** 1163
113. P S Ramanathan, H L Friedman *J. Chem. Phys.*, 1971, **54** 1086
114. B M Pettit, P Rossky *J. Chem. Phys.*, 1986, **84** 5836
115. N Schmelzer, J Einfeldt, M Grigo *J. Chem. Soc., Faraday Trans.*, 1990, **86** 489

Received 24th January 1992

Translated from *Uspekhi Khimii* **61** 1777–1804 (1992) U.D.C. 541.18+532.6

Line tension in the thermodynamics of thin liquid films

V G Babak
All-Union Correspondence Institute for the Food Industry, Moscow

ABSTRACT. The results of theoretical and experimental studies of line tension in thin liquid films and three-phase systems in the last 20 years have been examined and generalised. The main theories of line tension, the reported measurements of its magnitude and sign, and the results of numerical calculations of the line tension on the basis of various thermodynamic models have been analysed. The results of this analysis are discussed in terms of the generalised theory of line tension.

The bibliography contains 74 references.

Contents

I. Introduction 975
II. Different definitions of the line tension 976
III. Experimental determination of the line tension 978
IV. Theories of the line tension 980
V. Calculation of the line tension by numerical methods 983
VI. Conclusions 988

I. Introduction

Line tension manifests itself as a fundamental concept of the thermodynamics of surface phenomena in the description of the mechanical equilibrium and of the energy properties of thin liquid films and of three-phase systems of finite size. The line tension can be defined either as the force $æ(H)$ acting along the boundary line (or the three-phase contact line) of a thin liquid film and tending to shorten (for $æ > 0$) or to lengthen (for $æ < 0$) the contact line, or as the specific excess free energy (referred to unit length of the contact line) of the system, i.e. its grand thermodynamic potential æ, J m^{-1}. Being (by definition) an excess quantity the line tension can take different values, depending on the idealised thermodynamic model chosen to describe the real system including a film boundary or three-phase contact line.

The line tension concept is used in surface chemistry and in colloid chemistry to describe a variety of processes: the heterogeneous formation of a new phase,[1–3] the hydrodynamics of thin liquid films,[4] the breakdown of ordinary and of Newtonian black films,[5,6] bilayer membranes,[7] the adhesion of liquid particles,[8] etc.

According to theoretical calculations[9–15] the absolute numerical value of the line tension should be $10^{-11}-10^{-10}$ N. In spite of these low values the line tension makes a substantial contribution to the free energy and to the mechanical equilibrium of thin liquid films and of three-phase systems in highly dispersed and colloid systems. In particular, the lower work of formation of nuclei of a new phase (100 Å in diameter) on solid or liquid substrates than in homogeneous nucleation has been widely attributed[1,2,14,16–20] to negative line tension effects.

Positive line tension can explain the stability of Newtonian black films towards rupture in the theory of nucleational disintegration.[7,21–24] Positive line tension is associated with the stability of ordinary black films towards rupture or towards spontaneous conversion into Newtonian black films at the contact between air bubbles or microscopic solid spheres and the air–solution interface.[5,25] Allowance for the linear tension is necessary in calculations of the force of adhesion of solid particles to the air–water interface during flotation.[26] The observed dependence of the angle of contact in the region of the film meniscus on the radius of the film (r) is attributed to the existence of an excess two-dimensional pressure $æ/r$ (where r is the radius of curvature of the line of contact).[10,16,27–39]

However, we should note that no generally accepted experimental determinations of the line tension are available at present: data from various laboratories range between -10^{-7} and $+10^{-7}$ N, even for identical systems.[1,15,16,35]

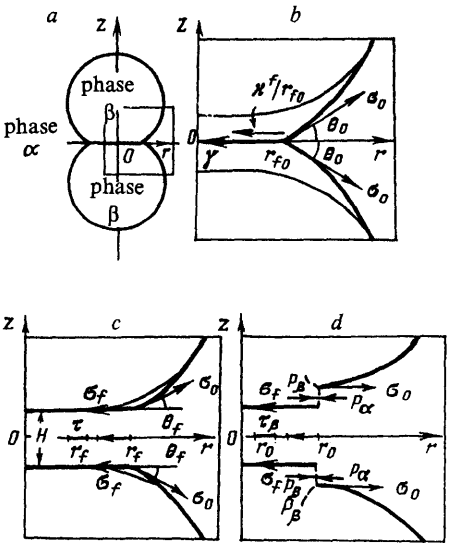


Figure 1. Different thermodynamic models of a thin liquid film used in the definition of the linear tension: *a*, contact of two identical fluid particles (phase β) in a liquid medium (phase α); *b*, membrane model of the liquid film; *c*, model of the liquid film which assumes two interfaces, used for a negative specific free energy of interaction in a film of thickness H_f; *d*, model of the liquid film for a positive specific free energy of interaction in a film of thickness H_f.

An analysis of experimental and of theoretical studies of line tension has shown[40–42] that different thermodynamic models are often used to define the line tension, and that this causes problems in comparing numerical values of æ.

The aim of this review is to analyse published work on the line tension problem in the thermodynamics of thin liquid films on the basis of the generalised theory of line tension developed by the writer.[40,42]

II. Different definitions of the line tension

All the reports on the line tension problem known to the writer can be arbitrarily divided into two groups. To the first we assign studies which have relied on the membrane approach to the thermodynamics of thin liquid films formulated by Deryagin and his co-workers.[43,44] In this approach the thermodynamic model of the thin liquid film is the interface (as defined by Gibbs,[45] i.e. a membrane of zero thickness) with respect to which the excess thermodynamic quantities are calculated (Fig. 1*b*).

Studies in which the film is treated as a layer of finite thickness H_f, bounded by two interfaces, are classified in the second group (Fig. 1*c*). This approach was proposed by Rusanov,[46–48] and has been further developed by the present writer and by others.[41,42,50–56]

In the membrane approach the condition of mechanical equilibrium of a symmetrical curved film of radius r_{f0} (see Fig. 1*b*) is defined as

$$\gamma + -\frac{æ^f}{r_{f0}} = 2\sigma_0 \cos\theta_0, \qquad (1)$$

where γ is the tension of the film, θ_0 is the contact angle corresponding to the radius of the film r_{f0}, σ_0 is the interfacial tension at the interface with the bulk phases, $æ^f$ is the line tension (in the symbols of Scheludko, et al.[1]). The term $æ^f/r_{f0}$ has the dimensions of N m^{-1} and can be interpreted as the two-dimensional pressure created by the curvature of the contact line (by analogy with the capillary pressure P_c created by the curvature of the interfacial surface). If the line of contact is straight (i.e. for $r_{f0}\to\infty$) the equilibrium equation of the film (or membrane) becomes

$$\gamma = 2\sigma_0 \cos\theta_{0\infty}, \qquad (2)$$

where $\theta_{0\infty}$ is the angle of contact corresponding to $r_{f0}\to\infty$. Ignoring the dependence of the film tension γ on its radius r_{f0} we obtain from Eqns. (1) and (2) the expression

$$æ^f = 2r_{f0}\sigma_0 (\cos\theta_0 - \cos\theta_{0\infty}), \qquad (3)$$

which is used as a basis for the experimental determination of the line tension $æ^f$ from the $\theta_0(r_{f0})$ relationship.

The line tension $æ^f$ defined in terms of the membrane approach is used, for example, by Scheludko, et al.[15,16] and by Churaev, et al.[57]

In the method of two interfaces the mechanical equilibrium condition of a symmetrical curved film is written (see Fig. 1*c*) as:[49]

$$2\sigma_f + \frac{\tau}{r_f} = 2\sigma_0 \cos\theta_f, \qquad (4)$$

where σ_f is the interfacial tension in a film of thickness H_f, which differs from the interfacial tension σ_0 and is related to it by the expression

$$2\sigma_f = 2\sigma_0 + \Delta\Omega(H_f), \qquad (5)$$

where $\Delta\Omega(H_f)$ is the specific free energy of the interaction between the interfaces in a film of thickness H_f, so that the condition for a finite angle of contact is $\Delta\Omega(H_f) < 0$; θ_f and r_f are the angle of contact and the radius of the film (note that $\theta_f \neq \theta_0$ and $r_f \neq r_{f0}$ for $H_f \neq 0$); τ is the line tension (in de Feijter and Vrij's symbols[49]).

If the thickness of the film H_f is unaffected by changes in the radius r_f we can write the expression [analogous to Eqn. (3)]

$$\tau = 2r_f\sigma_0 (\cos\theta_f - \cos\theta_{f\infty}), \qquad (6)$$

where $\theta_{f\infty}$ is the angle of contact for cylindrical films (i.e. for $r_f\to\infty$), which satisfies the condition

$$\sigma_f = \sigma_0 \cos\theta_f. \qquad (7)$$

Eqn. (6) is the basis of the experimental determination of the line tension τ from measurements of the $\theta_f(r_f)$ dependence.

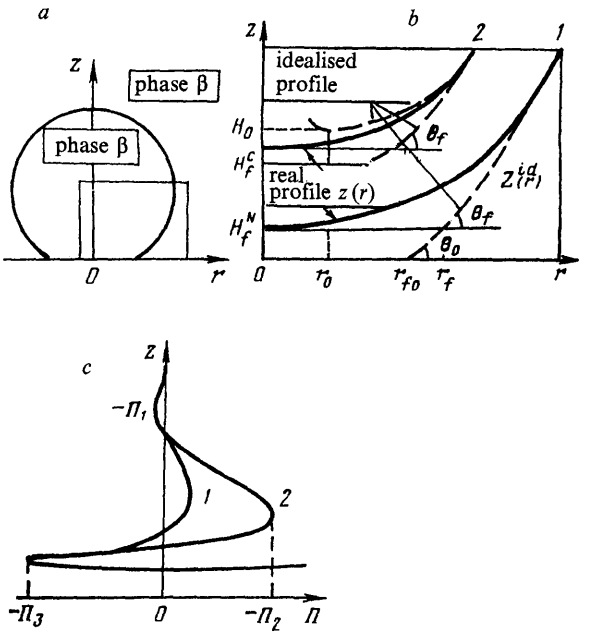


Figure 2. Definition of the parameters which characterise the profile of thin liquid films (see text).

We should stress the fact that the line tensions $æ^f$ and τ are different quantities, defined in terms of different thermodynamic models. As has been pointed out,[40,42] the difference between $æ^f/r_{f0}$ and τ/r_f is of the order of $\Delta P H_f$ (where $\Delta P = P_\beta - P_\alpha$, and P_α and

P_β are the hydrostatic pressures in the phases α and β respectively (see Fig. 1*a*), corresponding to $\sim 5 \times 10^{-6}$ N m^{-1} with $\Delta P \simeq 100$ Pa for films of thickness $H_f \sim 50$ nm thick. The error caused by identifying τ with $æ^f$ is $\sim 5 \times 10^{-10}$ N for films of radius $r_f \cong 100$ μm, and the relative error of the line tension $\tau \cong 10^{-12}$ N[49] is of the order of $\Delta P H_f/\tau = 500$. Thus failing to distinguish between the line tensions τ and $æ^f$ (as is often done in published work) can lead to serious errors in the determination of their numerical values for $H_f \neq 0$: the greater the product $\Delta P H_f$, the greater is the error.

It should be noted that the contact angles θ_f or θ_0 are determined by the following procedure (Fig. 2*a*). Since the real profile $z(r)$ of the film in the transition region of the meniscus can seldom be determined experimentally to the required precision (because of the very small size of this region) the idealised profile $z_{id}(r)$ is usually employed. This is by definition identical to the real profile $z(r)$ in the region of the main bulk of the meniscus, where the disjoining pressure is zero (Fig. 2*b*), and it can be extrapolated to the transition region of the film on the assumption that the interfaces do not interact in that region. The idealised profile of the film $z_{id}(r)$ is determined with high precision by an interference method (called the topographic method[58]). We know that the following relationship applies[49] for negative values of the specific free energy of interaction $\Delta\Omega(H_f)$ in a film of thickness H_f:

$$\Delta\Omega(H_f) = \int_{H_f}^{\infty} \Pi(H)dH, \tag{8}$$

and the idealised profile $z_{id}(r)$ must intersect the plane $z = z_f = H_f/2$, forming an angle of contact θ_f such that the condition (7) applies for cylindrical films. On the other hand if $\Delta\Omega(H_f)$ is negative and has a high absolute value the idealised profile $z_{id}(r)$ can also intersect the plane $z = 0$ (with a contact angle θ_0), and for cylindrical films the relationship (2) applies.

When $\Delta\Omega(H_f) > 0$ the idealised profile $z_{id}(r)$ passes above the plane $z = z_f = H_f/2$ (see Fig. 2*b*), and is characterised by a minimum ($z = H_0/2$) at $r = r_0$.[59–61] If the contact line is straight, i.e. if $r_0 \to \infty$, we can write

$$\Delta\Omega(H_f) = \Delta P(H_{0\infty} - H_f), \tag{9}$$

where $H_{0\infty} = 2z_{0\infty}$, and $z_{0\infty}$ is the minimum in the profile of the film for $r_0 \to \infty$.

The expression (9) was first used to determine experimentally the specific free energy of interaction $\Delta\Omega(H_f)$ in water films stabilised by adsorbed layers of polyvinyl alcohol,[62] and it was shown that under these conditions $\Delta\Omega(H_f) = +2 \times 10^{-7}$ J m^{-2}. The expression (9) was also used[63] in an experimental determination of $\Delta\Omega(H_f)$ for wetting films of aqueous solutions of electrolytes on quartz. For these films the result was $\Delta\Omega(H_f) = +2 \times 10^{-5}$ J m^{-2}.

The line tension τ_B for films with a positive $\Delta\Omega(H_f)$ was first determined by the present writer[55,64,65] as

$$\Delta\Omega(H_f) + \frac{\tau_B}{r_0} = \Delta P(H_0 - H_f), \tag{10}$$

or, using (5),

$$2\sigma_f + \frac{\tau_B}{r_0} = 2\sigma_0 + \Delta P(H_0 - H_f). \tag{11}$$

Eqn. (10) reduces to (9) for $r_0 \to \infty$. If the film thickness H_f and the difference in hydrostatic pressures stay constant, $\Delta\Omega(H_f)$ is also unchanged, and by combining (9) with (10) we obtain

$$\tau_B = r_0 \Delta P[H_0(r_0) - H_{0\infty}], \tag{12}$$

where $H_0(r_0)$ is the minimum thickness of the idealised profile of a film of radius r_0. Eqn. (12) can be used as the basis of the experimental determination of the line tension τ_B from the $H_0(r_0)$ dependence, but only under conditions of constant H_f and ΔP for changes in r_0.

In Fig. 1*c* we show a scheme which illustrates the condition of mechanical equilibrium of liquid films for a positive value of $\Delta\Omega(H_f)$.

These considerations, and the formulae for the line tensions $æ^f$, τ, and τ_B of symmetrical liquid films, can be extended to asymmetrical liquid films and three-phase systems (Fig. 3).

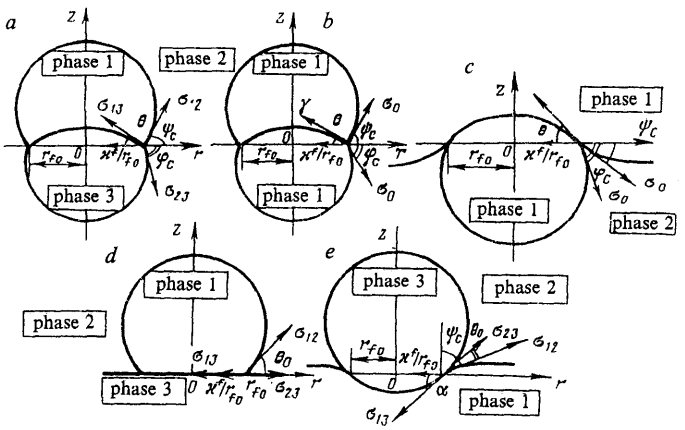


Figure 3. Definition of the line tension in asymmetric liquid films (see text).

At the contact of three fluid (liquid or gaseous) phases (Fig. 3*a*) the condition of mechanical equilibrium is

$$\sigma_{13}\cos\theta + \frac{æ^f}{r_{f0}} = \sigma_{12}\cos\psi_c + \sigma_{23}\cos\varphi_c. \tag{13}$$

If the inter-phase tensions σ_{12}, σ_{13}, and σ_{23} are known the line tension $æ^f$ can be determined by measuring the contact angles θ, ψ_c, and φ_c and the radius of the contact line r_{f0}.[18,31,39] If the interfacial tension σ_{13} is not known we must combine Eqn. (13) with the additional equilibrium equation

$$\sigma_{13}\sin\theta = \sigma_{23}\sin\varphi_c - \sigma_{12}\sin\psi_c. \tag{14}$$

When the phases 1 and 3 are identical we have $\sigma_{12} = \sigma_{23} = \sigma_0$, and $\sigma_{13} = \gamma$ (Fig. 3*b*), leading to a system of equations which describe the mechanical equilibrium of the phases and can be used to determine $æ^f$:[5,34,35]

$$\gamma\cos\theta_0 + \frac{æ^f}{r_{f0}} = \sigma_0(\cos\varphi_c + \cos\psi_c), \qquad (13')$$

$$\gamma\sin\theta_0 = \sigma_0(\sin\varphi_c - \sin\psi_c). \qquad (14')$$

If one of the phases is solid (Figs. 3*d* and 3*e*) the interfacial tensions σ_{13} and σ_{23} are unknown, and the condition of mechanical equilibrium of the three-phase line of contact of radius r_{f0} is written as follows (see Fig. 3*d* for a flat solid surface):

$$\sigma_{13} - \sigma_{23} + \frac{æ^f}{r_{f0}} = \sigma_{12}\cos\theta_0. \qquad (15)$$

On the assumption that the difference $\Delta\sigma = \sigma_{13} - \sigma_{23}$ stays constant during changes in the radius r_{f0} of the contact line we can write an expression analogous to (3):

$$æ^f = r_{f0}\sigma_{12}(\cos\theta_0 - \cos\theta_{0\infty}), \qquad (16)$$

which allows us to determine the line tension $æ^f$ from measurements of the $\theta_0(r_{f0})$ dependence.[32,38] In the case of a spherical solid surface (Fig. 3*e*) the mechanical equilibrium condition is

$$\sigma_{13} - \sigma_{23} + \frac{æ^f}{r_{f0}}\cos\alpha = \sigma_{12}\cos\theta_0. \qquad (15')$$

All these determinations of the line tension are based on the representation of the line tension as a force which stretches or compresses the line of contact. This approach to the determination of the line tension can nominally be called dynamic.

Another approach (arbitrarily termed the energy approach) depicts the line tension as the excess free energy æ referred to unit length of the contact line.[12,15,18,20] All these studies rely on the membrane model of liquid films and of three-phase systems. In particular, Rowlinson and Widom[12] determined the line tension æ by replacing the real system [including the three-phase contact line (Fig. 4*a*)], by an idealised model in which the surfaces A_{12}^{id}, A_{23}^{id}, and A_{13}^{id} have a constant average curvature and constant interfacial tensions σ_{12}, σ_{23}, and σ_{13} (up to the intersection of the surfaces with the contact line). Under these conditions the free energy (grand thermodynamic potential) of the idealised system Ω^{id} can be written

$$\Omega^{id} = -P_1V_1^{id} - P_2V_2^{id} - P_3V_3^{id} + \sigma_{12}A_{12}^{id} + \sigma_{23}A_{23}^{id} + \sigma_{13}A_{13}^{id} + æL, \qquad (17)$$

where L is the length of the contact line. The line tension æ is found from the condition of energy equivalence of the real and the idealised system, i.e. from the equality $\Omega = \Omega^{id}$, where Ω is the free energy of the real system, assumed to be known.

For the contact of a liquid drop (phase 1) with a solid surface (phase 3) in a gaseous medium (phase 2) the expression for the work of formation of the drop (assuming heterogeneous nucleation of water drops on a hydrophobic surface) can be written[1,15,20,66,67] (in our symbols) as

$$-W = \Delta\Omega = -\Delta PV_1^{id} + \sigma_{12}A_{12}^{id} + \Delta\sigma\pi r_{f0}^2 + 2\pi r_{f0}æ, \qquad (18)$$

where $\Delta\sigma = \sigma_{13} - \sigma_{23} - \sigma_{12}$; $\Delta P = P_1 - P_2$; V_1^{id} and A_{12}^{id} are the volume and surface area of the drop (for the idealised model of the drop, see above). All these workers determine the line tension æ on the basis of measurements of the work of heterogeneous nucleation of water drops from a supersaturated vapour onto hydrophobic (liquid or solid) substrates.

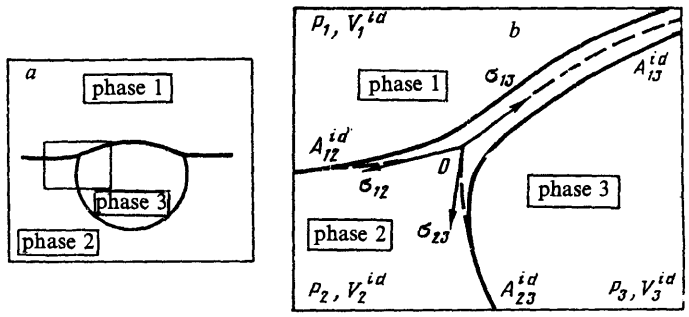


Figure 4. Definition of the line tension as the specific excess free energy of the system (referred to unit length of the contact line) which includes a thin liquid film (see text).

III. Experimental determination of the line tension

The results of experimental determinations of the line tension $æ^f$ are shown in Table 1.

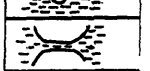
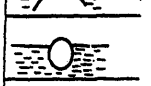
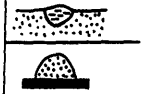
The lack of correlation between the magnitude and sign of the line tension (on the one hand) and other physicochemical parameters such as the angle of contact (on the other hand) is noteworthy. Furthermore the scatter of the $æ^f$ values measured by different workers for identical systems is 3–4 orders of magnitude.[33–35] Whereas Gaydos and Neumann,[38] and also Wallage and Schürch,[39] obtained positive values by measuring the dependence of the contact angle θ_0 on the radius of the contact line r_{f0} (i.e. they noted an increase in θ_0 upon decreasing r_{f0}), Good and Koo[32] found the opposite effect (i.e. they obtained a negative value of the line tension $æ^f$). However, the latter workers[32] attributed this $\theta_0(r_{f0})$ dependence to the roughness of their solid surface, and they called the measured $æ^f$ a pseudo-line tension.

The results of experimental determinations of the line tension $æ^f$ have led some workers[14–16,68] to the following conclusions on the effect of various physicochemical factors on $æ^f$.

For a relatively small coagulation barrier Π_2 (see curve *1* of Fig. 2*c*) very thin Newtonian black films (bilayer membranes) can be formed, with a thickness H_f^N less than 10 nm (curve *1* of Fig. 2*b*) and contact angles $\theta_0 \cong 10°$. These films are formed, for example, at the contact between air bubbles in an aqueous solution of sodium dodecyl sulphate containing NaCl ($c_{NaCl} > 0.36$ mol dm^{-3}).[5,26,34,36,68] In these films the line tension $æ^f$ is negative and equals $\sim 10^{-9}$ N. Upon raising the coagulation barrier Π_2 (curve *2* of Fig. 2*c*) by lowering the concentration of the NaCl electrolyte the contact angle θ_0 monotonically decreases, i.e. the negative specific free energy of the interaction $\Delta\Omega(H_f^N)$ decreases in absolute value. For example, for $c_{NaCl} = 0.32$ mol dm^{-3} the contact

angle is ~8°, and the line tension changes sign ($æ^f = +10^{-9}$ N) [5] (see Table 1).

Table 1. Results of experimental determinations of the magnitude and sign of the line tension æ.

æ, N	System	Experimental scheme	θ_0, deg	Refs.
$\pm 6 \times 10^{-8}$	Oil/aniline/water		> 10	[31]
-10^{-6} to -10^{-5}	Air/water/solid surface		> 10	[32]
$+1.25 \times 10^{-10}$	Air/solid surface/water		~ 25	[25]
$+10^{-10}$ to 10^{-9}	Air/water/air		~ 8	[5]
-1.7×10^{-11}	Air/water/air		< 1	[33]
-10^{-9} to 10^{-9}	ditto		~ 9	[34—36]
-1.9×10^{-10}	Gas/water/hexadecane		~ 50	[1, 20]
$+3 \times 10^{-6}$	Air/oil/Teflon		40—50	[38]
$+2.4 \times 10^{-8}$	Water/dibutyl phthalate/fluorocarbon		30—150	[39]

With an even higher coagulation barrier Π_2 (curve *2* of Fig. 2*c*), when the capillary pressure P_c in the film is less than Π_2, relatively thick ordinary black films are formed (of thickness $H_f^c > 10$ nm, see curve *2* of Fig. 2*b*). If $\Delta\Omega(H_f^c)$ is negative under these conditions the contact angle θ_f is formed. If the absolute value of $\Delta\Omega(H_f^c)$ is high enough we can find the contact angle θ_0, as in curve *1* of Fig. 2*b*. According to Kolarov and Zorin's measurements[33] the contact angle for $c_{NaCl} = 0.1$ mol dm^{-3} is $\theta_0 < 0.5°$. For ordinary black films Platikanov and Nedyalkov[68] found a positive value of $æ^f$, which is incompatible with Kolarov and Zorin's value:[33] a negative line tension $æ^f = -1.7 \times 10^{-11}$ N. This value of $æ^f$ agrees well with the numerical values of the line tension τ reported[49] for ordinary black films.

Let us examine some other methods of determining the line tension $æ^f$ experimentally.

Torza and Mason[31] measured the angles of contact formed by drops of silicone oil (phase 1) and aniline (phase 3) in water (phase 2) (see Fig. 3*a*), and calculated the line tension $æ^f$ by formula (13). The results lay in the range of $\pm 6 \times 10^{-8}$ N, denoting that the precision of the method was inadequate.

In the experiment reported by Mingins and Scheludko[25] glass microspheres (phase 1) of various diameters (< 50 μm) treated with an aqueous 0.01 M solution of octyltrimethylammonium bromide fell freely in water (phase 2) towards a water—air (phase 3) interface (see Fig. 3*e*). Spheres with a radius smaller than some critical value R_c formed ordinary black films with a relatively large thickness H_f^c (see curve *2* of Fig. 2*b*) because their mass was insufficient to overcome the coagulation barrier Π_2. According to those workers[25] a positive line tension $æ^f$ (tending to shorten the contact line) prevents the rupture of the liquid water film. Microspheres with a radius greater than R_c can overcome the line tension and fracture the black film, as can be seen in the microscope. The line tension was calculated by the formula[16,25]

$$æ^f = \frac{(2\rho g\sigma)^{1/2}}{3}(1 - \cos\theta_0)R_c^2, \tag{19}$$

which gives $R = 20$ μm and $æ^f = +1.25 \times 10^{-10}$ N for the known values $\theta_0 = 25°$, $\sigma = 70$ mJ m^{-2}, and $\rho = 1.48$ g cm^{-3}.

In the experiment reported by Platikanov, et al.[5] a similar method[25] was used, but the glass spheres were replaced by microscopic gas bubbles (phase 3) which floated in an aqueous solution of sodium dodecyl sulphate (phase 2) and came into contact with a water—air (phase 1) interface (Fig. 3*c*). The diffusion of gas through the film decreased the radius of the bubble but increased the capillary pressure P_c, and for $P_c > \Pi_2$ (see Fig. 2*c*) the ordinary black films of thickness H_f^c (curve *2* of Fig. 2*b*) which had been formed initially were spontaneously converted into thin Newtonian black films of thickness H_f^N (curve *1* of Fig. 2*b*), as noted in the microscope by the sudden change in reflectance (the grey colour being replaced by black) and by the increase in the radius of the bubbles.

As reported,[5,25] the conversion of ordinary black films into Newtonian black films opposes the positive line tension tending to shorten the contact line and thus to suppress the increase in area of the film. Under these conditions the expression for the line tension $æ^f$ obtained from the mechanical equilibrium condition of the bubble becomes (in our symbols)

$$æ^f = 2\sqrt{\frac{2}{3}\rho g\sigma_0}(1 - \cos\theta_{0\infty})R_{cr}^2, \tag{20}$$

where $\theta_{0\infty}$ is the angle of contact corresponding to infinitely large films (i.e. to a straight contact line), and R_{cr} is the critical radius of the gas bubble corresponding to the rupture of the ordinary black film.

The writer has pointed out[40] that this interpretation of the role of line tension in the stabilisation of ordinary black films is over-simplified and, in general, incorrect, because the same effect (i.e. the suppression of the increase in area of the film) is produced by negative line tension: it is the effect of bulk and surface forces contributing to the free energy, and not of line forces only, as could have been thought at first sight. An alternative explanation of the results, based on the theory of adhesion of liquid particles, has been suggested.[8]

Let us examine the results of measurements of the line tension æ through measurements of the work of heterogeneous nucleation of a water phase from the supersaturated vapour onto hydrophobic substrates.[1,15,20,66,67] The authors' interpretation of the results is based on the following arguments.

From measurements of the critical supersaturation S_0 of water vapour in the chamber the radius of curvature R of the surface of the nuclei is determined by the Thompson—Gibbs formula

$$P_c = \frac{kT}{\bar{v}}\ln S_0, \tag{21}$$

where $P_c = 2\sigma_0/R$ is the capillary pressure in the water nucleus, $\bar{v}$ is the molar volume of water, and k is Boltzmann's constant. Then, on the assumption that the heterogeneous creation of a new phase on reaching the critical supersaturation S_0 of water vapour is barrierless, i.e. that the work of formation W of the nuclei is zero, Eqn. (18) is re-written (for a solid hydrophobic surface, see Fig. 3*d*) as:

$$0 = W = \frac{2}{3}\sigma_{12}\pi R^2(1+\cos^3\theta_0) + \pi r_{f0}^2\Delta\sigma + 2\pi r_{f0}\text{æ}, \qquad (22)$$

where $r_{f0} = R\sin\theta_0$ is the radius of the contact between the nucleus and the solid substrate. Eqn. (22) establishes the relationship between the line tension æ and the parameters θ_0 (the angle of contact), R (the radius of the nucleus), and also σ_{12} and $\Delta\sigma$. Then, by using (15) (which relates the line tension æ^f to the contact angle θ_0) we can solve Eqn. (22) and obtain an expression for the line tension æ on the assumption that $\text{æ} = \text{æ}^f$.

The line tension can be obtained in a similar way from data on the heterogeneous nucleation on a liquid hydrophobic substrate (Fig. 4*a*).

Scheludko, et al.[1] give the results of one experiment (S_0 = 41.9% and $R \cong 3$ nm), and also the line tension calculated from them (æ = -0.8×10^{-10} N) by using the parameters σ_{12} = 24.1 mJ m^{-2}, σ_{23} = 53.2 mJ m^{-2}, σ_{13} = 73 mJ m^{-2}, $\theta_{0\infty}$ = 28.93°, and $\varphi_{c\infty}$ = 41.59° (see Fig. 3*c*).

Scheludko, et al.[1] believe that ignoring the negative line tension (which lowers the work of heterogeneous nucleation) would make the critical supersaturation very much higher: for the example given it would be S_0 = 105%, i.e. 2.5 times higher.

The reported line tension (æ = -0.8×10^{-10} N), and also the suggestion that this method can be used to determine the line tension, have attracted critical comments by the present writer.[40,42] The main objections to the determination of the line tension by this method are the following.

1. The precision claimed for the determination of the angles of contact $\theta_{0\infty}$ and $\varphi_{c\infty}$ is unacceptably high. The error in the measurement of these angles is about 0.5° (the uncertainty in the sessile drop method), corresponding to an error in the determination of the line tension of the order of $\Delta\text{æ} \simeq \pm 10^{-10}$ N, i.e. of the same order as the measured quantity æ = -0.8×10^{-10} N.

2. For drops with a diameter of 3 nm the interfacial tension σ_{12}, σ_{23}, and σ_{13} differ from the corresponding macroscopic values since the drop size is comparable with the radius of action of the surface forces (molecular and ionic/electrostatic). In this case the drop cannot be treated as a substance in the thermodynamic sense, and the replacement of the interfacial tensions by their macroscopic values is equivalent to ascribing bulk and surface excess thermodynamic parameters to the contact line markedly different from the corresponding values for the reference phase 3 (see Fig. 4). In particular, the decrease in the critical supersaturation for nucleation S_0 can be more convincingly attributed to the decreased interfacial tension of droplets with a diameter as small as R = 3 nm than to the effect of the line tension.

In the case of wetting films only one attempt to determine experimentally the line tension τ_B has so far been reported [see Eqn. (11)].[63] Those workers used Eqn. (12) to calculate the line tension τ_B, and obtained $\tau_B = \pm 3 \times 10^{-11}$ N from the experimental $H_0(r_0)$ dependence (see Fig. 3*d*) by assuming a constant film thickness H_f (h_0 in Zorin's symbols[63]). We should stress that since the film thicknesses H_0 and H_f can be measured only to within ± 5 nm as a function of the radius r_0, and since H_f could decrease when r_0 increases (i.e. when the difference in hydrostatic pressure ΔP increases), Eqn. (12) should be replaced by

$$\frac{\tau_\beta}{r_0} = \Delta P[H_0(r_0) - H_0(\infty)] - 2\Delta\sigma_f(r_0), \qquad (23)$$

where $\Delta\sigma_f(r_0) = \sigma_f(r_0) - \sigma_f(\infty)$, and the following approximate relation applies;

$$2\Delta\sigma_f(r_0) \simeq \int_{H_f(r_0)}^{H_f(\infty)} \Pi(H)dH \simeq \Delta P[H_f(r_0) - H_f(\infty)]. \qquad (24)$$

We shall use Zorin's experimental results[63] to calculate the error in the measurement of the line tension ($\Delta\tau_\beta$) due to the failure to allow for the possible change in the actual thickness of the film ($\Delta H \simeq \pm 5$ nm). Assuming $\Delta P \simeq 150$ Pa we obtain, for a film of radius r_0 = 50 μm,

$$\Delta\tau_B \simeq r_0\Delta\sigma_f(r_0) \simeq (50\times10^{-6})\times 1.50\times(\pm 5\times10^{-9}) = \pm 3.7\times10^{-11}\text{H}.$$

Evidently, the error in the determination of the line tension is of the same order as the measured quantity.

IV. Theories of the line tension

We shall now examine existing theories of the line tension, which give a relationship between the line tension and physicochemical parameters such as the radius r and the thickness H of the liquid film, the capillary pressure P_c, and the interfacial tension σ_0, and also parameters which characterise the form of the disjoining pressure isotherm $\Pi(H)$ as a function of the local thickness of the film (H).

An analytical expression for the line tension τ [see Eqn. (4)] was first proposed by de Feijter and Vrij,[49] who used a thermodynamic model of the film based on the presence of two interfaces (Fig. 2*c*). They discussed the mechanical equilibrium of the element of volume *ABCDEFGL* of a symmetrical curved liquid film (Fig. 5*a*), and they wrote the fundamental equation for the equilibrium of this film by equating to zero the projection on the 0r axis of the resultant of all the surface and bulk forces acting on the element of volume:

$$\frac{d}{dr} = [2\sigma(H)r\cos\varphi(H) + \Delta PHr] - [2\frac{\sigma(H)}{\cos\varphi(H)} + \Delta PH] = 0, \qquad (25)$$

where $\sigma(H)$ is the local interfacial tension in a film of thickness H; $\varphi(H)$ is the local value of the angle of contact; $\Delta P = P_\beta - P_\alpha$ is the difference in hydrostatic pressure between the α and β phases respectively. Then, by invoking the mechanical equivalence (in the sense of mechanical equilibrium) of the real film (Fig. 5*b*) and of its idealised model (Fig. 5*c*) they arrived at Eqn. (4) and the following analytical expression for the line tension (see Fig. 2*c*):

$$\tau = \int_0^R \left[\frac{2\sigma(H)}{\cos\varphi(H)} + \Delta PH\right]dr - \int_{r_f}^R \left[\frac{2\sigma_0}{\cos\varphi_{id}(H)} + \Delta PH_{id}\right]dr_{id} -$$

$$-(2\sigma_f + \Delta PH_f)r_f, \qquad (26)$$

where R is the distance along the 0$_r$ axis corresponding to a zero disjoining pressure, i.e. $\sigma(H) = \sigma_0$, where σ_0 is the interfacial tension of the noninteracting surfaces and *id* indicates a quantity

relating to the idealised profile. As we have pointed out,[41,42,55] Eqn. (26) (obtained[49] for curved films, i.e. for a curved contact line) is incorrect, though it approaches asymptotically the correct expression for a straight contact line (for $r_f \to \infty$):

$$\tau = \int_{H_f}^{\infty} \sigma(H)\sin\varphi(H)dH - \int_{H_f}^{\infty} \sigma_0 \sin\varphi_{id}(H)dH_{id}. \qquad (27)$$

For the case of a straight contact line the following expression relating the line tension τ to the specific free energy of the interaction $|\Delta\Omega(H_f)|$ [see Eqn. (8) in the limit of $\Delta\Omega(H_f) \ll \sigma_0$]:

$$\tau = \sigma_0^{1/2}\left\{\int_{H_f}^{\infty}\left[\Delta\Omega(H) - \Delta\Omega(H_f) + \Delta P(H - H_f)\right]^{1/2} dH - \right.$$
$$\left. - \int_{H_f}^{\infty}\left[-\Delta\Omega(H_f) + \Delta P(H_{id} - H_f)\right]^{1/2} dH_{id}\right\}, \qquad (28)$$

or for very small contact angles θ_f (ignoring the terms containing ΔP)

$$\tau = \sigma_0^{1/2}\left\{\int_{H_f}^{\infty}\left[\Delta\Omega(H) - \Delta\Omega(H_f)\right]^{1/2} - \left[-\Delta\Omega(H_f)\right]^{1/2}\right\}dH. \qquad (29)$$

The expressions (27) and (28) were used[49] for numerical calculations of the line tension in ordinary and in Newtonian black films.

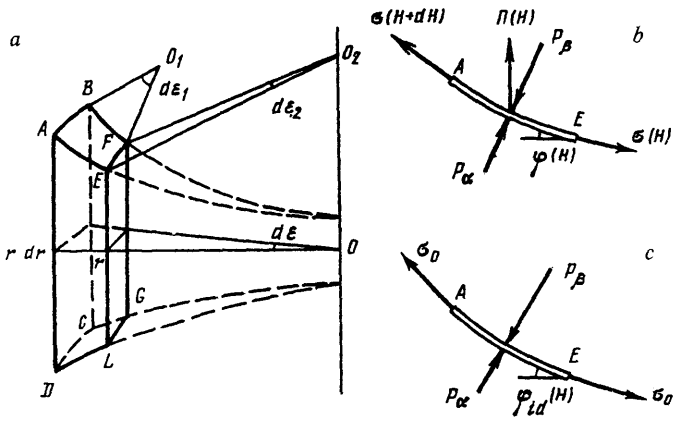


Figure 5. Formulation of the fundamental equilibrium equation of a thin liquid film [Eqn. (26)]: *a*, element of volume of a curved liquid film; *b*, equilibrium of the film surface in the transition region; *c*, equilibrium of the film surface in the Plateau region.

An approximate expression for τ, similar to Eqn. (26), was later obtained by other workers.[15,69,70]

The exact analytical expression (26) for the line tension τ was first obtained by Babak[55,64,65] in terms of the thermodynamics of the transition region of thin liquid films.[41] In particular, he showed[55] that the mechanical equilibrium of an element of volume of a thin liquid film (see Fig. 5*a*), like the element considered by de Feijter and Vrij,[49] is described by the system of equations:

$$\sigma(H)k(H) + \Pi(H)\cos\varphi(H) - \Delta P = 0, \qquad (30)$$

$$\Pi(H) = -\left.\frac{\partial\sigma(H)}{\partial H}\right|_{T,\mu_i,A} \qquad (31)$$

where $\Pi(H)$ is the disjoining pressure in the film as a function of the local thickness H, and $k(H)$ is the mean curvature of the film surface, which can be written (for a curved film)

$$k(H) = \frac{d\sin\varphi(H)}{dr} + \frac{\sin\varphi(H)}{r}. \qquad (32)$$

The Gibbs–Duhem equation (31) describes the equilibrium of the film surface in the direction of the tangent to this surface, since it can be rewritten [allowing for the fact that $dH = dl/2 \sin\varphi(H)$, where dl is an element of length of the tangent] as

$$\Pi(H)\sin\varphi(H)dl = -2d\sigma(H). \qquad (33)$$

Eqn. (30) describes the equilibrium of the film surface in the direction normal to the surface (see Fig. 5*a*) in the presence of a gradient of interfacial tension in the transition region of the film.

Eqn. (30) reduces to the well known equation for the mechanical equilibrium of a plane-parallel film of thickness H_f (which is also a definition of the disjoining pressure, proposed by Deryagin and Churaev[72]):

$$\Pi(H_f) = \Delta P = P_\beta - P_\alpha, \qquad (34)$$

allowing for the fact that in this region $k(H_f) = 0$ and $\varphi(H_f) = 0$, and that in the Laplace equation for noninteracting tension surfaces

$$\sigma_0 k_0 = \Delta P = P_\beta - P_\alpha, \qquad (35)$$

since $\sigma(H) = \sigma_0$ and $\Pi(H) = 0$.

The exact analytical expression for the line tension τ_d is[55,64,65]

$$\tau_d = r_f\left\{\int_{H_f}^{\infty}\frac{\sigma(H)\sin\varphi(H)}{r}dH - \int_{H_f}^{\infty}\frac{\sigma_0\sin\varphi_{id}(H)}{r_{id}}dH_{id}\right\}, \qquad (36)$$

where τ_d is the dynamic line tension (see Fig. 2*c*), obtained from the mechanical equilibrium condition of the element of volume of the liquid film (see Fig. 5*a*), in contrast to the energy line tension τ_e which appears in Eqn. (17) for the free energy of the film.

The expression for τ_d was obtained as follows. The integration of the fundamental mechanical equilibrium equation (30) over the thickness $H(r)$ of the real profile between the local value H and the value H_p in the Plateau region of the meniscus [where $\varphi(H_p) = \varphi_p$ and $\Pi(H_p) = 0$] leads to an invariant expression, independent of the local thickness of the film:

$$2\sigma_0\cos\varphi(H) + \Delta PH + \Delta\Omega(H) + \tau_0(H) +$$
$$+ \int_{H}^{H_p}\frac{\sigma(H)\sin\varphi(H)}{r}dH = 2\sigma_0\cos\varphi_p + \Delta PH_p, \qquad (37)$$

where the function

$$\tau_0(H)=\int_H^\infty\left[\frac{1}{2}\Delta\Omega(H)\frac{d\sin\varphi(H)}{dr}-\Pi(H)(1-\cos\varphi(H))\right]dH, \quad (38)$$

is identically equal to zero.[42]

Similarly, the integration of the Laplace equation (35) (see Fig. 5*b*) over the thickness of the idealised profile $H_{id}(r)$ between the limits H_{id} and H_p also gives an invariant, independent of the thickness of the idealised profile:

$$2\sigma_0\cos\varphi_{id}(H)+\Delta PH_{id}+\int_{H_{id}}^{H_P}\frac{\sigma_0\sin\varphi_{id}(H)}{r_{id}}dH_{id}=2\sigma_0\cos\varphi_P+\Delta PH_P. \quad (39)$$

By equating the invariants (37) and (39) we obtain a fundamental equation which was first proposed by the present writer:[55,64]

$$2\sigma_0\cos\varphi(H)+\Delta PH+\Delta\Omega(H)+\int_H^{H_P}\frac{\sigma(H)\sin\varphi(H)}{r}dH=$$

$$=2\sigma_0\cos\varphi_{id}(H)+\Delta PH_{id}+\int_{H_{id}}^{H_P}\frac{\sigma_0\sin\varphi_{id}(H)}{r_{id}}dH_{id}, \quad (40)$$

and which is valid for any values of $H(r)$ and $H_{id}(r)$ in the range of interest. This equation is universal, and it can be used to obtain all the known film equilibrium equations which have been used as the basis of the various thermodynamic models as well as the corresponding expressions for the line tensions. We shall prove this assertion with a few examples.

By inserting $H = H_f$ and $\varphi(H_f) = 0$ into the left-hand side of Eqn. (40), and $H_{id} = H_f$ and $\varphi_{id}(H_f) = \theta_f$ into the right-hand side (see Fig. 2*c*), and using the equality $\Delta\Omega(H_f) = 2\sigma_f - 2\sigma_0$, we obtain

$$2\sigma_f+\frac{\tau_d}{r_f}=2\sigma_0\cos\theta_f,$$

which is equivalent to Eqn. (4) and defines the equilibrium of the film in terms of the model of two interfaces, while the line tension τ_d is given by the exact analytical expression (36).

On the other hand if we use the membrane model of the film (see Fig. 2*b*) we must insert into the left-hand side $H = H_f$ and $\varphi(H_f) = 0$, and into the right-hand side $H = 0$ and $\varphi_{id(0)} = \theta_0$. In this case, using the definition of the film tension

$$\gamma = 2\sigma_f + \Delta PH_f, \quad (41)$$

we obtain from Eqn. (40) the condition of mechanical equilibrium of the film

$$\gamma+\frac{æ_d}{r_{f0}}=2\sigma_0\cos\theta_0,$$

which coincides with Eqn. (1), while the corresponding line tension $æ_d \equiv æ^f$ is determined by the exact analytical expression[55]

$$æ_d=r_{f0}\left\{\int_{H_f}^\infty\frac{\sigma_0\sin\varphi(H)}{r}dH-\int_0^\infty\frac{\sigma_0\sin\varphi_{id}(H)}{r_{id}}dH_{id}\right\}. \quad (42)$$

From (36) and (42) we obtain a relationship between the line tensions $æ_d$ and τ_d:[55]

$$\frac{æ_d}{r_{f0}}=\frac{\tau_d}{r_f}-\int_0^{H_f}\frac{\sigma_0\sin\varphi_{id}(H)}{r_{id}}dH_{id}. \quad (43)$$

In the case of a straight contact line (i.e. for $r_f\to\infty$) we obtain from Eqns. (36) and (42) the following expressions for the corresponding line tensions τ_d^0 and $æ_d^0$:

$$\tau_d^0=\int_{H_f}^\infty\sigma(H)\sin\varphi(H)dH-\int_{H_f}^\infty\sigma_0\sin\varphi_{id}(H)dH_{id}, \quad (44)$$

$$æ_d^0=\int_{H_f}^\infty\sigma(H)\sin\varphi(H)dH-\int_0^\infty\sigma_0\sin\varphi_{id}(H)dH_{id}, \quad (45)$$

and the following expression also applies:[55]

$$æ_d^0=\tau_d^0-\int_0^{H_f}\sigma_0\sin\varphi_{id}(H)dH_{id}. \quad (46)$$

Thus the generalised line tension theory[55,64] allows us to reconcile the various definitions of the line tension, corresponding to different thermodynamic models of a thin liquid film. This is a very valuable attribute, especially since it has been stated[15,33,57] that the line tensions τ_d [defined by Eqn. (4)] and $æ_d$ [defined by Eqn. (1)] are identical, and a good agreement has been reported between the values of æ (measured, or calculated theoretically) and of τ_d (calculated by de Feijter and Vrij[49]). Nevertheless the line tension $æ_d$ for ordinary black films can be 10^3 times greater than the line tension τ_d.[55,71] We shall examine this difference more closely below.

The following conclusion on the properties of $æ_d$ and τ_d have been formulated:[40] 1) the line tensions $æ_d$ and τ_d are different quantities; 2) $æ_d$ (unlike τ_d) depends on the film thickness H_f and coincides with τ_d when $H_f = 0$; 3) $æ_d$ is more "negative" than τ_d, since the integrals in Eqns. (43) and (46) are positive.

The writer has obtained[55,64,65] a definition of the line tension $\tau_{Bd} \equiv \tau_B$ [see Eqn. (11)], corresponding to the case of a positive $\Delta\Omega(H_f)$, for which a contact angle is not formed, and has derived an expression for this line tension:

$$\tau_{Bd}=r_0\left[\int_{H_f}^\infty\frac{\sigma(H)\sin\varphi(H)}{r}dH-\int_{H_0}^\infty\frac{\sigma_0\sin\varphi_{id}(H)}{r_{id}}dH_{id}\right], \quad (47)$$

where r_0 is the radius of the film (see Fig. 2*d*). In the case of a straight contact line Eqn. (47) reduces to

$$\tau_{Bd}^0=\int_{H_f}^\infty\sigma(H)\sin\varphi(H)dH-\int_{H_0}^\infty\sigma_0\sin\varphi_{id}dH_{id}. \quad (48)$$

The generalised line tension theory[40,41,42] also yields expressions for the "energy" line tensions, which appear in the expressions for the free energy of systems which include a liquid film. For example, for the model of a liquid film which stipulates two interfaces, the expression for the grand thermodynamic potential of the system (see Fig. 2*c*) becomes

$$\Omega^{id}=-P_\alpha V_\alpha^{id}-P_\beta V_\beta^{id}+\int_{A^{id}}\sigma(H)dA^{id}+2\pi r_f\tau_e, \quad (49)$$

where the integration is carried out over the surface of the idealised model of the film, with $\sigma(H) = \sigma_0$ on the side surface and $\sigma(H) = \sigma_f$ on the plane parallel surface.

From the condition of energy equivalence of the real film and its idealised model we obtain an expression for the line tension corresponding to a negative specific free energy of interaction $\Delta\Omega(H_f)$ in the film:[42]

$$\tau_e = \frac{1}{r_f}\int_0^R \left[\frac{2\sigma(H)}{\cos\varphi(H)} + \Delta PH\right] rdr - \int_{r_f}^R \left[\frac{2\sigma_0}{\cos\varphi_{id}(H)} + \Delta PH_{id}\right] rdr - \\ -[2\sigma_f + \Delta PH_f]r_f. \qquad (50)$$

By comparing the exact expression for the line tension τ_e [Eqn. (50)] with the approximate expression (26) obtained by de Feijter and Vrij[49] for the dynamical line tension τ we find substantial differences in spite of their structural similarity. Thus, we conclude that the first exact expression for the line tension τ_e was published in the current year.[42]

On the other hand it is clear that the dynamical line tension τ_d [defined by the expression (36)] differs from the energy line tension τ_e [defined by the expression (50)] in the case of a curving contact line. For a straight contact line the dynamical (τ_d^0) and the energy line tension coincide and are defined by the relationship (44).

The first exact analytical expression[42] for the energy line tension $æ_e$, corresponding to the membrane model of the film for $\Delta\Omega(H_f) < 0$, and the expression for the energy line tension τ_{Be}, corresponding to $\Delta\Omega(H_f) < 0$, are shown below:

$$æ_e = \frac{1}{r_{f0}}\int_0^R \left[\frac{2\sigma(H)}{\cos\varphi(H)} + \Delta PH\right] rdr - \frac{1}{r_{f0}}\int_{r_0}^R \left[\frac{2\sigma_0}{\cos\varphi_{id}(H)} + \Delta PH_{id}\right] rdr - \gamma r_0, \qquad (51)$$

$$\tau_{Be} = \frac{1}{r_0}\int_0^R \left[\frac{2\sigma(H)}{\cos\varphi(H)} + \Delta PH\right] rdr - \frac{1}{r_0}\int_{r_0}^R \left[\frac{2\sigma_0}{\cos\varphi_{id}(H)} + \right. \\ \left. + \Delta PH_{id}\right] rdr - [2\sigma_f + \Delta PH_f]r_0. \qquad (52)$$

In particular we showed that the equalities $æ_d^0 = æ_e^0$ and $\tau_{Bd}^0 = \tau_{Be}^0$ apply for a straight line of contact [see Eqns. (45) and (48) respectively].

Thus the first exact analytical expressions for the line tensions in terms of various thermodynamic models of thin liquid films have been derived from our generalised theory of line tension.[40,64] These expressions have been used[40–42,55,64,71] in numerical calculations of the line tension.

V. Calculation of the line tension by numerical methods

As was pointed out by de Feijter and Vrij,[49] the line tension τ_d^0 defined by Eqn. (27) can only be negative if the specific free energy of interaction $\Delta\Omega(H_f)$ in a film of thickness H_f is negative, i.e. when finite contact angles θ_f exist and the disjoining pressure isotherm is characterised by one coagulation minimum. This conclusion is self-evident, since in this case the product $\sigma(H)\sin\varphi$ is smaller than the product $\sigma_0 \sin\varphi_{id}$ over the whole integration range in Eqn. (27). We have shown[55,64] that under these conditions the line tension $æ_d^0$ determined in terms of the membrane model of the film [see Eqn. (1)] is even more negative if the sign of the integral in Eqn. (46) is taken to be positive. In the case of positive $\Delta\Omega(H_f)$ the line tension τ_{Bd}^0 defined by the expression (10) can only be positive[55,64] if the disjoining pressure $\Pi(H)$ is positive over the whole transition region. This obvious corollary follows from Eqn. (48) if we stipulate that the product $\sigma(H)\sin\varphi$ is greater than the product $\sigma_0 \sin\varphi_{id}$ over the whole integration region.

In the more complex disjoining pressure isotherms the sign of the line tension cannot be predicted from the form of Eqns. (44), (45), or (48). In this case the problem of the magnitude and sign of the line tensions determined on the basis of different thermodynamic models can be solved only by direct numerical calculations. The results of these calculations are examined in this section.

1. Choice of disjoining pressure isotherm for numerical calculations of the line tension

Figure 6 shows different types of disjoining pressure isotherm [$\Pi(H)$] used in line tension calculations.

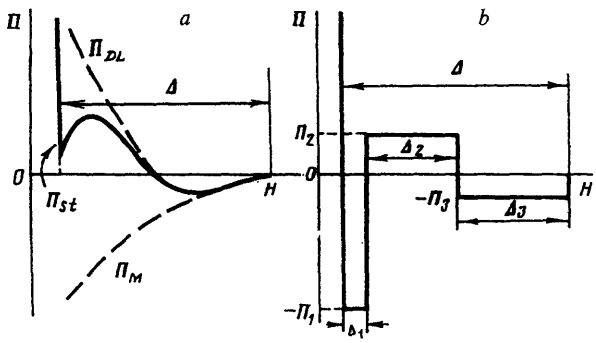


Figure 6. $\Pi(H)$ disjoining pressure isotherms used to calculate the line tension by de Feijter and Vrij[49] (*a*) and by Babak[40–42,55,64,65,71] (*b*).

De Feijter and Vrij[49] used a $\Pi(H)$ isotherm corresponding to the Deryagin–Landau–Verwey–Overbeek (DLVO) theory (see Fig. 6*a*), but including a very strong repulsion for $H \leqslant 4$ nm. This isotherm is thought to be characteristic of foam films stabilised by SAS and able to form stable Newtonian black films. The $\Pi(H)$ isotherm had the following analytical form:

$$\Pi(H) = -\frac{A}{6\pi H^3} + 1.59 \times 10^8 c \exp(-æH);\ H > 4 \text{ nm};$$

$$\Pi(H) = +\infty,\ H \leqslant 4 \text{ nm}, \qquad (53)$$

where A is the Hamaker constant, c is the concentration of electrolyte, and $æ = 3.28 \times 10^9$ s$^{1/2}$ m^{-1} is the Debye length. The line tension τ was calculated by formula (29) for several values of the parameters: $A = (0.2-4) \times 10^{-19}$ J, $c = 10^{-3}-\infty$ mol dm^{-3}, and $\Delta P = 25-100$ Pa.

As can be seen from Table 2 the line tension depends on the difference in hydrostatic pressures, on the contact angle (or specific free energy of interaction in the film), on the equilibrium thickness of the film, and on the radius of action of the molecular forces. De Feijter and Vrij[49] concluded that in ordinary and in Newtonian black films the line tension τ has a negative sign if the contact angle θ_f is finite, because varying these parameters over their actual existence range did not change the sign of the line tension from negative to positive. This conclusion is inconsistent with the experimental results of Platikanov, et al.[5,34,37,68] and of Scheludko, et al.,[16] who obtained positive linear tensions for ordinary black films.

Table 2. Line tension τ calculated[49] by the approximate formula (29) for different values of the concentration of electrolyte c, of the difference in hydrostatic pressure ΔP, of the film thickness H_f, of the contact angle θ_f, and of the specific free energy of interaction $\Delta\Omega(H_f)$ in a film of thickness H_f and radius of action of the surface forces Δ (σ_0 = 30 mJ m^{-2}).

No.	c, mol dm^{-3}	ΔP, Pa	H_f, nm	θ_f, min	$10^{-6}\Delta\Omega(H_f)$, J m^{-2}	Δ, μm	$10^{-12}\tau$, N
1	0.001	25	81	5	-0.063	18.5	-2.1
2	0.002	25	60	13	-0.42	14.4	-3.1
3	0.01	25	26	34	-2.93	7.6	-4.8
4	0.05	25	10	87	-19.21	2.0	-5.6
5	∞	25	4	248	-256.1	1.0	-5.2
6	0.01	25	31	12	-0.37	11.5	-1.5
7	0.01	25	26	34	-2.93	7.6	-4.8
8	0.01	25	19	89	-20.1	3.8	-11.3
9	0.01	25	26	34	-2.93	7.6	-4.8
10	0.01	50	25.5	34	-2.93	6.0	-4.6
11	0.01	100	25	34	-2.93	4.7	-4.2

It follows from Table 2 that the effects of the parameters H_f, θ_f [or $\Delta\Omega(H_f)$], ΔP, and Δ on the line tension τ are inter-related: this prevents us from identifying the effects of the individual parameters on τ and from constructing the appropriate analytical expressions. In order to study the individual contribution of these parameters to the line tension the writer[55,64,71] has suggested using the idealised $\Pi(H)$ isotherm shown in Fig. 6*b*.

The main advantage of this isotherm over the DLVO isotherm of Fig. 6*a* is that in numerical calculations the equilibrium film thickness H_f can be kept constant, and the form parameters of the $\Pi(H)$ isotherm change in a way which keeps the angle of contact θ_f [or the parameter $\Delta\Omega(H_f)$] constant. Thus we are able to distinguish the effects of the contact angle θ_f on τ_d for constant values of the other parameters (H_f, ΔP, Δ_i, Π_i), and therefore we can establish the appropriate correlation dependences.

We should also note that the writer[64] used a $\Pi(H)$ isotherm which allows for the steric repulsion between adsorption layers of macromolecules in a liquid film, given by the Hesselink–Vrij–Overbeek (HVO) theory[73] as

$$\Pi(H) = a(1 - bH^2)H \exp(-cH^2), \qquad (54)$$

where a, b, and c are functions of the parameters which characterise the conformational state of macromolecules in the solution and their interactions.

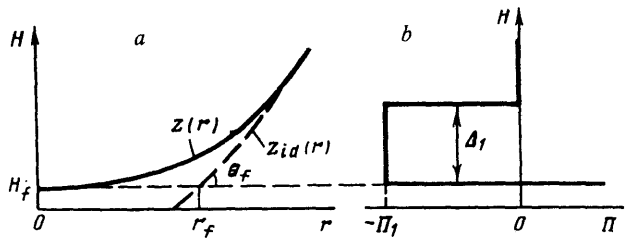


Figure 7. Idealised disjoining pressure isotherm $\Pi(H)$ with one coagulation minimum (see text).

Table 3. Line tension τ_d^0 calculated[79] by the exact formula (44) for different values of the parameters Δ_1 and Π_1 which describe the idealised disjoining pressure isotherm shown in Fig. 7, and also different values of the hydrostatic pressure ΔP, the contact angle θ_f, and of the specific free energy of interaction $\Delta\Omega(H_f)$ in a film of thickness H_f (σ_0 = 30 mJ m^{-2}).

ΔP, Pa	Δ_1, nm	Π_1, Pa	θ_f, min	$10^{-6}\Delta\Omega(H_f)$, J m^{-2}	$10^{-12}\tau_d^0$, N
10	10	10^2	49	-2	-0.92
10^2	10	10^2	49	-2	-0.78
10^3	10	10^2	49	-2	-0.44
10^4	10	10^2	49	-2	-0.17
10^5	10	10^2	49	-2	-0.06
10^3	10	10^3	154	-20	-2.45
10^3	10	10	16	-0.2	-0.02
10^3	1	10^3	49	-2	-0.08
10^3	100	10	49	-2	-1.71
10^2	10	10^3	154	-20	-29.10
10^2	10	10^4	482	-200	-94.00
10^2	1	10^5	482	-200	-9.43

2. Magnitude and sign of the line tension for a $\Pi(H)$ isotherm with one coagulation minimum

Let us first consider the $\Pi(H)$ disjoining pressure isotherm characterised by a single coagulation minimum (Fig. 7). It is obtained from the isotherm shown in Fig. 6*b* by the formal substitution $\Pi_2 = \Pi_3 = 0$, and it can describe Newtonian black films at relatively high concentrations of electrolyte (when the ionic–electrostatic repulsive forces in the electrical double layer are effectively suppressed and the coagulation barrier Π_2 disappears). Furthermore this disjoining pressure isotherm can describe ordinary black films (in which the radius of action of the molecular forces is much greater than the Debye length æ and the disjoining pressure Π_2 is greater than the capillary pressure in the film). The effect of the

height of the coagulation barrier on the magnitude and sign of the line tension will be discussed in depth below.

Table 3 shows the results of calculations of the line tension τ_d^0 by formula (44) as a function of the parameters Δ_1 and Π_1, which characterise the form of the idealised disjoining pressure isotherm $[\Delta P, \theta_f, \Delta\Omega(H_f)]$ for a constant interfacial tension.[40–42,55,64,71]

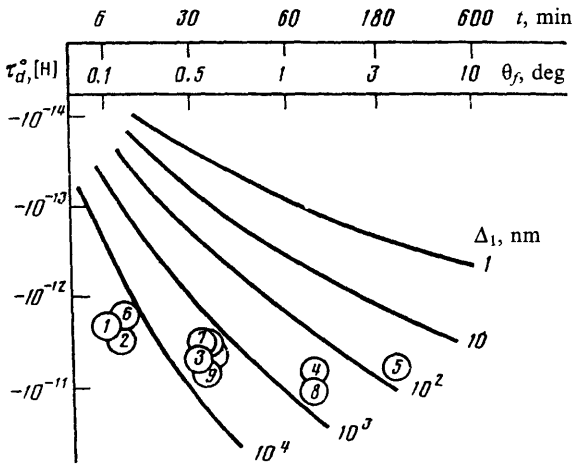


Figure 8. Plots of the line tension τ_d^0 against the contact angle θ_f for some values of the parameter Δ_1 which characterises the radius of action of the surface forces. The numbers by the curves denote the line tension value (τ) in Table 2 calculated by de Feijter and Vrij[49] by the approximate formula (29).

We note that the line tension τ_d^0 is negative for all forms of the $\Pi(H)$ isotherm, and also for the whole range of contact angles θ_f and of differences in hydrostatic pressure Δp examined. It is clear from the plots of the line tension τ_d^0 against the contact angle shown in Fig. 8 for constant values of the parameter Δ_1 (the action radius of the molecular forces) that the line tension tends towards zero as the angle of contact tends towards zero. Under these conditions the line tension is very sensitive to Δ_1, increasing as Δ_1 increases. We can see from Table 3 that the line tension τ_d^0 decreases as the difference in hydrostatic pressure ΔP increases while the other parameters stay constant.

Fundamental differences are revealed by comparing the dependences on the contact angle θ_f of the line tension τ obtained by de Feijter and Vrij,[49] and shown in Fig. 8, with the calculated $\tau_d^0(\theta_f)$ dependences.[42] For example, a change in the angle of contact from 0.5° to 3° is reported[49] to produce only a slight increase in the line tension (see the numbered points in Fig. 8). However, the line tensions in this range of θ_f actually increase by a factor of 30–100, depending on the parameter Δ_1 [see the corresponding $\tau_d^0(\theta_f)$ curves in Fig. 8]. The reason for this large difference between the calculated $\tau_d^0(\theta_f)$ dependences is self-evident when one notes that the disjoining pressure isotherm used in the calculations of de Feijter and Vrij (see Fig. 6*a*) cannot be used while keeping constant the film thickness, which decreases as the contact angle is increased (see Table 2), thus masking the true dependence of τ_d^0 on θ_f. The advantages of the $\Pi(H)$ isotherm used by the present writer[55,64,71] therefore seem obvious: it enables the film thickness H_f and the parameter Δ_1 to be held constant during changes in the contact angle θ_f, and it gives the true dependence of the line tension on θ_f.

We should also note that the use[49] of the approximate working formula (29) to calculate the line tension gives values at least 10 times too high, as can be seen by comparing the data in Table 2 with the numerical values of τ_d^0 calculated by the exact formula (44) (Table 3) for equal values of the parameters θ_f, ΔP, and Δ_1.

As was pointed out above, according to the generalised theory of the line tension[40] the tension $æ_d$, defined in terms of the membrane model of the film by Eqn. (1), differs from the line tension τ_d in the thermodynamic model, based on the assumption of a film with two interfaces [see Eqn. (4)]. The relationship between $æ_d^0$ and τ_d^0 in the case of a straight contact line is described by Eqn. (46). An analysis of the data in Table 4 leads to the important conclusion that the film thickness H_f has a marked influence on $æ_d^0$ but none on τ_d^0. Under these conditions the numerical value of the line tension $æ_d^0$ can exceed that of τ_d^0 by a factor of 10 or more.[55,71]

Table 4. Line tension $æ_d^0$ calculated[42] by the exact formula (45) as a function of the parameters Δ_1 and Π_1 which describe the idealised disjoining pressure isotherm shown in Fig. 7, and also for different hydrostatic pressures ΔP, contact angles θ_f, and specific energies of interaction $\Delta\Omega(H_f)$ in a film of thickness H_f and line tension τ_d^0 (σ_0 = 300 mJ m^{-2}).

ΔP, Pa	Δ_1, nm	Π_1, Pa	θ_f, min	$10^{-6}\Delta\Omega(H_f)$, J m^{-2}	$10^{-12}\tau_d^0$, N J m^{-2}	H_f, nm	θ_0, deg	$10^{-12}æ_d^0$, N
10	10	10^3	2.57	-20	-2.98	0.2	2.57	-3.06
10	10	10^3	2.57	-20	-2.98	2	2.57	-3.87
10	10	10^3	2.57	-20	-2.98	20	2.55	-11.9
10	10	10^3	2.57	-20	-2.98	200	2.43	-90.1
10^2	10	10^2	0.81	-2	-0.78	20	0.00	-2.67
10^2	10	10^3	2.57	-20	-2.91	20	2.43	-11.6
10^2	1	10^5	8.11	-200	-0.94	2	8.11	-2.35
10^2	10	10^4	8.11	-200	-9.40	20	8.07	-37.5
10^2	1	10^5	8.11	-200	-0.94	20	8.07	-29.1
10^3	10	10^3	2.57	-20	-2.45	20	0.00	-8.42

3. Magnitude and sign of the line tension for a $\Pi(H)$ isotherm without a coagulation minimum

As we have already noted, in the case of a positive specific free energy of interaction $\Delta\Omega(H_f)$ in a film of thickness H_f the idealised profile of the film lies above the real profile (see Fig. 2*b*), and the line tension τ_{Bd}^0 is defined by Eqn. (10).[55,64,65] Table 5 shows the results of calculations of the line tension τ_{Bd}^0 by the exact formula (48) for the idealised $\Pi(H)$ isotherm shown in Fig. 9. This $\Pi(H)$ isotherm, in the form of a step, allows us to keep constant the film thickness H_f and to identify the effects of the shape of the $\Pi(H)$ isotherm (the parameters Δ_2 and Π_2) and also of ΔP and $\Delta\Omega(H_f)$ on the line tension τ_{Bd}^0.

Table 5. Line tension τ^0_{Bd} calculated[42] by the exact formula (48) as a function of the parameters Δ_2 and Π_2 which characterise the idealised disjoining pressure isotherm shown in Fig. 9, and also of the difference in hydrostatic pressure ΔP, the difference in film thickness $\Delta H = H_0 - H_f$, and the specific free energy of interaction $\Delta\Omega(H_f)$ in a film of thickness H_f (σ_0 = 30 mJ m^{-2}).

ΔP, nm	Δ_2, nm	Π_2, Pa	ΔH, nm	$10^{-6}\Delta\Omega(H_f)$, J m^{-2}	$10^{-12}\tau^0_{Bd}$, N
10^2	100	10	20	+2.0	+5.66
10^2	20	50	20	+2.0	+1.89
10^2	2	50	2	+0.2	+0.06
10^2	10	10	2	+0.2	+0.18
20	10	10	10	+0.2	+0.30
10^3	10	10	0.2	+0.2	+0.06

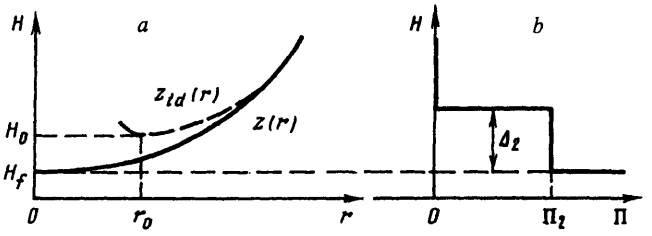


Figure 9. Idealised disjoining pressure isotherm $\Pi(H)$ without a coagulation minimum, used in calculations[41,42,71] of the line tension τ_{Bd} (see text).

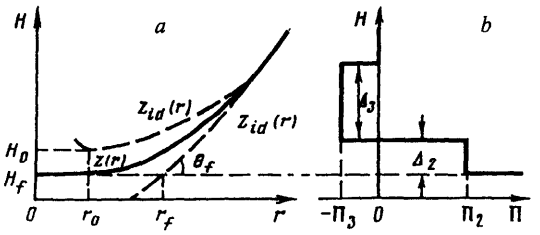


Figure 10. Idealised disjoining pressure isotherm $\Pi(H)$ with a long-range minimum and a coagulation barrier (see text).

The main conclusion from this analysis of the calculations is that the sign of the line tension τ^0_{Bd} is positive, i.e. it corresponds to the sign of $\Delta\Omega(H_f)$.[55,64] The line tension τ^0_{Bd} increases with Δ_2 and $\Delta\Omega(H_f)$, and as ΔP decreases.[55,64] More detailed results or the writer's calculations of τ^0_{Bd} as a function of these parameters have already been reported.[71]

4. Effect of the coagulation barrier on the magnitude and sign of the line tension

Let us first examine the idealised profile of the $\Pi(H)$ isotherm shown in Fig. 10, which can be used to model the change from wetting ordinary black films (which do not form a finite contact angle) to non-wetting ordinary black films (which form a finite contact angle θ_f). If the specific free energy of interaction in the film [which is equal, in our case of an idealised $\Pi(H)$ isotherm to $\Delta\Omega(H_f) = -2\Delta_3\Pi_3 + 2\Delta_2\Pi_2$] is less than zero the idealised profile $z_{id}(r)$ lies below the real profile $z(r)$ and forms the contact angle θ_f. If $\Delta\Omega(H_f) > 0$ the contact angle is not formed because $z_{id}(r)$ lies above $z(r)$. For $\Delta\Omega(H_f) = 0$ the contact angle θ_f is zero.

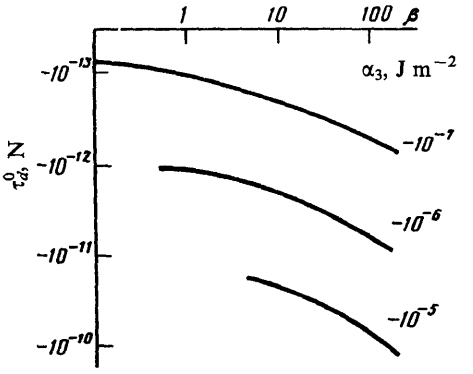


Figure 11. Dependence of the line tension τ^0_d on the parameter β for different values of the parameter α_3; ΔP = 100 Pa, σ_0 = 30 mJ m^{-2}, $\Delta\Omega(H_f) = 0$.

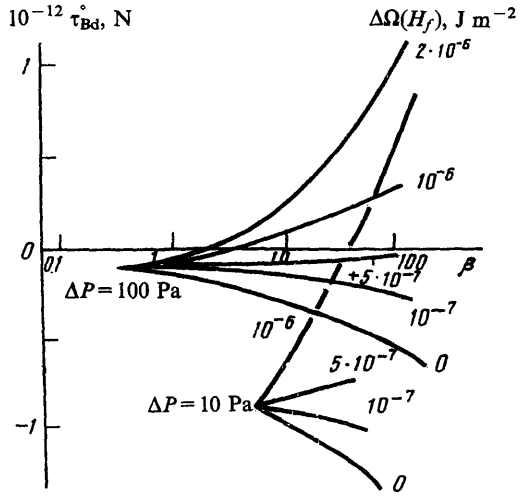


Figure 12. Dependence of the line tension τ^0_{Bd} on the parameter β for different positive values of the specific interaction energy $\Delta\Omega(H_f)$ in a film of thickness H_f and of the difference in hydrostatic pressure ΔP (σ_0 = 30 mJ m^{-2}, $\alpha_3 = -5 \times 10^{-7}$ J m^{-2}).

The latter case is illustrated in Fig. 11,[42] where the different $\tau^0_d(\beta)$ curves correspond to the condition $\Delta\Omega(H_f) = 0$ but to a different form of $\Pi(H)$ isotherm, characterised by the parameters $\beta = \Delta_2/\Delta_3$ and $\alpha_3 = -2\Delta_3\Pi_3$.

The most important conclusion suggested by the $\tau_d^0(\beta)$ curves of Fig. 11 is that the line tension τ_d^0 (and, even more, $æ_d^0$) is negative when the films have a finite angle of contact θ_f. This conclusion coincides with the results of numerical calculations of the line tension by de Feijter and Vij,[49] who obtained only negative values of τ_d^0 for ordinary black films, but is incompatible with the experimental results of Platikanov, et al.,[5,34] who obtained positive values of the line tension $æ_d$ for those films.

We also note that increasing the depth α_3 of the coagulation minimum (or the height of the coagulation barrier) for $\Delta\Omega(H_f) = 0$ (or $\theta_f = 0$) increases the absolute value of the (negative) line tension almost in proportion to the parameter α_3. This feature can be used as a criterion of the form of the $\Pi(H)$ isotherm under the conditions of a reliable experimental determination of both τ_d^0 and the contact angle θ_f.

When $\Delta\Omega(H_f) > 0$ the contact angle is not formed (see Fig. 10). In Fig. 12 we show the results of calculations of the line tension τ_{Bd}^0 as a function of the parameter $\beta = \Delta_2/\Delta_3$ for constant values of $\Delta\Omega(H_f)$ ($\alpha_3 = -5 \times 10^{-7}$ J m^{-2} in all the calculations). The upper family of curves corresponds to $\Delta P = 100$ Pa, the lower to $\Delta P = 10$ Pa.

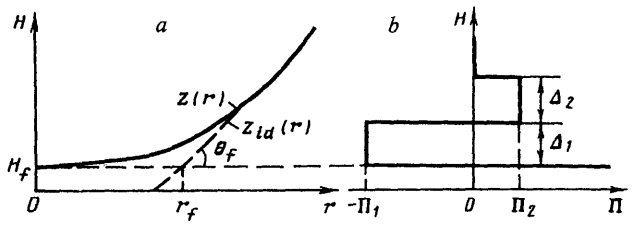


Figure 13. Idealised disjoining pressure isotherm $\Pi(H)$ with a coagulation barrier and a short-range coagulation minimum (see text).

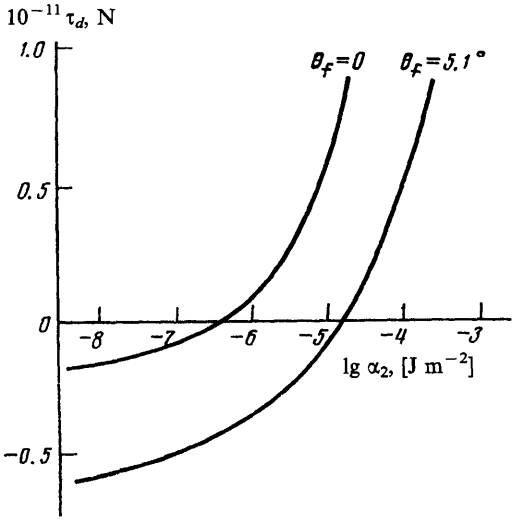


Figure 14. Dependence of the line tension τ_d^0 on the parameter α_2 for two values of the contact angle θ_f ($\Delta P = 100$ Pa, $\sigma_0 = 30$ mJ m^{-2}, $\Delta_1 = \Delta_2 = 10$ nm).

The line tension τ_{Bd}^0 determined according to Eqn. (48) can (in principle) have both negative and positive values.[42,74] However, since in ordinary black films the parameter β cannot be greater than 1 we may conclude that the line tension τ_{Bd}^0 is more likely to be negative than positive. The measured[63] positive value $\tau_{Bd}^0 = +3 \times 10^{-11}$ N for $\Delta\Omega(H_f) = 10^{-5}$ J m^{-2} and $\Delta P \simeq 100$ Pa is not incompatible with the numerical calculations of the line tension τ_{Bd}^0 shown in Fig. 12 provided that the films of aqueous solutions of electrolytes studied in that work[63] do not possess a long-range coagulation minimum, i.e. long-range molecular forces are entirely absent.

Let us now examine another generalised $\Pi(H)$ isotherm (Fig. 13), which models the Newtonian black films when the effect of the long-range coagulation barrier can be ignored. The dependence of the line tension $\tau_d^0(\alpha_2)$ on the parameter $\alpha_2 = 2\Delta_2\Pi_2$ for a constant $\Delta P = 100$ Pa is shown in Fig. 14 ($\Delta_2 = \Delta_1 = 10$ nm), where constant values of $\Delta\Omega(H_f)$ are also assumed (i.e. constant angles of contact θ_f).

We can see from Fig. 14 that upon increasing the height of the coagulation barrier Π_2 (i.e. upon increasing the parameter α_2) the line tension τ_d^0 passes from the negative into the positive region: this transition takes place at a higher value of α_2 when the contact angle θ_f is increased.

Lastly, if the effect of the long-range coagulation minimum cannot be ignored, the $\Pi(H)$ isotherm shown in Fig. 5*b* (characterised by two coagulation minima and a coagulation barrier) must be used in the calculation of the line tension.

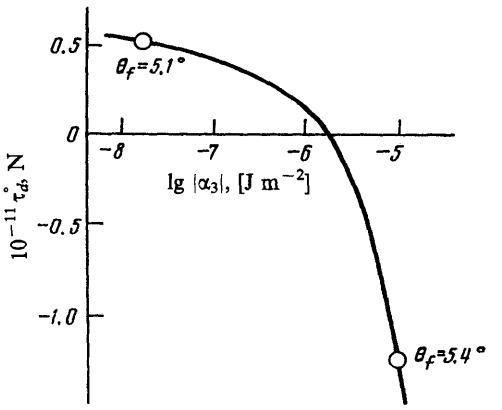


Figure 15. Dependence of the line tension τ_d^0 on the absolute value of the parameter α_3 ($\Delta P = 100$ Pa, $\sigma_0 = 30$ mJ m^{-2}, $\alpha_1 = -0.98 \times 10^{-4}$ J m^{-2}, $\alpha_2 = +1.8 \times 10^{-5}$ J m^{-2}, $\Delta_1 = \Delta_2 = \Delta_3 = 10$ nm).

In Fig. 15 we show the dependence of the line tension $\tau_d^0(\alpha_3)$ on the parameter $\alpha_3 = -2\Delta_3\Pi_3$ for constant $\Delta P = 10$ Pa, $\Delta_1 = \Delta_2 = \Delta_3 = 10$ nm, $\alpha_1 = -0.98 \times 10^{-4}$ J m^{-2}, and $\alpha_2 = +1.8 \times 10^{-5}$ J m^{-2}. Increasing the depth of the long-range coagulation minimum, i.e. increasing the absolute value of the parameter α_3, changes the sign of the line tension from positive to negative. Under these conditions the angle of contact θ_f is almost unaffected (at least,

any change in this angle is experimentally undetectable, since $\Delta\theta_f$ = 0.3° for an absolute value of $\theta_f \simeq 5°$).

Thus we may conclude that the most significant effects on the magnitude and sign of the line tension are produced by the form of the $\Pi(H)$ disjoining pressure isotherm rather than by the absolute value of the specific free energy of the interaction in the film, $\Delta\Omega(H_f)$, i.e. by the contact angle θ_f. This justifies the effort now being directed towards the experimental determination of the line tension, since a knowledge of the magnitude and sign of this parameter should provide new information on the form of the disjoining pressure isotherm.

As to the sign of the line tension τ_d^0 in Newtonian black films, in principle this parameter can be either positive or negative, depending on the form of the idealised $\Pi(H)$ isotherm. However, for real $\Pi(H)$ isotherms, for example those described by the DLVO theory, de Feijter and Vrij showed[49] that the line tension has only negative values in Newtonian black films, characterised by relatively large angles of contact. The same conclusion was reached by the present writer from the first calculations of the line tension τ_d of microscopic curved films[55] by the exact analytical formula (36).

VI. Conclusions

The following conclusions can be formulated from the analysis of the line tension problem in the thermodynamics of thin liquid films given in the present review.

Line tensions are defined by different workers in terms of different thermodynamic models of thin liquid films, and therefore they are physically different quantities. Identifying line tensions defined in different ways leads to incompatible numerical values and even signs of these parameters. The writer's generalised theory of the line tension[40] reconciles the different definitions and establishes their mutual relationships.

Exact analytical expressions for the line tension have been proposed.[40–42,55,64,65,71] In particular, it has been shown that the well known expression for the line tension [Eqn. (26)] obtained by de Feijter and Vrij,[49] which is widely used at present, is incorrect for the general case of a curved line of contact though it approaches asymptotically the correct expression as the radius of curvature of the contact line tends towards infinity.

The writer has reported[40–42,71] the first calculations of the line tension by numerical methods, and has obtained the dependence of the line tension on the form parameters of the disjoining pressure isotherm and on the capillary pressure in the film, the interfacial tension, the contact angle (the specific free energy of interaction in the film), and the film thickness. The numerical values of the line tension have been compared with known experimental results for this quantity.

References

1. A Scheludko, V Chakarov, B Toshev *J. Colloid Interface Sci.*, 1981, **82** 83
2. G Navascues, L Mederos *Surf. Techn.*, 1982, **17** 79
3. J F Joanny, P G de Gennes *J. Colloid Interface Sci.*, 1986, **111** 94
4. I B Ivanov, Thesis, Sofia, 1977
5. D Platikanov, M Nedyalkov, A Scheludko *J. Colloid Interface Sci.*, 1980, **75** 612
6. B V Derjaguin, A V Prokhorov *J. Colloid Interface Sci.*, 1981, **81** 108
7. V S Markin, Yu A Chizmadzhev, E Neiman *Biol. Membrany*, 1990, **7** 543
8. V G Babak *Colloids Surf.*, 1987, **28** 123
9. F P Buff, H Saltsburg *J. Chem. Phys.*, 1957, **26** 23
10. B A Pethica *J. Colloid Interface Sci.*, 1977, **62** 567
11. J Kerins, B Widom *J. Chem. Phys.*, 1982, **77** 2061
12. J S Rowlinson, B Widom *Molecular Theory of Capillarity*, Oxford University Press, 1982, 375 pp
13. J S Rowlinson *J. Chem. Soc., Faraday Trans. 2*, 1983, **79** 77
14. A Scheludko *Colloids Surf.*, 1983, **7** 81
15. B V Toshev, D Platikanov, A Scheludko *Langmuir*, 1988, **4** 489
16. A I Rusanov, F C Goodrich (Editors) *Sovremennaya Teoriya Kapillyarnosti* (Modern Theory of Capillarity), Khimiya, Leningrad, 1980, p. 274
17. V Chakarov, A Scheludko, M Zembala *J. Colloid Interface Sci.*, 1983, **92** 35
18. A Scheludko, V Chakarov *Colloid Polymer Sci.*, 1983, **261** 776
19. A Scheludko *J. Colloid Interface Sci.*, 1985, **104** 471
20. V Chakarov, M Zembala, O Novozhilova, A Scheludko *Colloid Polymer Sci.*, 1987, **265** 347
21. B V Deryagin, Yu V Gutop *Kolloidn. Zh.*, 1982, **24** 431
22. D Kashiev, D Exerova *J. Colloid Interface Sci.*, 1980, **77** 501
23. B V Deryagin, A V Prokhorov *Kolloidn. Zh.*, 1982, **42** 621
24. A V Prokhorov, B V Deryagin *Kolloidn. Zh.*, 1987, **49** 903
25. J Mingins, A Scheludko *J. Chem. Soc., Faraday Trans. 1*, 1979, **75** 1
26. P A Kralchevsky, I B Ivanov, A D Nikolov *J. Colloid Interface Sci.*, 1986, **112** 108
27. I Langmuir *J. Chem. Phys.*, 1933, **1** 756
28. V S Veselovskii, V N Pertsov *Zh. Fiz. Khim.*, 1936, **8** 245
29. W D Harkins *J. Chem. Phys.*, 1937, **5** 135
30. N L Gershfeld, R J Food *J. Theor. Biol.*, 1967, **17** 246
31. S Torza, S G Mason *Kolloid Z.-Z. Polym.*, 1971, **246** 593
32. R J Good, M N Koo *J. Colloid Interface Sci.*, 1979, **71** 283
33. T Kolarov, Z M Zorin *Colloid Polymer Sci.*, 1979, **257** 1292
34. D Platikanov, M Nedyalkov, V Nasteva *J. Colloid Interface Sci.*, 1980, **75** 620
35. P A Kralchevsky, A D Nikolov, I B Ivanov *J. Colloid Interface Sci.*, 1986, **112** 132
36. B V Deryagin (Editor) *Poverkhnostnye Sily i Granichnye Sloi Zhidkostei* (Surface Forces and Boundary Layers in Liquids), Nauka, Moscow, 1983, p. 200
37. D Platikanov, M Nedyalkov, N Rangelova *Colloid Polymer Sci.*, 1987, **265** 72
38. J Gaydos, A W Neumann *J. Colloid Interface Sci.*, 1987, **120** 76
39. J A Wallage, S Schürch *J. Colloid Interface Sci.*, 1988, **124** 452
40. V G Babak *Colloids Surf.*, 1987, **25** 205
41. V G Babak *Fizikokhimiya Mikroskopicheskikh Zhidkikh Plenok Stabilizirovannykh Polimerami. Ch. 1* (Physical Chemistry of Microscopic Liquid Films Stabilised by Polymers. Part 1), Izd. Ural'sk. Univ., Sverdlovsk, 1988, p. 172
42. V G Babak *Voprosy Termodinamiki Geterogennykh Protsessov i Teorii Poverkhnostnykh Yavlenii* (Problems in the Thermodynamics of Heterogeneous Processes and in the Theory of Surface Phenomena), Izd. Sankt-Peterburgsk. Univ., St. Petersburg, 1992, p. 82

43. B V Deryagin, G A Martynov, Yu V Gutop *Kolloidn. Zh.*, 1965, **27** 357
44. B V Deryagin (Editor) *Research in Surface Forces,* Consultants Bureau, New York, 1966, p. 9
45. J W Gibbs *The Collected Works of J Willard Gibbs*, Dover Publ., New York, 1971, Vol. 1
46. A I Rusanov *Kolloidn. Zh.*, 1966, **28** 718
47. A I Rusanov *Kolloidn. Zh.*, 1967, **29** 113
48. B V Deryagin (Editor) *Research in Surface Forces*, Consultants Bureau, New York, 1971, Vol. 3, p. 103
49. J A de Feijter, A Vrij *J. Electroanal. Chem.*, 1979, **37** 9
50. B V Toshev, I B Ivanov *Colloid Polymer Sci.*, 1975, **253** 558
51. I B Ivanov, B V Toshev *Colloid Polymer Sci.*, 1975, **253** 593
52. J A de Feijter, J B Rijnbout, A Vrij *J. Colloid Interface Sci.*, 1978, **64** 258
53. B V Toshev *Colloids Surf.*, 1981, **2** 243
54. J C Eriksson, B V Toshev *Colloids Surf.*, 1982, **5** 241
55. V G Babak *Colloids Surf.*, 1987, **25** 1
56. V G Babak *Proceedings of the International Symposium on Calorimetry and Chemical Thermodynamics*, Moscow State University Press, Moscow, 1991, p. 121
57. N V Churaev, V M Starov, B V Derjaguin *J. Colloid Interface Sci.*, 1982, **89** 16
58. T Kolarov, A Scheludko, D Exerova *Trans. Faraday Soc.*, 1968, **64** 2864
59. G A Martynyuk, I B Ivanov, B V Toshev *Kolloidn. Zh.*, 1976, **38** 474
60. J F Paddat (Editor) *Wetting, Spreading, and Adhesion,*, Academic Press, London, 1977, p. 37
61. W G M Agterof *J. Colloid Interface Sci.*, 1982, **86** 384
62. V G Babak *Kolloidn. Zh.*, 1985, **47** 435
63. Z M Zorin, D Platikanov, T Kolarov *Colloids Surf.*, 1987, **22** 147
64. V G Babak *Dep TsNIITEIPishcheprom*, No. 1109, Moscow, 1985, p. 26
65. V G Babak, R A Monissova *J. Dispersion Sci. & Technol.*, 1985, **6** 539
66. A Scheludko *Colloids Surf.*, 1980, **1** 191
67. B Radoev, A Scheludko, B Toshev *J. Colloid Interface Sci.*, 1986, **113** 1
68. D Platikanov, M Nedyalkov *Microscopic Aspects of Adhesion and Lubrication,* Elsevier, Amsterdam, 1982, p. 97
69. P A Kralchevsky, I B Ivanov *Chem. Phys. Lett.*, 1985, **121** 116
70. B V Toshev *Compt. Rend. Acad. Bulgare des Sciences*, 1986, **39** 87
71. V G Babak *Colloids Surf.*, 1987, **25** 25
72. B V Deryagin, N V Churaev *Kolloidn. Zh.*, 1976, **38** 438
73. F Th Hesselink, A Vrij, J Ph G Overbeek *J. Phys. Chem.*, 1971, **75** 2094
74. V G Babak, P A Kralchevsky, I B Ivnaov *Abstracts of the Ninth International Symposium on Surfactants in Solutions,* Varna, 1992, p. 62

Received 1st January 1992

Translated from *Uspekhi Khimii* **61** 1805–1821 (1992) U.D.C. 541.2+546.65+546.66+546.799

The anomalous stabilisation of the oxidation state 2+ of lanthanides and actinides

N B Mikheev, L N Auerman, I A Rumer, A N Kamenskaya, M Z Kazakevich
Institute of Physical Chemistry, Russian Academy of Sciences

ABSTRACT. The present review deals with the anomalous stabilisation of the oxidation state 2+ of a number of lanthanides and actinides. This stabilisation of the oxidation state 2+ is due to the lowering of the energy of a *d*-orbital as a result of crystal field splitting in the ligand field and *d*-electron participation in chemical bonding.

The bibliography contains 68 references.

Contents

I. Introduction 990
II. Reduction of lanthanides and actinides to the oxidation state 2+ in chloride melts and determination of the standard oxidation potentials ($E^0_{M^{3+}/M^{2+}}$) 991
III. Hydration energies of divalent lanthanides 993
IV. Electron configuration of divalent lanthanides and actinides 994
V. Characteristics of the behaviour of divalent actinides in melts 995
VI. Stabilisation of the oxidation state 2+ of lanthanides and actinides in condensed clusters 995

I. Introduction

The lanthanides (Ln) and actinides (An) are transition *f*-elements characterised by the gradual filling of the 4*f*- and 5*f*-orbitals with electrons. The lanthanides from praseodymium to ytterbium (except gadolinium) and the actinides from plutonium to nobelium (except curium) in the ground state of the neutral atoms have the same electron configuration $f^n s^2$, so that these elements should be divalent. In fact, however, for all the lanthanides and for the actinides from americium onwards, the most stable oxidation state is 3+ (except for No, for which the most stable oxidation state is 2+). Connick[1] was the first to emphasise that the predominant oxidation state 3+ for the lanthanides is not related to the ground state of the neutral atoms, but is determined purely by the quantitative ratio of the ionisation potentials I_n and the chemical stabilisation (hydration, solvation, etc.) of the divalent and trivalent ions. A measure of the stability of the divalent state relative to the trivalent state in solution is provided by the oxidation potential $E^0_{M^{3+}/M^{2+}}$. For aqueous solutions, the standard oxidation potential can be expressed as follows:

$$E^0_{M^{3+}/M^{2+}} + 4.43 = \Delta G^\circ_{ion} + \Delta G^0_h(M^{3+}) - \Delta G^0_h(M^{2+}), \quad (1)$$

where 4.43 V is the standard electrode potential of the hydrogen electrode;[2] ΔG°_{ion} the ionisation energy, calculated from the values of the third ionisation potential I_3; and $\Delta G^\circ_h(M^{2+})$ and $\Delta G^\circ_h(M^{3+})$ the hydration energies of the divalent and trivalent ions.

Nugent and co-workers[3] obtained theoretical estimates of $E^0_{M^{3+}/M^{2+}}$ for the lanthanides and actinides. The improved theory of electron spin-pairing due to Jørgenson[4] was used in the calculations, and a correlation was found between the energy of the first electron-transfer band in the spectra of trivalent Ln and An complexes on the one hand and the energy of the first *f*–*d*-transition band of divalent Ln and An and the corresponding oxidation potentials on the other. The observed relationships are semi-empirical. Because of the lack of experimental data, the relationship between the oxidation potentials and the spectral parameters was established from a small number of points (divalent Sm, Eu, and Yb for Ln, and Cf for An) (Tables 1 and 2).

Table 1. Standard oxidation potentials of the Ln^{3+}/Ln^{2+} couples ($E^0_{Ln^{3+}/Ln^{2+}}$) and *fd*-excitation energies of the free ions Ln^{2+} (E_{fd}).

Ln	$E^0_{Ln^{3+}/Ln^{2+}}$, V			E_{fd}, eV (Ref.18)
	experimental (Ref.17)	calculated		
		(Ref.3)	(Ref.5)	
La	−2.94±0.08	−3.1±0.2	−3.8	−0.891
Ce	−2.92±0.08	−3.2±0.2	−3.5	0.406
Pr	−2.84±0.06	−2.7±0.2	−3.0	1.593
Nd	−2.62±0.05	−2.6±0.2	−2.8	1.892
Pm	−2.44±0.06	−2.6±0.2	−2.5	not known
Sm	−1.50±0.01	−1.6±0.2	−1.5	3.259
Eu	−0.34±0.01	−0.3±0.2	−0.35	4.740
Gd	−2.85±0.07	−3.9±0.2	−3.6	−0.295
Tb	−2.83±0.07	−3.7±0.2	−3.5	1.112
Dy	−2.56±0.05	−2.6±0.2	−2.6	not known
Ho	−2.79±0.06	−2.9±0.2	−2.9	2.236
Er	−2.87±0.08	−3.1±0.2	−3.0	2.105
Tm	−2.22±0.05	−2.3±0.2	−2.1	2.839
Yb	−1.18±0.01	−1.1±0.2	−1.10	4.139

Table 2. Standard oxidation potentials of the An^{3+}/An^{2+} couples ($E^0_{An^{3+}/An^{2+}}$) and *fd*-excitation energies of the free ions An^{2+} (E_{fd}).

An	$E^0_{An^{3+}/An^{2+}}$, V		E_{fd}, eV (Ref.19)
	experimental (Ref.17)	calculated (Ref.3)	
Ac	not known	−4,9±0.2	−3.434
Th	not known	−4,9±0.2	−1,872
Pa	not known	−4,7±0.2	−0.570
U	−2.60±0.06	−4,7±0.2	0.00
Np	−2.83±0.07	−4,7±0.2	0,508
Pu	−2.79±0.07	−3.5±0.2	1,699
Am	−2.28±0.06	−2,3±0.2	2.963
Cm	−2.78±0.07	−4,4±0.2	0,880
Bk	−2.52±0.06	−2.8±0.2	2.343
Cf	−1.63±0.02	−1.6±0.2	3.447
Es	−1.45±0.02	−1,3±0,2	3,744
Fm	−1.18±0.02	−1,1±0.2	3.992
Md	−0.15±0.01	0,0±0.2	4,972
No	+1.45±0.01	+1,3±0.2	6,249

Another method for estimating $E^0_{M^{3+}/M^{2+}}$ for the lanthanides, used by Johnson,[5] is based on calculations from thermodynamic cycles. Experimental data for samarium, europium, and ytterbium were used in these calculations. The method is based on the assumption that the crystal lattice energies and the hydration energies of the ions change regularly with increase in atomic number and that the formation of a solid phase and the interaction of the ions with a solvent are not accompanied by a change in the number of *f*-electrons of the elements being considered. The calculated values of $E^0_{M^{3+}/M^{2+}}$ are given in Table 1.

The experimental data on the long familiar divalent state of samarium, europium, and ytterbium were supplemented in the late seventies by the preparation of the divalent state of many lanthanides (Pr,[6] Nd,[7] Pm,[8] Dy,[9] Ho,[10] Er,[11] Tm [12]) and actinides Am,[13] Bk,[14] Cf,[15] Es,[15] Fm[16]) and the determination of the standard oxidation potentials. The standard oxidation potentials of the M^{3+}/M^{2+} couples were determined for these elements[17] (Tables 1 and 2).

Tables 1 and 2 show that for most Ln and An the experimental values of $E^0_{M^{3+}/M^{2+}}$ agree with the theoretical estimates. From the theoretically calculated $E^0_{M^{3+}/M^{2+}}$ values, the existence of the divalent states of the elements La, Ce, Gd, Tb, U, Np, Pu, and Cm should not be expected. In fact, Tables 1 and 2 show that the calculated standard oxidation potentials of the M^{3+}/M^{2+} couples for Gd, Tb, U, Np, Pu, and Cm lie below −3 V. This oxidation potential (−3 V) is reached in the presence of the strongest known reducing agent—lithium—and a lower oxidation potential cannot be obtained in a condensed medium. Nevertheless, it has been established experimentally that these elements exist in the divalent state and that the standard oxidation potentials of their M^{3+}/M^{2+} couples are appreciably higher than the theoretically calculated values (Tables 1 and 2).

It will be shown in the present work that the anomalous stabilisation of the oxidation state 2+ of these elements is due to the participation of *d*-orbitals in chemical bonding.

II. Reduction of lanthanides and actinides to the oxidation state 2+ in chloride melts and determination of the standard oxidation potentials $E^0_{M^{3+}/M^{2+}}$

Since various actinides are available only in micro-quantities, the possibility of obtaining the *f*-elements in the oxidation state 2+ was investigated, and the values of $E^0_{M^{3+}/M^{2+}}$ determined, by cocrystallisation in the molten salt systems $(LnOCl)_{solid}-(LnCl_3-LnCl_2-SrCl_2)_{melt}$, where Ln = Pr, Nd, Sm, and Ho, the subscript solid denotes the solid phase, and the subscript melts denotes the melt. The oxide chlorides of all the actinides and lanthanides except thulium and ytterbium have the PbFCl crystal structure. Thus the cocrystallisation of micro-quantities of Ln^{3+} and An^{3+} will take place as a result of true isomorphism or isodimorphism. On the other hand, the divalent lanthanides and actinides resemble the alkaline earth elements, which do not form oxide chlorides. Thus Ln^{2+} and An^{2+} should not cocrystallise with solid LnOCl. Preliminary experiments confirmed this assumption. The entrainment of Sr^{2+} and Eu^{2+}, and also Cs^+, by the solid phase did not exceed 0.1%. This resolved the question of the possible formation of anomalous mixed crystals of the reduced forms of the elements being studied with LnOCl. In these experiments, the potential of the system was determined by the ratio Ln^{3+}/Ln^{2+} in the system. The use of the dichlorides of praseodymium, neodymium, samarium, and holmium made it possible to study the reduction of the lanthanides and actinides over a wide range of values of the oxidation potentials and, which is particularly important, at a low concentration of the elements being studied.

The method developed made it possible to determine the extent of the reduction of the *f*-element being studied and the difference between the standard oxidation potentials of the element being studied and the potential-determining element. For this it was necessary to know the equilibrium distribution of the micro-component between the solid phase LnOCl and the $LnCl_3-SrCl_2$ melt when both components are in the trivalent state:

$$D_0=[m^{3+}/m^{3+}]_{solid}[M^{3+}/M^{3+}]_{melt}, \quad (2)$$

where D_0 is the cocrystallisation coefficient, and m and M the quantities of the micro- and macro-components.

Since the micro-component in the reduced form does not cocrystallise with the solid phase, the distribution of the elements in the system containing the reducing agent, $(LnOCl)_{solid}-(LnCl_3-LnCl_2-SrCl_2)_{melt}$, will be described by the equation:

$$D_0=\left(\frac{m^{3+}}{M^{3+}}\right)_{solid}\left(\frac{M^{3+}+M^{2+}}{m^{3+}+m^{3-n}}\right)_{melt}, \quad (3)$$

where n is the number of electrons involved in the reduction of the micro-element.

From Eqns. (2) and (3) and the Nernst equation, the equilibrium state in the system is described by the equation:

$$\ln\left[\frac{D_0}{D}\left(1+\frac{M^{2+}}{M^{3+}}\right)-1\right]=\frac{-\Delta E_{M-m}}{RT/nF}+n\cdot\ln\frac{M^{2+}}{M^{3+}}. \quad (4)$$

where $\Delta E_{M-m}=E_{M^{3+}/M^{2+}}-E_{m^{3+}/m^{(3-n)+}}$, and n is the number of electrons in the reaction $m^{3+}+ne^-\rightarrow m^{(3-n)+}$. Thus if D_0 and D are known for different ratios M^{2+}/M^{3+}, Eqn. (4) can be used to

determine the value of n, that is the number of electrons involved in the reduction of the ion of the micro-element, and ΔE_{M-m}—the difference between the oxidation potentials of the couples M^{3+}/M^{2+} (for the potential-determining macro-element) and $m^{3+}/m^{(3-n)+}$ (for the micro-element).

In a large number of experimental studies,[20-27] Eqn. (4) has been used to calculate n, that is the number of electrons involved in the reduction of Ln^{3+} and An^{3+}. In all cases the value was practically equal to 1. This indicates that reduction takes place to the oxidation state 2+. This is illustrated for the reduction of Pu^{3+} in Fig. 1. The result of the reduction is independent of the reducing agent used—Pr^{2+} or Nd^{2+}. The authors cited[20-27] also calculated the difference between the oxidation potentials of the potential-determining elements and the elements being studied (ΔE_{M-m}) (Table 3).

Table 3. Differences between the oxidation potentials $\Delta E_{M-m} = E_{M^{3+}/M^{2+}} - E_{M^{3+}/M^{2+}}$ in chloride melts.[38]

M–m	ΔE_{M-m}, V	M–m	ΔE_{M-m}, V	M–m	ΔE_{M-m}, V
Pr — La	+0.10±0.04	Nd — Pm	-0.18±0.02	Sm — Yb	-0.31±0.02
Pr — Ce	+0.08±0.04	Nd — Dy	-0.07±0.04	Sm — Cf	+0.13±0.02
Pr — Nd	-0.22±0.04	Nd — Pu	+0.17±0.05	Sm — Es	-0.05±0.01
Pr — Gd	+0.01±0.03	Nd — Am	-0.34±0.03	Sm — Fm	-0.32±0.01
Pr — Tb	-0.01±0.03	Nd — Bk	-0.10±0.01	Ho — Dy	-0.26±0.03
Pr — Cm	-0.06±0.02			Ho — Er	+0.08±0.06
				Ho — Tm	-0.38±0.15

Table 4. Differences between the oxidation potentials of the M^{3+}/M^{2+} couples in solutions and melts $\Delta E_{M_1-M_2}$, V.

Pair of elements	Water		Ethanol	Acetonitrile	Chloride melts	
	electrochemistry (Refs. 3, 31)	thermochemistry (Ref.30)	cocrystallisation (Refs. 32, 33)	electrochemistry (Refs. 36, 37)	electrochemistry (Ref.35)	cocrystallisation (Ref.28)
Sm — Yb	-0.40±0.02; -0.32±0.01	-0.36±0.08	—	—	-0.354±0.007	0.31±0.02
Sm — Eu	-1.20±0.03; -1.16±0.01	-1.06±0.08	—	-1.2	-1.175±0.009	—
Yb — Eu	-0.80±0.03; -0.84±0.01	0.70±0.08	—	—	-0.821±0.008	—
Nd — Dy	—	-0.06±0.08	—	—	—	-0.07±0.04
Yb — Fm	—	—	0±0.02	—	—	+0.01±0.02
Sm — Es	—	—	0±0.04	—	—	-0.05±0.01
Sm — Cf	—	—	0.05±0.04	+0.03	—	+0.13±0.02

Thus the values of ΔE in chloride melts were determined experimentally (Table 3). Subsequent studies[28,29] established how the $\Delta E_{M_1-M_2}$ values change on going to other systems, in particular aqueous solutions (Table 4). Table 4 shows that the values of $\Delta E_{M_1-M_2}$ in chloride melts, aqueous solutions, and organic solutions are similar, irrespective of the nature of the liquid phase and temperature. On this basis, the known values of $E^0_{M^{3+}/M^{2+}}$ for various lanthanides and the experimentally determined values of $\Delta E_{M_1-M_2}$ were used to calculate the previously unknown standard oxidation potentials of M^{3+}/M^{2+} couples for lanthanum, cerium, praseodymium, promethium, gadolinium, terbium, holmium, erbium, uranium, neptunium, plutonium, curium, and berkelium (Tables 1 and 2).

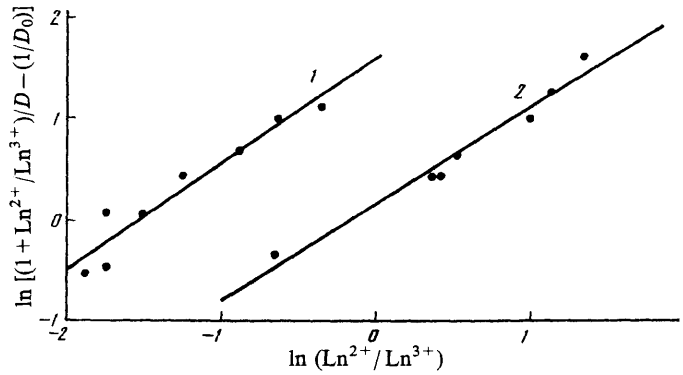


Figure 1. Determination of the number of electrons involved in the reduction of Pu^{3+} by Pr^{2+} (1) and Nd^{2+} (2).[22]

The M—MCl_3 equilibrium diagrams for many f-elements show that the metallic lanthanides and actinides are soluble to a greater or lesser extent in their molten trichlorides. This phenomenon can be regarded as resulting from the reaction

$$M + 2MCl_3 \longrightarrow 3MCl_2.$$

Since in these systems the element is present in three oxidation states (M^0, M^{2+}, M^{3+}) in equilibrium, the following equation can be written for T = 1173 K:

$$E_{M^{3+}/M^{2+}} + \frac{RT}{F}\ln\left[M^{3+}/M^{2+}\right] = E_{M^{3+}/M^0} + \frac{RT}{3F}\ln\left[M^{3+}\right]. \quad (5)$$

In this equation the values of $E_{M^{3+}/M^{2+}}$ and E_{M^{3+}/M^0} in the molten salts at 1173 K are unknown. As shown in Table 4, however, $E_{M_1-M_2}$ is independent of temperature and the composition of the liquid phase. Thus the standard oxidation potential of the M^{3+}/M^{2+} couple in the melt at 1173 K and the standard oxidation potential of the same couple in aqueous solution at 298 K $E^0_{M^{3+}/M^{2+}}$ will differ from one another by a constant quantity

$$E_{M^{3+}/M^{2+}} - E^0_{M^{3+}/M^{2+}} = a.$$

An analogous equation can be written for the oxidation potentials of the M^{3+}/M^0 couple:

$$E_{M^{3+}/M^0} - E^0_{M^{3+}/M^0} = b.$$

Replacing $E_{M^{3+}/M^{2+}}$ and E_{M^{3+}/M^0} in Eqn. (5) by the corresponding values of the standard oxidation potentials gives:

$$E^0_{M^{3+}/M^{2+}} + \frac{1173R}{F}\ln\left[\frac{M^{2+}}{M^{3+}}\right] + a = E^0_{M^{3+}/M^0} + \frac{1173R}{3F}\ln\left[M^{3+}\right] + b, \quad (6)$$

from which it is possible to calculate the quantity $a - b$:

$$a - b = E_{M^{3+}/M^0} - E^0_{M^{3+}/M^{2+}} + \frac{1173R}{3F}\ln\left[M^{3+}\right] - \frac{1173R}{F}\ln\left[\frac{M^{3+}}{M^{2+}}\right]. \quad (7)$$

Table 5 gives the mole fractions $[M^{3+}]$ and $[M^{2+}]$ found from the solubility of the metal in the molten trichloride at 1173 K,[38] and also the standard oxidation potentials of the couples M^{3+}/M^{2+} and the couples M^{3+}/M^0.[17,39,40] Table 5 also gives the values of $(a - b)$ for various lanthanides and actinides, calculated from the above data. Table 5 shows that the values of $(a - b)$ remain contant to within 45 mV.

Table 5. Solubilities (S) of the metals in the molten trichlorides, the mole fraction $[M^{3+}]$ and $[M^{2+}]$ in the melts, the standard oxidation potentials of the couples M^{3+}/M^{2+} and M^{3+}/M^0, and the calculated differences $a - b$.

M	S M in MCl_3, mol%	$[M^{3+}]$ (Ref.38)	$[M^{2+}]$ (Ref.38)	$E^0_{M^{3+}/M^{2+}}$, V (Ref.17)	$E^0_{M^{3+}/M^0}$, V (Ref.39)	$a-b$, V (Ref.38)
La	9 [41]	0.73	0.27	−2.94	−2.36	0.47
Ce	9 [42]	0.73	0.27	−2.92	−2.33	0.48
Pr	19 [42]	0.43	0.57	−2.84	−2.34	0.50
Nd	30 [43]	0.10	0.90	−2.62	−2.32	0.44
Gd	5 [44]	0.85	0.15	−2.85	−2.28	0.39
Ho	20 [10]	0.40	0.60	−2.79	−2.37	0.43
Er	7 [45]	0.79	0.21	−2.87	−2.32	0.41
Pu	8 [46]	0.76	0.24	−2.59	−2.02	0.44

average 0.44±0.04

The established correlation between the standard oxidation potentials of the couples M^{3+}/M^{2+} and M^{3+}/M^0 and the solubility of the metal in the molten trichloride is observed irrespective of whether M^{2+} is present in the melt in the configuration $f^n d^0 s^0$ or in the configuration $f^{n-1}d^1s^0$. Although the dichlorides of the lanthanides and the actinides in these two electronic states show different chemical properties, the differences between their free energies of reaction with the molten chlorides and with water are the same. All this made it possible to construct a single scale of standard oxidation potentials of the M^{3+}/M^{2+} couples (Tables 1 and 2).

III. Hydration energies of divalent lanthanides

Tables 1 and 2 show that for many of the elements, the experimentally determined values of the standard oxidation potentials of the M^{3+}/M^{2+} couples[17] agree well with the calculated values.[3,5] In the lanthanide series, the exceptions are Gd and Tb. Calculations of the hydration energies of Ln^{2+} from Eqn. (1)[47] were used to determine possible reasons for the anomalous behaviour of Gd and Tb. Fig. 2 (straight lines *1a* and *1b*) shows the dependence of the hydration energies of Ln^{2+} on their atomic number. It follows from Fig. 2 that for most of the elements the hydration energies change linearly with increase in the atomic number (Z); this is due to the linear dependence of the ionic radius on the atomic number of the element (straight line *2* in Fig. 2).[48] La, Ce, Gd, and Tb, however, do not correspond to this relationship. La^{2+} and Gd^{2+} even as the free ions have the electron configuration $f^{n-1}d^1$. When the Ln^{2+} ion is converted from the free state to the coordinated state, the d-state is stabilised by the splitting of the d-level in the crystal field of the ligands, and also by the increase in the covalent character of the chemical bonding with the ligands. The stabilisation energy of the d-level of Ce^{2+} and Tb^{2+} is greater than the fd-excitation energy of their free ions (0.406 eV and 1.112 eV respectively[18]), but on conversion into the coordinated state these elements will have the same electron configuration as the La^{2+} and Gd^{2+} ions. In this case it is convenient to calculate the hydration energies of Gd^{2+} and Tb^{2+} from Eqn. (1) using not the total ionisation energy but the energy of ionisation from the d-level, which can be calculated using the equation:

$$I_d = I_3 - E_{fd}, \quad (8)$$

where I_d is the energy of ionisation from the d-level, and E_{fd} the fd-excitation energy of the free doubly-charged ion.[18] Eqn. (1) then takes the form:

$$E^0_{M^{3+}/M^{2+}} + 4.43 = \Delta G^0_{ion}(d) + [\Delta G^0_h(M^{3+}) - \Delta G^0_h(M^{2+})], \quad (9)$$

where $\Delta G^0_{ion}(d)$ is the ionisation energy, calculated from the value of I_d.

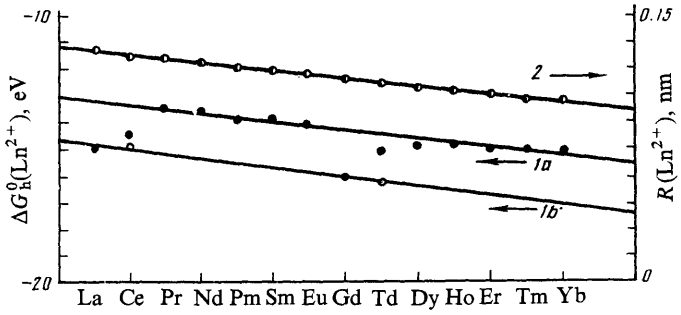


Figure 2. Hydration energies $[\Delta G^0_h(Ln^{2+})]$ (*1a*, *1b*) and ionic radii $[R(Ln^{2+})]$ (*2*) of Ln^{2+}.[47,48]

A feature of undoubted interest is that in this case the hydration energies for the neighbouring elements La^{2+}, Ce^{2+} and Gd^{2+}, Tb^{2+} have similar values, all of which lie on the straight line 1*b* (Fig. 2), lying almost parallel to straight line *1a*. This indicates that the hydrated doubly-charged ions of La, Ce, Gd, and Tb have an

electron configuration involving *d*-electrons. Moreover, the fact that the two straight lines (*1a* and *1b* in Fig. 2) are almost parallel indicates a similarity in the changes in the ionic radius of Ln^{2+} with change in atomic number in the two different electron configurations. The difference between the hydration energies of Ln^{2+} in different electron configurations might be regarded as the stabilisation energy of the *d*-level. This is true, however, only if the ionic radii of La^{2+}, Ce^{2+}, Gd^{2+}, and Tb^{2+} are independent of their electron configurations, and there is obviously no justification for this assumption. Moreover, the ionic radius of all the above elements in the $f^{n-1}d^1$ configuration should be greater than that expected if they had the electronic structure f^nd^0. Thus the stabilisation energy of the *d*-level for these elements will be greater than the differences between the hydration energies of the elements in the two different electron configurations (~1.6 eV for La^{2+} and Ce^{2+} and ~1.8 eV for Gd^{2+} and Tb^{2+}). At the same time, the order of magnitude of the values obtained for the stabilisation is consistent with the energy of splitting of the *d*-level of La and Gd in a CaF_2 matrix, obtained by Johnson and Sandoe[49] (3 eV).

In addition to Ln, yttrium was also obtained in the divalent state, and the standard oxidation potential of the Y^{3+}/Y^{2+} couple was determined (−2.82 V).[50] Yttrium is a typical *d*-element, whose doubly-charged ion has the electron configuration $4d^1$. It was therefore of interest to calculate the hydration energy of the Y^{2+} cation using Eqn. (1). The hydration energy of the Y^{2+} ion was found to lie on straight line *1b* (Fig. 2) in the range corresponding to the second half of the Ln family, confirming the electron configuration of La^{2+}, Ce^{2+}, Gd^{2+}, and Tb^{2+}.

IV. Electron configuration of divalent lanthanides and actinides

The electron configuration of hydrated Ln^{2+} ions was dealt with in a study[51] of the dependence of the standard oxidation potentials of the M^{3+}/M^{2+} couples on the *fd*-excitation energy of the free doubly-charged ion. Figs. 3 and 4 give this relationship for the first and second halves of the Ln family, and show that the standard oxidation potential of the M^{3+}/M^{2+} couple for most of the elements is linearly dependent on the *fd*-excitation energy (straight line *1*). This relationship can be explained if Eqn. (8) is used to express the ionisation energy ΔG^0_{ion} in terms of its two components. Eqn. (1) then becomes:

$$E^0_{M^{3+}/M^{2+}} + 4.43 = E_{fd} + [\Delta G^0_{ion}(d) + \Delta G^0_h(M^{3+}) - \Delta G^0_h(M^{2+})]. \quad (10)$$

The relationship $E^0_{M^{3+}/M^{2+}} = f(E_{fd})$ will obviously be linear if the quantity in square brackets does not depend or is linearly dependent on the *fd*-excitation energy. For elements such as La and Ce (Fig. 3) or Gd and Tb (Fig. 4), the standard oxidation potential of the M^{3+}/M^{2+} couple for the two elements being compared is practically independent of the *fd*-excitation energy (straight line *2*). As noted above, this is related to the fact that in these elements in the coordinated state an electron is localised in a *d*-orbital. The anomalous position of La^{2+}, Ce^{2+} and Gd^{2+}, Tb^{2+} reflects their position in the sequence of change in the hydration energies of Ln^{2+} with change in the atomic number (Fig. 2). Figs. 3 and 4 can be used to estimate the stabilisation energy of the *d*-level in aqueous solutions. It will obviously correspond to that *fd*-excitation energy of the free ion (the 4*f*-orbitals undergo practically no splitting in the crystal field of the ligands) which correspond to the point of intersection of straight lines *1* and *2* (Figs. 3 and 4). The values obtained using this approach for the stabilisation energy of the *d*-state are 1.6 eV for the first half of the lanthanide family, and 2.1 eV for the second, in good agreement with the values obtained from the hydration relationships (Fig. 2).

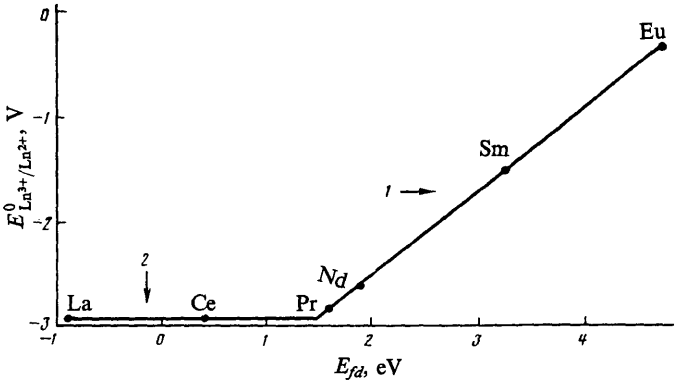


Figure 3. Dependence of the standard oxidation potentials of the Ln^{3+}/Ln^{2+} couples ($E^0_{Ln^{3+}/Ln^{2+}}$) on the *fd*-excitation energy of Ln^{2+} (E_{fd}) for the first half of the lanthanide family.[47]

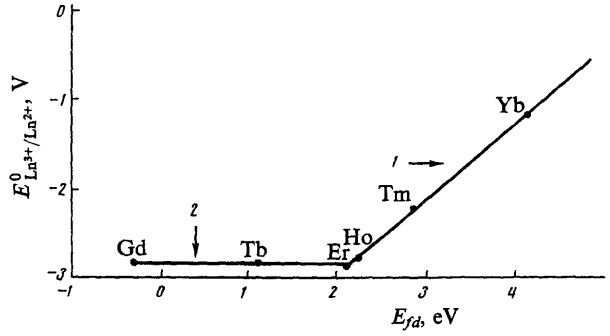


Figure 4. Dependence of the standard oxidation potentials of the Ln^{3+}/Ln^{2+} couples on the *fd*-excitation energy of Ln^{2+} for the second half of the lanthanide family.[47]

For An, the hydration energies of the An^{2+} ions cannot be calculated using Eqn. (1) as in the case of Ln, since there are no experimental values of the third ionisation potentials and hydration energies of the An^{3+} ions. The *fd*-excitation energies of the doubly-charged ions have been calculated for all An,[19] however, so that it has been possible to study the dependence of $E^0_{An^{3+}/An^{2+}}$ on the *fd*-excitation energies of the free doubly-charged ions (Fig. 5). Fig. 5 shows that the standard oxidation potential of the M^{3+}/M^{2+} couple for U, Np, Pu, and Cm is independent of E_{fd}, as already observed for La, Ce, Gd, and Tb. Thus these elements of the An family in the divalent state apparently have an electron configuration with a *d*-electron. The stabilisation energy of the *d*-state for An is 2.1 eV, which coincides with the value obtained for the second half of the Ln family.

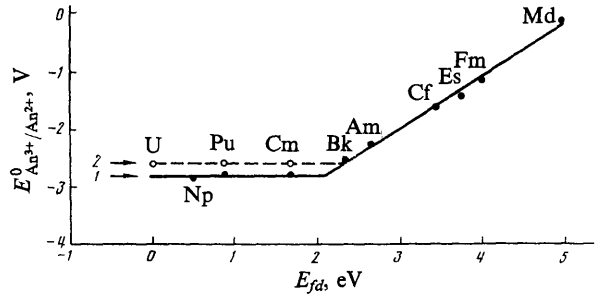


Figure 5. Dependence of the standard oxidation potentials of the An^{3+}/An^{2+} couples ($E^0_{An^{3+}/An^{2+}}$) on the *fd*-excitation energy of An^{2+} (E_{fd}) for the second half of the actinnide family.[47]

V. Characteristics of the behaviour of divalent actinides in melts

An interesting feature is that the oxidation potential of the Pu^{3+}/Pu^{2+} couple depends on the Pu concentration even in the micro-concentration range. With change in the Pu concentration from $\sim 10^{-4}$ mol% to $\sim 10^{-6}$ mol% the standard oxidation potential of the Pu^{3+}/Pu^{2+} couple changes from -2.59 V to -2.79 V (Fig. 5). In addition, the standard oxidation potential of the Cm^{3+}/Cm^{2+} couple in the presence of $\sim 10^{-4}$ mol% Pu also changes from -2.78 V to -2.59 V and coincides with the value for Pu at a concentration of 10^{-4} mol%. In addition to Cm, Pm was also added to the system; at the oxidation potential of the Nd^{3+}/Nd^{2+} couple, Pm is reduced to the divalent state. In contrast to the case of Cm, the oxidation potential of $E^0_{Pm^{3+}/Pm^{2+}}$ remained unchanged in the presence of Pu.[52] Thus Pu^{2+} is apparently able to form dimers or simple clusters. This distinguishes it from Pm^{2+} and other divalent Ln and An with the electronic structure $f^n d^0$. The probability of this process evidently depends on the Pu concentration. In addition, Cm^{2+} can also take part in the formation of clusters with Pu, and in this case its standard oxidation potential increases to the oxidation potential of the Pu^{3+}/Pu^{2+} couple. The values of the standard An^{3+}/An^{2+} oxidation potentials obtained for ponderable quantities of the elements of this family are given by straight lines *2* in Fig. 5. The "dimerisation" is an additional factor stabilising the oxidation state 2+, and was observed by us only for 5*f*-elements characterised in the divalent state by the participation of *d*-orbitals in chemical bonding.

For U there are no data on the standard oxidation potential of the U^{3+}/U^{2+} couple in the micro-concentration range ($\sim 10^{-6}$ mol%), since the experiments on its reduction were carried out using the ^{233}U isotope at a concentration of $\sim 10^{-4}$ mol%.[53] The value of $E^0_{U^{3+}/U^{2+}}$ coincides with that of $E^0_{Pm^{3+}/Pm^{2+}}$ at the same concentration (Fig. 5). Thus uranium is apparently dimerised in the divalent state in the melt. This was confirmed by subsequent studies which showed that the oxidation potential of Cm increases to -2.6 V in the presence of ponderable quantities of uranium.

The behaviour of Np is of particular interest. Change in the Np concentration from 10^{-3} mol% to trace quantities has no influence on the value of $E^0_{Np^{3+}/Np^{2+}}$ (straight line *1* in Fig. 5). Thus Np^{2+} does not form dimers in melts and in this respect differs from U, Pu, and Cm.[54]

The suggestion that dimers are formed was confirmed by studying the behaviour of Pu^{2+} during the directed crystallisation of $NdBr_2$. In contrast to the case of Am^{2+} and Eu^{2+}, for which the coefficient of cocrystallisation with $NdBr_2$ differs little from 1, the cocrystallisation coefficient of Pu^{2+} is characterised by the presence of a maximum as the crystallisation of $NdBr_2$ proceeds (Fig. 6).[52,55] The authors cited explain the appearance of the maximum as follows. As the crystallisation tube moves from the hot zone of the melt to the cooled zone, decrease in temperature is accompanied by dimerisation. The resulting dimers cocrystallise with the $NdBr_2$ matrix with a high coefficient. Thus the crystallising $NdBr_2$ as it were "draws out" Pu^{2+} from the melt. This is facilitated by the hindering of the back diffusion of dimerised plutonium into the hot zone of the melt. As a result, there is an appreciable decrease in the concentration of plutonium in the melt, so that the dimerisation stops and the cocrystallisation coefficient of Pu decreases in the final stage of the directed crystallisation. The directed-crystallisation experiments confirm the anomalous behaviour of Pu^{2+} compared with Am^{2+} and Eu^{2+}, resulting from the participation of *d*-orbitals of Pu^{2+} in chemical bonding.

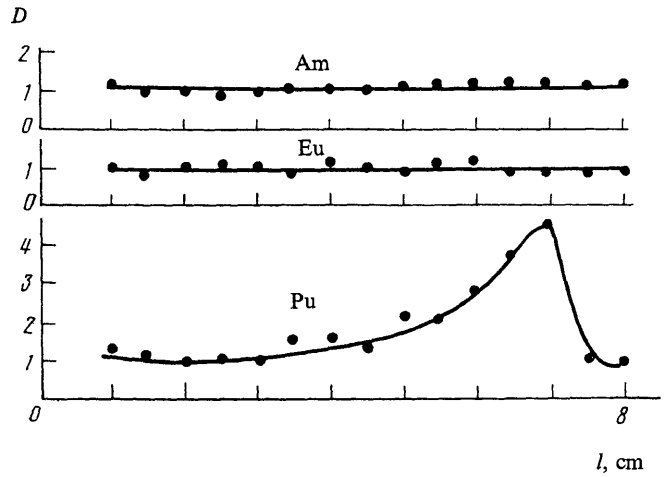


Figure 6. Distribution of Pu^{2+}, Eu^{2+}, and Am^{2+} along the crystal (*l*) in the directed crystallisation of $NdBr_2$.[55]

VI. Stabilisation of the oxidation state 2+ of lanthanides and actinides in condensed clusters

In recent years a number of condensed cluster compounds containing lanthanides having oxidation states from 1+ to 2.5+ have been synthesised.[56–61] It has been established[60] that the *d*-orbitals of the lanthanides take part in the formation of the M–M bond. The compound Gd_2Cl_3 was first obtained by the reaction of metallic Gd with molten Gd trichloride.[44] This cluster forms acicular crystals made up of chains of octahedra of gadolinium atoms joined to one another via shared edges. The mechanism of formation of the cluster has not been studied, however.

Two possible mechanisms of formation of the cluster have been proposed. The first is based on the disproportionation of gadolinium dichloride formed by the reaction of Gd^0 with $GdCl_3$:

$$Gd^0 + 2GdCl_3 \rightarrow 3GdCl_2 ,$$
$$\frac{3GdCl_2 \rightarrow Gd_2Cl_3 + GdCl_3}{Gd^0 + GdCl_3 \rightarrow Gd_2Cl_3} .$$

The second mechanism assumes reduction by metallic gadolinium sorbed on the cluster by a mechanism involving the primary sorption of the trivalent gadolinium ion:

$$Gd^0 \rightarrow Gd^{3+} + 3e^- ,$$
$$2GdCl_3 + 3e^- \rightarrow Gd_2Cl_3 + 3Cl^- ,$$
$$\frac{Gd^{3+} + 3Cl^- \rightarrow GdCl_3}{Gd^0 + CdCl_3 \rightarrow Gd_2Cl_3} .$$

The overall reaction is the same for both processes, so that it is difficult to establish the mechanism of formation of the cluster. At the same time it should be noted that a necessary condition for the first mechanism is the existence of divalent gadolinium. In this case, if a micro-component which is also reduced to the oxidation state 2+ and which like Gd^{2+} has the electron configuration $f^{n-1}d^1$ is introduced into the system, then the extent of its cocrystallisation will be proportional to the fraction of this element in the divalent state. For the second mechanism, which assumes the participation of the trivalent form of the element in the cocrystallisation, the opposite relationship should be observed, that is decrease in the cocrystallisation with increase in the fraction of the reduced form of the cocrystallising element.

Equations have been derived,[62] describing the distribution of a micro-component between solid Gd_2Cl_3 and molten $GdCl_3$ for the two mechanisms, namely

$$\ln\frac{a}{a-x} = \frac{2(1+k)}{1+k\cdot\exp\left(\frac{\Delta E^0_{M-m}}{RT/F}\right)}\lambda_1\cdot\ln\frac{2b}{2b-y} , \qquad (11)$$

for the first mechanism and

$$\ln\frac{a}{a-x} = \frac{2(1+k)\cdot\exp\left(\frac{\Delta E^0_{M-m}}{RT/F}\right)}{1+k\cdot\exp\left(\frac{\Delta E^0_{M-m}}{RT/F}\right)}\lambda_2\cdot\ln\frac{2b}{2b-y} , \qquad (12)$$

for the second mechanism of formation of the cluster, where a and b are the initial concentrations of the micro-component and the macro-component in the $GdCl_3$ melt, x and y their concentrations in the cluster Gd_2Cl_3, k the ratio of the concentrations $[Gd^{3+}]$ and $[Gd^{2+}]$ in the melt, and λ the cocrystallisation coefficient.

It can be seen that if $\Delta E^0_{M-m} = 0$, both equations become

$$\ln\frac{a}{a-x} = 2\lambda\cdot\ln\frac{2b}{2b-y} , \qquad (13)$$

and in this case the mechanism of formation of the cluster cannot be determined. Thus to establish the mechanism of formation of the cluster it is necessary to determine the cocrystallisation coefficient λ for elements which are chemically similar to Gd but which differ from gadolinium in the values of the standard oxidation potential of the M^{3+}/M^{2+} couple. This requirement is satisfied by Np, Pu, and Cm (Table 2). Since we are considering actinides with similar ionic radii, the coefficients of their cocrystallisation with Gd_2Cl_3 should be close to one another.

Table 6 gives the values of the cocrystallisation coefficients λ_1 and λ_2 for Np, Pu, and Cm with Gd_2Cl_3, calculated from Eqns. (11) and (12), which describe respectively the first and second mechanisms of formation of the cluster.[62]

Table 6. Cocrystallisation coeffcients λ_1 and λ_2 for Np, Pu, and Cm with Gd_2Cl_3.[17]

An	$E^0_{M^{3+}/M^{2+}}$, V	λ_1	λ_2
Np	−2.86	1.16	2.21
Pu	−2.59	0.072	2.03
Cm	−2.78	0.70	1.73

Table 6 shows that the values of λ_1, obtained assuming that the cocrystallisation takes place by the first mechanism, show poor agreement with one another. The situation is quite different if it is assumed that the second mechanism of cocrystallisation is correct. In this case the values of λ_2 for all three elements are close to one another, as expected for elements with similar properties It was therefore concluded[62] that the formation of the Gd_2Cl_3 cluster passes through a stage involving the sorption of the trivalent ion on the surface of the growing crystal and the subsequent reduction of Ln^{3+} to the oxidation state 1.5+.

Subsequent studies showed that not every trivalent ion can enter the Gd_2Cl_3 matrix. For example, Nd^{3+} and Pu^{3+}, which have similar ionic radii (0.0983 nm and 0.100 nm respectively) and practically identical standard oxidation potentials of the M^{3+}/M^{2+} couples (−2.62 V and −2.59 V respectively), show completely different behaviour on cocrystallisation with the Gd_2Cl_3 cluster. Plutonium cocrystallises with Gd_2Cl_3, but Nd^{2+} does not.[17] The explanation is that after sorption, the trivalent ion is reduced to the lower oxidation state by the "electron gas" in the Gd_2Cl_2 matrix. As can be seen from Fig. 5, Pu then acquires an electron configuration analogous to that of Gd, and takes part in the chemical bonding using its *d*-orbitals. In the case of Nd, the situation is quite different. As can be seen from Fig. 3, divalent neodymium does not have valence *d*-orbitals, and cannot take part in the construction of the Gd_2Cl_3 crystal lattice. Thus by studying the cocrystallisation with Gd_2Cl_3 it is possible to reach conclusions about the electron configuration of an *f*-element in the divalent state. Some elements which in the melt have the electron configuration f^nd^0, for example, Pr, Er, and Ho, cocrystallise with Gd_2Cl_3.[63,64] Figs. 3 and 4 show that Pr and Er lie at the intersection of straight lines *1* and *2*, corresponding to two different electron configurations of the ions in the divalent state, and the slight increase in the stabilisation energy of the *d*-level in the Gd_2Cl_3 crystal converts all of the above three elements into the $f^{n-1}d^1$ configuration. For Ho,

the *fd*-excitation energy is 0.13 eV greater than the stabilisation energy in melts. From this it follows that the stabilisation energy in the Gd_2Cl_3 matrix is approximately 0.13 eV greater than the stabilisation energy in the chloride melt. Our recent studies have shown that the same applies to the actinides. Thus berkelium cocrystallises with Gd_2Cl_3, whereas in the melt it has the configuration $[f^n d^0]^{2+}$. This indicates that for the actinides, the stabilisation energy of the *d*-level in Gd_2Cl_3 is 0.2 eV greater than that in the melt.

An important factor in cocrystallisation with the cluster is the ionic radius of the cocrystallising element. For example, in the series Pr–Ce–La the coefficient of cocrystallisation with the Gd_2Cl_3 cluster decreases from 0.5 for Pr to almost zero for La. The ionic radius of La^{3+}, which undergoes almost no cocrystallisation with Gd_2Cl_3, differs from that of Gd^{3+} by about 10%. According to Mitscherlich, this difference between the ionic radii should lead to a sharp decrease in the miscibility of the elements in the solid phase, as observed in the cocrystallisation of Ce and more particularly La with Gd_2Cl_3.[63] The opposite dependence of the cocrystallisation coefficients on ionic radius is observed for the actinides, however, where λ decreases in the series Pa–Np–Pu–Cm–Bk (Table 7). A possible explanation for this relationship and the comparatively high values of λ for these elements may be that in addition to *d*-orbitals, the 5*f*-orbitals are also involved in chemical bonding.

Table 7. Cocrystallisation coefficients for actinides with the cluster Gd_2Cl_3

An	Cocrystallisation coefficient λ (Ref.17)	Ionic radius of An^{3+}, nm (Ref.65)
Pa	3.00	0.104
Np	2.21	0.101
Pu	2.03	0.100
Cm	1.73	0.097
Bk	1.20	0.096

The study of the cocrystallisation of Ln and An with the Gd_2Cl_3 matrix has shown which elements of these families in the divalent state have a valence-electron configuration analogous to that of Gd^{2+}. Among the lanthanides these are La, Ce, Pr, Gd, Tb, Er, Ho, and Lu. To these can be added Y, which also has a *d*-electron in the divalent state. The actinides having an electron configuration with a *d*-electron are Pa, Np, Pu, Cm, and Bk.

Thus experimental data and information on the electronic structure of the free ions Ln and An show that a considerable number of elements of the *f*-series in the oxidation state 2+ are characterised by the participation of a *d*-electron in chemical bonding, leading to anomalous stabilisation of the oxidation state 2+, revealed by an increase in the oxidation potentials, an increase in the hydration energies, and the ability to form dimers and clusters.

* * *

The anomalous stabilisation of lantanides and actinides in the oxidation state 2+ has made it possible to reduce La, Ce, Gd, Tb, U, Np, Pu, and Cm to the divalent state. The chemical properties of these ions are similar to those of divalent yttrium. Until now it has been considered that the divalent lanthanides and actinides are analogues of the alkaline earth elements. This is true for those elements, such as Eu, for which the *fd*-excitation energy is greater than the stabilisation energy of the *d*-level. For these elements the stability of the divalent state is linearly dependent on the *fd*-excitation energy. For those divalent elements which are analogues of divalent yttrium, the stability of the divalent state is determined not by the *fd*-excitation energy by by factors stabilising the *d*-level: the splitting of the *d*-level in the crystal field of the ligands, the covalent character of the bonds with the ligands, dimerisation, and possibly others.

The elements of a given family, Ln or An, may be analogues of elements of the *s*- or *d*-groups of Mendeleev's periodic system depending on the *f*–*d*-excitation energy.[66]

The observed constant value of the standard oxidation potential of the An^{3+}/An^{2+} couples for U, Np, Pu, and Cm makes it possible to predict the value of this quantity for Ac and Pa (betwen −2.6 V and −2.9 V). There are no published data on the possible existence of Pa in the divalent state. For Ac^{2+}, the published values of its potential are −1.5 V[67] and above −1.6 V.[68] Both values are apparently too high.

Further studies will undoubtedly reveal many new and unusual features in the properties of *f*-elements showing anomalous stability of the oxidation state 2+.

References

1. R E Connick *J. Chem. Soc. Suppl.*, 1949, (235)
2. E A Kanevskii *Dokl. Akad. Nauk SSSR*, 1981, **257** 926
3. L J Nugent, R D Baybarz, J L Burnett, J L Ryan *J. Phys. Chem.*, 1973, **77** 1528
4. C K Jørgensen *Chem. Phys. Lett.*, 1968, **2** 549
5. D A Johnson *J. Chem. Soc., Dalton Trans.*, 1974, 1671
6. L F Druding, J D Corbett, B N Ramsey *Inorg. Chem.*, 1963, **2** 869
7. L F Druding, J D Corbett *J. Am. Chem. Soc.*, 1959, **81** 5512
8. N B Mikheev, V I Spitsyn, L N Auerman, et al. *Radiokhimiya*, 1976, **18** 556
9. J D Corbett, B C MacCollum *Inorg. Chem.*, 1956, **5** 538
10. U Loechner, J D Corbett *Inorg. Chem.*, 1975, **14** 426
11. N B Mikheev, B G Korshunov, L N Auerman, et al. *Radiokhimiya*, 1981, **23** 624
12. P E Caro, J D Corbett *J. Less-Common Met.*, 1969, **18** 1
13. R D Baybarz, L B Asprey, C E Strouse, E Fukushima *J. Inorg. Nucl. Chem.*, 1972, **34** 3427
14. N B Mikheev, R A D'yachokva, V I Spitsyn *Dokl. Akad. Nauk SSSR*, 1979, **244** 109
15. N B Mikheev, V I Spitsyn, A N Kamenskaya, et al. *Radiokhimiya*, 1972, **14** 486
16. N B Mikheev, V I Spitsyn, B A Gvozdev, et al. *Dokl. Akad. Nauk SSSR*, 1971, **201** 1393
17. N B Mikheev, A N Kamenskaya *Coord. Chem. Rev.*, 1991, **109** 1
18. W C Martin, R Zalubas, L Hagan *Atomic Energy Levels—The Rare-Earth Elements*, NSRDS–NBS, 1978, No.60
19. K L Vander Sluis, L J Nugent *J. Opt. Soc. Am.*, 1974, **64** 687

20. N B Mikheev, R A D'yachkova, L N Auerman *Acta Chim. Acad. Sci. Hung.*, 1981, **108**(3) 249
21. V I Spitsyn, N B Mikheev, L N Auerman *Dokl. Akad. Nauk SSSR*, 1981, **261** 1154
22. N B Mikheev, L N Auerman, R A D'yachkova, I A Rumer *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 818
23. N B Mikheev, R A D'yachkova, L N Auerman, I A Rumer *Radiokhimiya*, 1982, **24** 112
24. N B Mikheev, L N Auerman, I A Rumer, R A D'yachkova *Radiokhimiya*, 1983, **25** 65
25. N B Mikheev, L N Auerman, I A Rumer *Zh. Neorg. Khim.*, 1983, **28**(5) 1329 [English translation in *Russ. J. Inorg. Chem.*, 1983(5)]
26. N B Mikheev, L N Auerman, I A Rumer *Radiokhimiya*, 1984, **26** 718
27. N B Mikheev, L N Auerman, I A Rumer, S A Kulyukhin, *Radiokhimiya*, 1984, **26** 415
28. N B Mikheev, L N Auerman, I A Rumer *Radiokhimiya*, 1984, **26** 646
29. N B Mikheev, L N Auerman, I A Rumer *Inorg. Chim. Acta*, 1985, **109** 217
30. L R Morss, M C McCue *Inorg. Chem.*, 1975, **14** 1624
31. D E Hobart, Ph. D. Thesis, University of Tennessee, Knoxville, 1981
32. N B Mikheev, V I Spitsyn, A N Kamenskaya, et al. *Radiokhimiya*, 1978, **20** 564
33. N B Mikheev, I A Rumer *Radiokhimiya*, 1972, **24** 492
34. C Musikas, R G Haire, J R Peterson *J. Inorg. Nucl. Chem.*, 1981, **43** 2935
35. K E Johnson, J R Mackenzie *J. Electrochem. Soc., Electrochem. Sci.*, 1969, **116** 1697
36. B F Myasoedov, Yu M Kulyako, I S Sklyarenko *Inorg. Nucl. Chem. Lett.*, 1972, **8** 433
37. H A Friedman, J R Stokely, R D Baybarz *Inorg. Nucl. Chem. Lett.*, 1972, **8** 433
38. N B Mikheev, L N Auerman, I A Rumer *Electrokhimiya*, 1987, **33** 638
39. V I Minkin (Editor) *Lantanoidy* (The Lanthanides), Izd. Rostov. Univ., Rostov-on-Don, 1980, p. 26
40. L L Borin, A I Karelin *Termodinamika Okislitel'no-vosstanovitel'nykh Protsessov v Tekhnologii Aktinidov* (The Thermodynamics of Redox Processes in the Technology of the Actinides), Atomizdat, Moscow, 1977, p. 207
41. D Brown *Halides of the Lanthanides and Actinides* (Translated into Russian), Atomizdat, Moscow, 1972, p. 161
42. H R Bronstein *J. Phys. Chem.*, 1969, **73** 1320
43. L F Druding, J D Corbett *J. Am. Chem. Soc.*, 1961, **83** 2462
44. J E Mee, J D Corbett *Inorg. Chem.*, 1965, **4** 88
45. J D Corbett, D L Pollard, J D Mee *Inorg. Chem.*, 1966, **5** 761
46. K W R Johnson, J A Leary *J. Inorg. Nucl. Chem.*, 1964, **26** 103
47. N B Mikheev, I L Rumer, L N Auerman *Radiokhimiya*, 1985, **27** 539
48. N B Mikheev *Radiokhimiya*, 1988, **30** 297
49. K E Johnson, J N Sandoe *J. Chem. Soc. A*, 1969, 1694
50. N B Mikheev, M Z Kazakevich, I L Rumer *Radiokhimiya*, 1990, **32** 40
51. N B Mikheev, I A Rumer, L N Auerman *Radiochem. Radioanal. Lett.*, 1983, **59** 317
52. N B Mikheev *Radiokhimiya*, 1988, **30** 16
53. N B Mikheev, E R Merts *Radiokhimiya*, 1990, **32** 1
54. N B Mikheev, I A Rumer, M Z Kazakevich *Radiokhimiya*, 1991, **33** 9
55. N B Mikheev, M Z Kazakevich I A Rumer *Radiokhimiya*, 1986, **28** 773
56. H J Mattausch, J B Hendricks, R Eger, et al. *Inorg. Chem.*, 1980, **19** 2128
57. A Simon, N Holzer, H J Mattausch *Z. Anorg. Allg. Chem.*, 1979, **456** 207
58. H J Mattausch, A Simon, N Holzer, R Eger *Z. Anorg. Allg. Chem.*, 1980, **466** 7
59. A Simon *Angew. Chem. Int. Ed. Engl.*, 1981, **20** 1
60. G Ebbinghaus, A Simon, A Griffith *Z. Naturforsch.*, 1982, **37a** 564
61. A Simon *J. Solid State Chem.*, 1985, **57** 2
62. N B Mikheev, I A Rumer, A N Kamenskaya, M Z Kazakevich *Radiokhimiya*, 1989, **31** 23
63. N B Mikheev, A N Kamenskaya, I A Rumer *Radiokhimiya*, 1991, **33** 10
64. N B Mikheev, A N Kamenskaya, I A Rumer *Radiokhimiya*, 1991, **33** 13
65. R D Shannon *Acta Crystallogr., Sect. A*, 1976, **32** 751
66. N B Mikheev *Naturwissenschaften*, 1989, **76** 107
67. F David *Radiochem. Radioanal. Lett.*, 1970, **5** 275
68. H Yamana, T Mitsugashira, Y Shiokawa, et al. *J. Radioanal. Chem.*, 1983, **76** 16

Received 8th May 1992

Translated from *Uspekhi Khimii* **61** 1822–1838 (1992) U.D.C. 541.127:577.151

Kinetic isotope effects in the enzymic reactions of tritium- and deuterium-containing substrates

G P Akulov
Khlopin Radium Institute (Scientific-Industrial Association), St. Petersburg

ABSTRACT. The kinetic differences between the enzymic reactions involving substrates containing heavy hydrogen isotopes are examined. Theoretical estimates and numerous examples of experimentally measured kinetic isotope effects in various enzymic reactions are presented. The kinetic isotope effects are widely used in studies of the mechanisms of enzymic reactions and of the structures of the enzyme–substrate complexes, for the enrichment of labelled compounds in heavy hydrogen isotopes, and also in certain fields of medicine and biochemistry.

The bibliography includes 99 references.

Contents

I. Introduction 999
II. Theoretical estimates of kinetic isotope effects 999
III. Classification of kinetic isotope effects in enzymic reactions 1000
IV. Methods for the determination of kinetic isotope effects in enzymic reactions 1001
V. Applications of kinetic isotope effects 1002

I. Introduction

The use of labelled compounds as radioactive tracers is based on the hypothesis of the identity of the physicochemical properties of the labelled and unlabelled molecules of the given compound.[1] This assumption is to some extent arbitrary. The introduction of an isotope label and especially of heavy hydrogen isotopes induces the appearance of isotope effects—definite changes in the physical, chemical, and biochemical, pharmacokinetic, and certain other properties of the labelled compounds.[2]

Among the numerous studies devoted to isotope effects, a large proportion referred to studies of the kinetic differences between the chemical reactions of isotopic molecules, i.e. to kinetic isotope effects (KIE).[3] KIE referring to enzymic reactions have been studied to a lesser extent, although recently there has been a continuous growth of interest in such effects, which is indicated by the constantly increasing number of published (mainly abroad) review and original (see, for example, Refs. 17–21) papers. Unfortunately, one must conclude that this field of enzyme kinetics has as yet attracted little attention by the investigators in our country.

The current interest in studies on KIE in enzymic reactions is caused, on the one hand, by the fact that the KIE may serve as a potential source of possible errors in the use of labelled compounds in radiochemical studies on enzymic reactions[22,23] and, on the other hand, KIE can serve as a powerful means of investigating a number of important problems in enzymology.[5, 11–14]

While our aim is not a detailed examination of the negative aspect of KIE, we may note, for example, that the difference between the rates of enzymic reactions of labelled and unlabelled substrates can be the cause of errors in radiometric measurements of the catalytic activities of enzymes, in the isotopic determinations of the rates of individual stages of the process, and in the establishment of the kinetic orders of the reactions of the substrates. Failure to take into account KIE in the studies on metabolism and pharmacokinetics with the aid of labelled preparations can also lead to serious errors. These and certain other complications associated with KIE become particularly significant in polyenzymic processes and also when substrates with a high degree of isotope substitution (multiply labelled compounds) are used. Comprehensive study of KIE makes it possible not only to foresee the possibility of such errors but also to avoid them by selecting conditions in the use of labelled compounds under which KIE are minimal or are fully excluded.

As regards the positive aspect of KIE, one should note in the first place the enormous importance which they have in studies on the mechanisms of enzymic reactions and the structures of enzyme–substrate complexes. One of the promising fields also involves the use of KIE for the enrichment of labelled compounds in heavy isotopes.

II. Theoretical estimates of kinetic isotope effects

The ratios of the rate constants for the corresponding pairs of isotopic molecules have come to be used for the quantitative characterisation of the kinetic differences in reactions of labelled and unlabelled compounds. Since these differences are determined primarily by the relative differences between the masses of the isotopes, the maximum KIE are to be expected for compounds labelled with hydrogen isotopes, for which the mass ratios are maximal ($^1H:^2H:^3H = 1:2:3$).

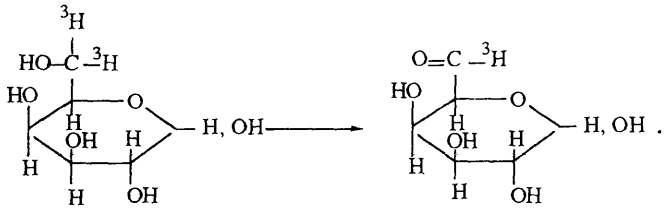
Theoretical calculations of KIE are based on the kinetic transition state theory or the theory of rate processes.[24] Without dwelling on the details of the conclusions which have been described quite fully in the familiar monograph by Melander and Saunders,[3] we shall quote the principal predictions by these authors concerning the values of the KIE for reactions involving compounds labelled with hydrogen isotopes.

The simplest calculations of KIE in which the absence of differences between the energies of the zero-point vibrations of the C–H, C–D, and C–T bonds in the transition complexes is assumed yield the quantities $k_H/k_D = 6.9$ and $k_H/k_T = 16$. In calculations where the disappearance of the deformation vibration

frequencies in the transition state is assumed, the following limiting isotope effects were obtained: from 15 to 20 for k_H/k_D and from 50 to 75 for k_H/k_T. However, the available data show that even if the deformation modes are weakened, this occurs to a very slight extent and the appreciably higher values of the KIE sometimes observed in practice compared with the above results of semiclassical calculations (6.9 for deuterium and 16 for tritium) is more likely to be attributable to quantum mechanical tunnelling. Melander and Saunders believe[3] that the isotope effects k_H/k_D below 12 and k_H/k_T below 36 may contain a definite contribution due to tunnelling, while higher values of the KIE cannot be explained at all without resorting to the tunnel effect.

The experimental protium–deuterium and protium–tritium KIE for many chemical and enzymic reactions are close to the values predicted by semiclassical calculations. There are numerous examples in the literature of a significant retardation (sometimes by several tens) of a wide variety of chemical (see, for example, Rosenberg[25]) and enzymic[26,27,34–42] reactions involving deuteriated and tritiated substrates.

As an example of such high KIE, one may quote the results of kinetic studies of the oxidation reaction of tritium-labelled galactose catalysed by galactose oxidase:[27]



It has been established that galactose doubly labelled with tritium in the 6-position is oxidised at a rate which is lower almost by a factor of 150 than the rate of oxidation of normal galactose. Such a high KIE is due both to the different isotopic composition of the bond subjected to chemical change and to the different isotopic composition of the neighbouring bond.

There exists a fairly well justified theoretical and experimentally confirmed relation between the protium–deuterium and protium–tritium KIE. It was first established by Swain, et al.[28] in the form of the equation

$$\frac{\ln (k_H/k_T)}{\ln (k_H/k_D)} = 1.44$$

or

$$\frac{k_H}{k_T} = \left(\frac{k_H}{k_D}\right)^{1.44}.$$

These relations are used widely to predict the KIE in the reactions of substrates labelled with one of the heavy hydrogen isotopes, provided that the KIE for the other isotope has been established experimentally.

The same relations can be used to confirm the reliability of the experimental results. For example, markedly different results of spectrophotometric measurements of the KIE in D-[1-^{2}H]glucose enzymic oxidation reaction have been published: the protium–deuterium KIE has been estimated as 10–15 by Bright and Gibson[29] and as 2.2–2.5 by Hauge et al.[30] Radiometric measurements of the protium–tritium KIE in a similar D-[1-^{3}H]-glucose oxidation reaction yielded k_H/k_T = 3.0–3.1.[31] When the latter was used to calculate the expected protium–deuterium effect from the equations presented above, it was found that the KIE is 2.2, which confirms the reliability of the value found by Hauge, et al.[30]

III. Classification of kinetic isotope effects in enzymic reactions

The classification adopted for chemical processes[3] can be used for the KIE in enzymic reactions. As in chemical reactions, the KIE can be divided into primary and secondary and intramolecular and intermolecular. The primary isotope effects are determined by the different isotopic compositions of the bond being dissociated with the same isotopic composition of the neighbouring bond. The secondary isotope effect is determined by the different isotopic compositions of the neighbouring bond for the same isotopic composition of the bond being dissociated. The combined isotope effect is determined simultaneously by the different isotopic compositions of the bonds being dissociated and the neighbouring bond. The intramolecular isotope effect (or the intramolecular competition factor) is determined by the different isotopic compositions of two chemically equivalent bonds in the same molecule. The intermolecular isotope effect is determined by the different isotopic compositions of molecules in the same incubation system.

The characteristic features of the kinetics of enzymic reactions, associated primarily with the multistage nature of the process and the phenomenon involving the saturation of the enzyme by the substrate, require the expansion of the classification of the KIE using special kinetic parameters which are not used in the kinetics of chemical reactions. Such a classification has been mainly developed by Northrop.[5,7]

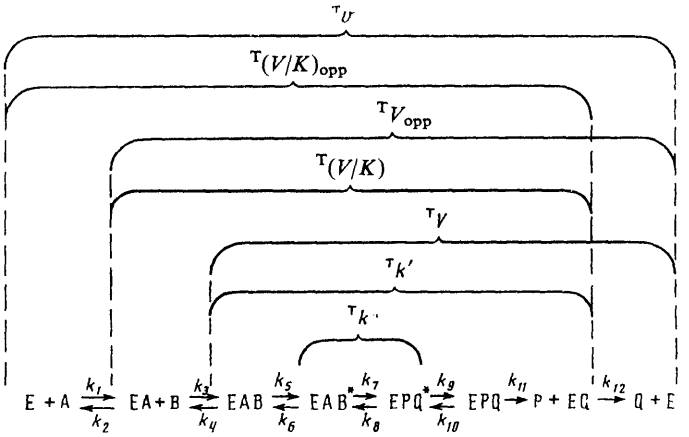


Figure 1. Classification of kinetic isotope effects in a two-substrate enzymic process.[5,7]

In the multistage enzymic process illustrated schematically in Fig. 1, the presence of a tritium (or deuterium) label in one of the substrates (for example, A) can affect the rates of individual stages

and the kinetic parameters entering into the main kinetic equation for enzymic processes (the Michaelis–Menten equation):[32]

$$v = \frac{V\,[S]}{K + [S]},$$

where v is the rate of reaction, V the maximum rate for the complete saturation of the enzyme by the substrate, [S] the substrate concentration, and K the Michaelis–Menten constant. The braces in the scheme enclose the stages in which the KIE can be determined experimentally. The symbols above the braces denote the KIE in terms of definite kinetic parameters and the superscript T means that in the given instance the isotope effect refers to tritium, i.e. one is dealing with the ratio of the corresponding parameter for the protium form to the parameter for the tritium form of the substrate.

The KIE indicated have been given the following names:[7] the isotope effect ^{T}v is the "observed isotope effect", the isotope effects $^{T}(V/K_{app})$ and $^{T}V_{app}$ are the "apparent isotope effects" (they are obtained by extrapolating the observed isotope effects to infinitely small and infinitely large concentrations of the substrate A for a fixed concentration of the cosubstrate B), the isotope effects $^{T}(V/K)$ and ^{T}V are the "limiting isotope effects" (they refer respectively to low and high concentrations of the cosubstrate B), the isotope effect $^{T}k'$ is the "internal isotope effect", and finally the isotope effect ^{T}k is the "true isotope effect" (it is analogous to the KIE in chemical reactions). The true isotope effects in the forward and reverse reactions may not be the same, which leads to the appearance of an isotope effect in the equilibrium constants.

IV. Methods for the determination of kinetic isotope effects in enzymic reactions

The observed KIE is determined from v as the ratio of the observed rates of conversion of the unlabelled and labelled substrates under identical conditions.

In order to determine the apparent or limiting isotope effects in terms of V and V/K, the concentration variations of the observed rates of conversion of the labelled and unlabelled substrates are investigated. Figure 2*a* presents typical relations of this type. For a high substrate concentration, where the enzyme is saturated by the substrate and the order of the enzyme reaction approaches zero, the labelled and unlabelled molecules are converted at the maximum rates V_H and V_T. The KIE ^{T}V corresponds to this boundary condition (Fig. 2*b*).

In the other boundary situation—at low substrate concentrations—where the process is of first order with respect to substrates, the slope of the initial sections of the curves is equal to the ratio V/K according to the Michaelis–Menten equation. The KIE $^{T}(V/K)$ corresponds to this condition.

The isotope effects in the Michaelis constants can be calculated from the KIE in terms of V and V/K obtained in this way.

Such concentration variations of the KIE can be investigated for the majority of labelled substrates and enzymes. However, limitations are possible for tritium-containing substrates. This applies to reactions for which the Michaelis constants are large and when the attainment of saturation by the enzyme requires the introduction of an appreciable amount (frequently unavailable) of the labelled substrate into the incubation system. We encountered such a case (see, for example, Akulov and Smetkova[31]) in a study of the KIE in the oxidation of glucose labelled with tritium in the 1-position in the presence of glucose oxidase. For this reaction, K has been estimated as 3.3×10^{-2} mol litre^{-1}.[33] In this case, the saturation of the enzyme by the substrate requires the use of a labelled substrate having an activity amounting to tens of Curies. Furthermore, difficulties associated with radiation processes arise under these conditions.

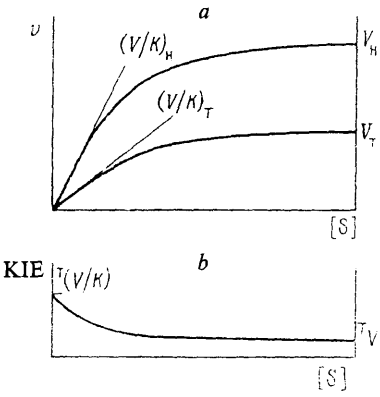


Figure 2. Determination of KIE from the concentration variations of the observed rates of reaction (*a*) and the variation of the KIE with substrate concentration (*b*).

The true ^{T}k or ^{D}k, which reflect the influence of the isotopic composition of the substrate on the true chemical reaction within the activated enzyme–substrate complex, cannot be measured experimentally but they can be calculated from the protium–deuterium and protium–tritium isotope effects in terms of V/K.[7] Thus the true protium–deuterium KIE ^{D}k can be determined with the aid of the equation

$$\frac{^{D}(V/K) - 1}{^{T}(V/K) - 1} = \frac{^{D}k - 1}{^{D}k^{1,44} - 1}.$$

The equation for the calculation of the true tritium KIE has a similar form.

Thus, in order to determine the individual KIE, it is necessary to carry out enzymic reactions of labelled substrates with complete isotope substitution at the reaction centre. Whereas for deuterium such compounds are entirely available, for tritium the production of preparations with complete isotope substitution at a given position within the molecule has begun comparatively recently. Studies in which the KIE in enzymic reactions were investigated using substrates containing exclusively tritium atoms in this position within the molecules reacting chemically in the given process began to be published only in the very latest years. However, there are still frequent claims in the literature that, owing to the absence of tritiated preparations without carriers, the protium–tritium KIE cannot be determined from the individual rates of reaction of the labelled and unlabelled substrates and that the only method which can be used in such investigations is that of competitive reactions in which the incubation system contains simultaneously labelled and unlabelled substrate molecules [Melander and Saunders (Ref. 3, p. 312) and Cleland[14]].

Owing to the difference between the rates of reaction of the labelled and unlabelled molecules, the specific radioactivity of the substrate changes in such competitive experiments. In the determination of the KIE by the competitive method, the reaction is stopped at specified time intervals and the degree of enzymic reaction and the specific radioactivity of the unreacted substrate or product are determined. The kinetic isotope effect in terms of the V/K ratio is calculated from the formula (Ref. 3, p. 105).

$$^{T}(V/K) = \frac{\lg(1-F)}{\lg[1-(FA_p/A_S^0)]},$$

where F is the extent of reaction and A_S^0 and A_p are the initial molar radioactivity of the substrate and the specific radioactivity of the product. In order to achieve the maximum accuracy, it is recommended to determine the limiting value of the function for F tending to zero:

$$^{T}(V/K) = \left|(A_S^0/A_p)\right|_{F\to 0}.$$

Thus the competitive method makes it possible to measure only the KIE in terms of V/K. This constitutes its disadvantage.

The methods for the determination of KIE examined require specially synthesised labelled substrates enriched in deuterium or tritium. However, in certain cases it is possible to use preparations with the natural isotopic composition for such purposes.

All hydrogen-containing compounds are known to contain approximately 0.015% of natural deuterium and 4×10^{-15}% of natural tritium. Unfortunately, modern experimental techniques do not allow the employment of natural tritium for the measurement of KIE; however, in the case of deuterium highly sensitive NMR spectrometers permit the measurement of the content of such deuterium in various positions within molecules and to follow its variation in chemical and biochemical processes.

It has been shown with the aid of NMR analysis that the distribution of deuterium can differ fairly appreciably as a function of the source of the preparation. For example, it has been established that specimens of synthetic and natural anethole[43] and camphor,[44] differing in their chemical history, have different distributions of natural deuterium. The cause of this difference is the KIE, which lead to the enrichment of specific positions within the molecules in deuterium. Using the NMR method based on natural deuterium, Pascal, et al.[45] established that C(10) position is appreciably enriched in deuterium in the biosynthesis of β-pinene from mevalonic acid. The KIE calculated from this enrichment proved to 2.1.

It is noteworthy that the method for the determination of KIE in terms of natural deuterium examined above is based on the competitive principle and therefore it permits the determination of KIE solely in terms of the V/K ratio.

V. Applications of kinetic isotope effects

1. Kinetic and chemical mechanisms of enzymic reactions

One of the important problems in enzyme kinetics is the determination of the kinetic mechanism of reactions occurring with participation of two or more substrates (or products), i.e. the specification of the order of the addition of substrates and of the liberation of the products. In order to estimate the kinetic order by classical methods, use is normally made of the technique involving inhibition or equilibrium exchange.[46] However, for enzyme systems, in which the conversion of the substrate into the product via a ternary complex is irreversible, such methods proved to be extremely inconvenient. Additional experimental difficulties arise when one of the substrates is oxygen and one of the products is water.

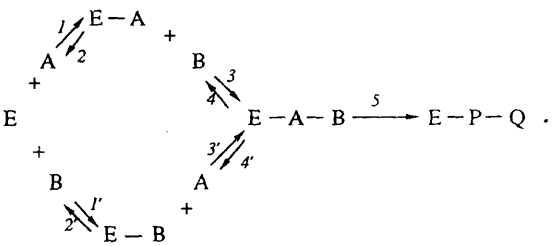
Unique possibilities in the study of the kinetic order of enzymic reactions are provided by the apparent and limiting isotope effects in terms of the V/K ratio, which are determined, as noted above, from the concentration variations of the rate of the process at a fixed concentration of one of the substrates.

Suppose that a substrate A, containing a tritium (or deuterium) label, and substrate B participate in the reaction. The order of the addition of the substrates to the enzyme involves one of the two ordered mechanisms

$$E + A \underset{2}{\overset{1}{\rightleftharpoons}} E-A + B \underset{4}{\overset{3}{\rightleftharpoons}} E-A-B \xrightarrow{5} E-P-Q, \quad (1)$$

$$E + B \underset{2}{\overset{1}{\rightleftharpoons}} E-B + A \underset{4}{\overset{3}{\rightleftharpoons}} E-B-A \xrightarrow{5} E-P-Q \quad (2)$$

or can occur at random:



Kinetic analysis of mechanism (1) yields the following expression for the KIE:[12]

$$^{T}(V/K) = \frac{^{H}k_5/^{T}k_5 + [^{H}k_5(1 + k_3[B]/k_2)/k_4]}{1 + [^{H}k_5(1 + k_3[B]/k_2)/k_4]}.$$

At an infinitely high concentration of the substrate B, the terms of the equation in square brackets become dominant and the KIE tends to unity.

On the other hand, in those cases where the addition of the substrate A precedes the addition of the substrate B [mechanism (2)], the KIE is defined by the equation

$$^{T}(V/K) = \frac{^{H}k_5/^{T}k_5 + {}^{H}k_5/k_4}{1 + {}^{H}k_5/k_4},$$

i.e. is independent of the concentration of the substrate B. In this case, the KIE can assume values from unity to the theoretical maximum value and depends on the ratio $^{H}k_5/k_4$. Here it is important that the ratio is the same for all concentrations [B]. Thus, if it has been established that the concentration of B does not affect the KIE, it follows that B is bound to the enzyme after A.

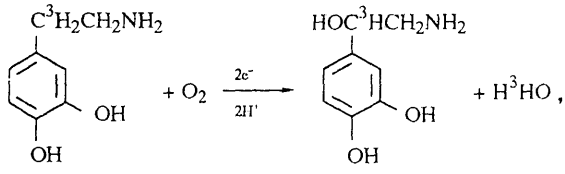
For a random sequence of the addition of the substrates A and B, the expression for the KIE becomes more cumbersome[12] but significantly simplified when the concentration [B] tends to zero:

$$^{T}(V/K) = \frac{^{H}k_5/^{T}k_5 + {}^{H}k_5/(k_4 + k_{4'})}{1 + {}^{H}k_5/(k_4 + k_{4'})}$$

or to infinity:

$$^{T}(V/K) = \frac{^{H}k_5/^{T}k_5 + ^{H}k_5/k_4'}{1 + ^{H}k_5/k_4'} .$$

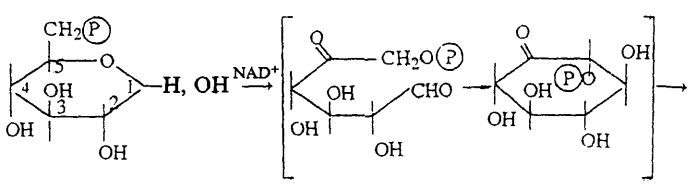
Using the KIE, Miller and Klinman established[10,47] that the oxidation of tritium-labelled dopamine catalysed by the enzyme dopamine β-monooxygenase, i.e.



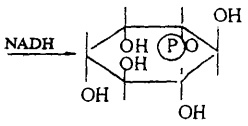
is accompanied by an appreciable KIE (V/K) which decreases from 8.8 at an oxygen concentration of 0.02 mM to 4.1 at $[O_2]$ = 1 mM. Analysis of the experimental dependences of the KIE on the oxygen concentration yielded the following limiting values of the KIE: $^{T}(V/K)_{O_2\to 0} \simeq 15$ and $^{T}(V/K)_{O_2\to\infty} \simeq 3.6$. The data obtained indicate a non-ordered kinetic mechanism of this reaction.

Analysis of the KIE in the enzyme oxidation reactions of 2-[2-^{2}H]propanol and [1-^{2}H]cyclohexanol made it possible to establish the kinetic mechanisms of processes catalysed by alcohol dehydrogenases isolated from both yeast and liver.[48–50] When liver alcohol dehydrogenase is used, the liberation of NAD from the ternary complex E–NAD–cyclohexanol takes place at a negligible rate, while cyclohexanol is liberated much faster than it reacts with formation of products, i.e. the process is ordered. In the 2-propanol oxidation reaction catalysed by yeast alcohol dehydrogenase, the liberation of 2-propanol and NAD from the complex E–NAD–propanol takes place at approximately the same rates, i.e. the reaction is random. In the study of the mechanisms of the same reactions, use was also made of secondary KIE.[51] Together with the determination of the kinetic mechanisms of enzymic reactions, the KIE can yield valuable information about their chemical mechanisms.[12,52–55]

For example, the study of the KIE in the reactions involving the conversion of *D*-[5-^{3}H]-, *D*-[3-^{3}H]-, and *D*-[4-^{3}H]-glucose-6-phosphate[34,56,57] and also *D*-[5-^{2}H]- and *D*-[G-^{2}H]- glucose-6-phosphate[58,59] into the corresponding tritiated and deuteriated isotopic forms of myoinosotol-1-phosphate, catalysed by myoinositol-1-phosphate syntheses of plant and animal origin, established the following process mechanism:



D-glucose-6-phosphate

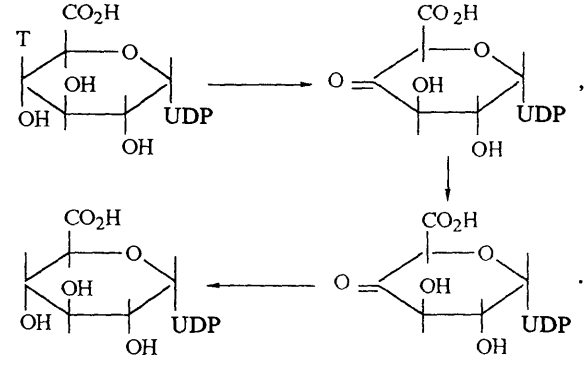


myoinosotol-1-phosphate

Isotope effects were observed only in those cases where tritium or deuterium was present in the initial substrate in the 5-position, while in the remaining cases the labelled substrates reacted at the same rate as the unlabelled *D*-glucose-6-phosphate. This shows that only hydrogen atoms in the 5-position participate in the oxidation stage and in the subsequent cyclisation of *D*-glucose-6-phosphate to myoinositol-1-phosphate.

A difference between the mechanisms of two parallel transmethylation reactions catalysed by catechol *O*-methyltransferase, involving the transfer of [^{3}H]methyl groups from the labelled *S*-adenosylmethionine to the *m*- and *p*-hydroxy-groups of dopamine, has also been established with the aid of KIE.[42] It was found that for *meta*-methylation, the secondary KIE is 1.16, whereas for *para*-methylation it is 1.35. The latter value is close to the value of 1.29 determined previously for the S_N2 transfer of the methyl group in the methylation of 3,4-dihydroxyacetophenone in the presence of the same enzyme.[60] On this basis, it was concluded[42] that the methylation of the *para*-position of dopamine proceeds via an S_N2 mechanism. The lower value of the KIE for *meta*-methylation indicates the influence of other stages on the rate of the process as a whole.

An appreciable KIE (3.1) has been observed in the decarboxylation of uridine-diphospho-*D*-[4-^{3}H]glucuronic acid in the presence of UDP-*D*-glucuronate decarboxylase, whereas the presence of the tritium label in the 3- and 5-positions in the initial compound did not affect the rate of the process.[61,62] These results show that the decarboxylation reaction is accompanied by oxidation at C(4):



Similar conclusions concerning process mechanisms have been drawn from the KIE in the reaction involving the conversion of UDP-*D*-[4-^{3}H]glucose into UDP-*D*-[4-^{3}H]galactose catalysed by UDP-*D*-glucose 4-epimerase.[63]

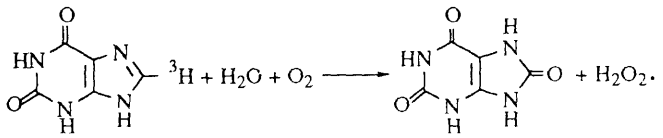
KIE have also been used in the study of the mechanisms of reactions catalysed by fumarase,[64] protease,[17] alcohol dehydrogenase,[62,65–67] aminoxidase,[68,69] chorismate synthase,[19] yeast hexokinase,[70] lacate dehydrogenase,[71] phosphoribosyltransferases,[72] succinoxidase,[73] adenosine deaminase,[74] liver monoxygenase,[75] and lipoxygenase.[54]

Useful information about the mechanisms of enzymic reactions is also provided by KIE when deuteriated solvents are used (the dependence of the KIE on the solvent).[76–78]

2. Determination of the rate-limiting stage in the enzymic process

Analysis of the principal types of KIE makes it possible to discover the rate-determining stage in enzymic reactions. An example of such use of KIE is provided by a study[21] in which kinetic

differences in the oxidation of the protium and tritium forms of xanthine catalysed by xanthine oxidase were investigated.



A marked dependence of the KIE on the xanthine concentration in the incubation mixture was observed. If the kinetic data are presented graphically using the method of the double reciprocal quantities 1/v and 1/[S], then linear relations are observed for all the cases investigated, as can be seen from Fig. 3, which is consistent with the Lineweaver–Burk equation:

$$\frac{1}{v} = \frac{K}{V[S]} + \frac{1}{V} \quad .$$

Here it is significant that all the experimental straight lines have different slopes but intersect the ordinate axis at virtually the same point at a given pH. It follows from the equation that the slopes of the straight lines are equal to the ratios K/V; the intercept on the abscissa axis is $-1/K$, while that on the ordinate axis yields $1/K$.

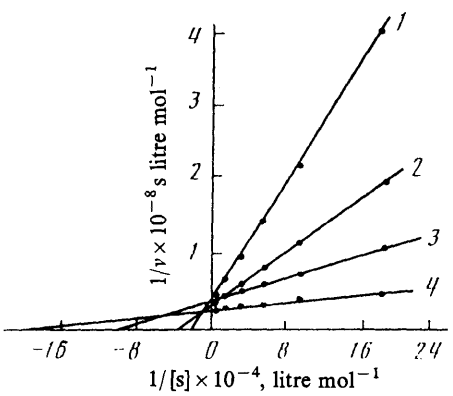


Figure 3. Graphical representation of the rates of enzymic oxidation of labelled (lines *1* and *2*) and unlabelled (lines *3* and *4*) xanthine at different pH; *1*, 10.2; *2*, 8.5; *3*, 10; *4*, 8.5.

The following conclusions can be drawn from the results: the maximum rates of oxidation of the labelled and unlabelled xanthine at the same pH are virtually identical, i.e. at high substrate concentration there is no KIE or it is insignificant; the kinetic isotope effect is manifested mainly in the value of the Michaelis constant.

The following binary mechanism has been established for the enzymic oxidation of xanthine:[79]

$$E + K \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} EX \xrightarrow{k_2} E_{red} + U,$$

$$E_{red} + O_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} E_{red}\cdot O_2 \xrightarrow{k_4} E + H_2O_2,$$

where E is the enzyme, X is xanthine, and U is uric acid. It is also known that the rate of oxidation of the reduced enzyme E_{red} is significantly greater than the rate of its formation and the rate of the process as a whole is therefore determined by the first two stages. At fairly high xanthine concentrations, [X] ≫ [E], the entire enzyme is bound in the enzyme–substrate complex EX and the rate of reaction has a maximum:

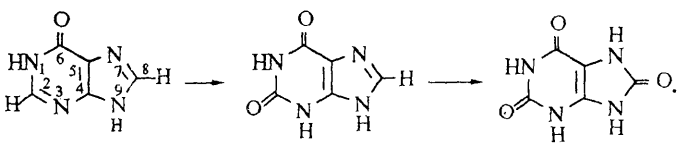
$$V = k_2[EX] = k_2[E] \quad .$$

Since the enzyme concentration was the same in the measurement of the KIE in all the experiments, the similarity of the values of V published for the protium and tritium substrates indicates a small difference between the rate constants for the decomposition of the complexes EX containing [^{1}H]- or [^{3}H]-xanthine.

On the other hand, the Michaelis constant is defined as $K = (k_1 + k_2)/k_1$. Bearing in mind that the constants k_2 have been shown to be equal, the observed difference between the Michaelis constants for the labelled and unlabelled xanthine may be explained by the difference between the rate constants for the formation and decomposition of the enzyme–substrate complexes. Thus the KIE in the reaction investigated is determined by the different rates of formation of the transition complexes of the labelled and unlabelled xanthine.

A similar discrimination between the labelled molecules was observed in the formation of enzyme–substrate complexes in the oxidation of xanthine containing deuterium in the 8-position.[79]

The rate-determining stage in the formation of the complex EX was also established in a study of the KIE in the two-stage oxidation of [2-^{3}H]-, [8-^{3}H]- and [2,8-^{3}H$_2$]-hypoxanthine catalysed by the same enzyme, i.e.



hypoxanthine xanthine uric acid

But in this case the stage involving the decomposition of the complex is partly rate-determining.[80] Isotope effects in the stage where the reaction is inhibited by the substrate were also observed under these conditions.

An effective use of KIE in order to establish the rate-limiting stages in the decarboxylation of *L*-malate catalysed by *L*-malate $NADH^+$-oxidoreductase has been reported by Schimerlik, et al.[81]

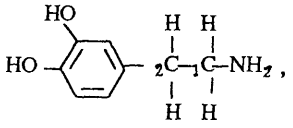
3. The structure of the transition state

The isotope effects in chemical reactions are used widely in the study of the structure of the transition state.[3] On the other hand, such use of the KIE for enzymic reaction is difficult because the chemical bond dissociation stage is usually not fully rate-determining, while other reactions such as, for example, the formation of the products or conformational changes, which precede or follow the chemical bond dissociation stage, are usually partly rate-determining. Therefore, in order to obtain information about the structure of the transition state in enzymic reactions, it is necessary to measure the true KIE, i.e. the isotope effect in the chemical bond dissociation stage. As mentioned above, this KIE can be calculated by Northrop's method. Conclusions concerning the structural characteristics of the transition state derived from the KIE

are based on theoretical considerations put forward by Melander,[3] which have been described by Cleland in relation to enzymic reactions.[11]

Unfortunately, whereas the theoretical aspect of the problem has been developed in fair detail, there have been few practical applications of KIE in the analysis of the structure of the transition state. For example, the KIE found in kinetic studies on the biosynthesis of S-adenosylmethionine from [5′-^{14}C]- and [5′-^{3}H]-ATP (catalysed by the enzyme S-adenosylmethionine synthetase) permitted the conclusion that the transition state has an S_N2-like structure in which the binding to C(5′) is symmetrical in relation to the leaving phosphate group and the arriving methionine sulphur atom.[18]

In the oxidation reactions of dopamines, chirally tritium-labelled in the 1-position {[(1*R*)-^{3}H]- and [(1*S*)-^{3}H]-dopamines}, i.e.



catalysed by ox plasma aminoxidase, strong stereochemical isotope effects were observed: 5–6 for [(1*R*)-^{3}H]- and 26–34 for [(1*S*)-^{3}H]-dopamines, which permitted a conclusion concerning the stereochemistry of the binding of dopamine to the enzyme.[68]

4. Enrichment of labelled substrates in heavy hydrogen isotopes

In those cases where the initial substrate consists of two different varieties of molecules—deuterium- or tritium-labelled molecules and the usual unlabelled molecules—the reactions of the two forms are qualitatively the same, but, by virtue of the manifestation of the KIE, are quantitatively different. The ratio of the two varieties of molecules therefore gradually changes during the reaction in favour of those labelled with heavy hydrogen isotopes.

If the initial ratio of the concentrations of the labelled and unlabelled substrate molecules $[S]_0^*/[S]_0$ is designated by R_0, while the corresponding concentration ratio after the attainment of a degree of enzymic reaction F is designated by $R = [S]^*/[S]$, the enrichment in the heavy isotope of the substrate remaining unreacted in the incubation system can be determined from the equation (Ref. 3, p. 105)

$$\frac{R}{R_0} = (1-F)^{(k^*/k)-1},$$

where k^*/k is the KIE.

When tritium-labelled substrates are used, the ratio R/R_0 in the above equation can be replaced by the ratio of the molar radioactivity of the enriched product A to the initial molar radioactivity of the substrate A_0.

This enzymic method of enriching labelled preparations in the heavy isotope is of great practical importance because the use of compounds with the maximum content of the label is of greatest interest. Furthermore, the KIE can be used to regenerate the labelled compounds after the experiments in which they were diluted by the unlabelled ("cold") compounds.

KIE have been used[20,27] in the enzymic oxidation of labelled *D*-galactose in order to increase significantly the tritium content in preparations comprising different isotopic forms of galactose. The results of these experiments are presented in Table 1.

When KIE are used to enrich substrates in heavy hydrogen isotopes, the choice of incubation conditions and primarily of the substrate concentration is important. For example, when the enzymic oxidation of xanthine is carried out at a high substrate concentration, the molar radioactivity of [8-^{3}H]xanthine does not increase appreciably since under these conditions there are virtually no KIE in terms of V.[21] On the other hand, at low xanthine concentrations, where there is an appreciable KIE in terms of V/K, it was possible to increase the molar radioactivity of the [8-^{3}H]xanthine preparations.

Table 1. Results of the enzyme-catalysed increase in the molar radioactivity of tritium-labelled *D*-galactose preparations.

Initial mixture of isotopic forms	A_0, Ci mmol^{-1}	t, min	A, Ci mmol^{-1}	A/A_0
[6-$^{3}H_1$]Gal, Gal	0.15	60	0.32	2.2
[6-$^{3}H_1$]Gal, Gal	4.6	90	20.3	4.4
[6-$^{3}H_1$]Gal, Gal	4.6	90	18.2	4.0
[6-$^{3}H_1$]Gal, Gal	4.6	240	21.3	4.6
[6-$^{3}H_1$]Gal, Gal	14.6	60	24.5	1.7
[6-$^{3}H_2$]Gal, Gal	4.2	30	6.5	1.5
[6-$^{3}H_2$]Gal, Gal	4.2	240	26.2	6.2
[6-$^{3}H_2$]Gal, [6-$^{3}H_1$]Gal	48.0	240	53.0	1.1

Note. Gal = *D*-galactose; A_0 = initial Moner activity; A = final Moner activity; t = incubation time; A/A_0 = degree of enrichment.

Examples of the analogous use of KIE in certain other enzymic reactions can be found in other studies.[31,80,82]

The observed biological fractionation of isotopes is also based on KIE.[83,84]

5. Kinetic isotope effects in pharmacology and medicine

Bearing in mind the familiar claim that enzymes are the basis of life and that the basis of biological processes is enzymic reactions, the KIE in such reactions can be regarded as the basis of the biological isotope effects, i.e. of the definite difference in the behaviour of labelled and unlabelled compounds in living organisms.

Such differences can be manifested, for example, by a change in the biotransformation of labelled products. Thus deuteriation of ethyl radicals in the anaesthetics methoxyflurane, haloctan, and enflurane leads to an appreciable slowing down of their metabolism.[85] Since the products of the biotransformation of these preparations determine to a large extent their toxicity, the weakening of the metabolism of the deuteriated compounds results in a decrease of toxicity.

The difference in the metabolic behaviour of deuteriated compounds, defined by the KIE in enzymic processes, has also been noted for certain other medicinal preparations.[86–89]

It has not been ruled out that, when deuteriated medicinal preparations are used, the KIE can in certain cases produce a greater therapeutic effect or prolong the activity of the preparations as a result of their greater concentration in certain organs.

Radioisotope diagnosis and positron emission tomography are promising fields where KIE can be applied. In such cases, it is essential to use preparations with a double isotope label: one (deuterium) label is used to achieve the KIE and the other radionuclide) label is used to investigate the distribution and location of the radiopharmaceutical preparation in the organism. In a number of instances, on the basis of the deuterium KIE it has been possible to alter the increase in the concentration in and the rate of elimination of a preparation from the test organ, achieving thereby a definite diagnostic effect. For example, such an effect has been observed by Wenzel[90] in a study of the kinetics of the process in which *N*-alkylamphetamine labelled with iodine-131 in the *para*-position was concentrated in rat and mouse brains. This radiopharmaceutical preparation is capable of being concentrated in the brain and is therefore used for various studies on this organ. It has been established that, when deuterium is introduced into the side chain of N-alkyl-*p*-[^{131}I]iodoamphetamine, the degree of concentration of this preparation in the brain increases appreciably.

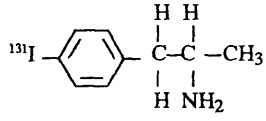


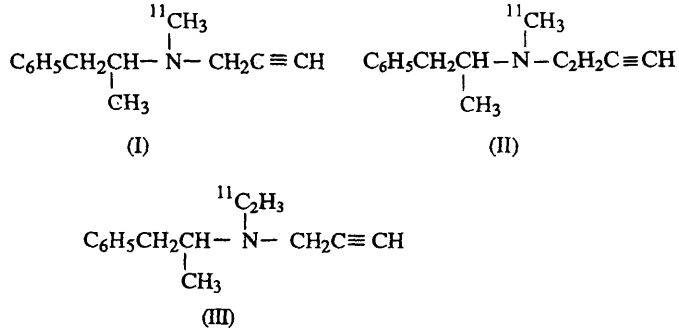
Figure 4 illustrates the kinetics of the alteration of the radioactivity in the brain of the protium form and of one of the deuteriated forms of *p*-[^{131}I]iodoamphetamine investigated by Wenzel. The figure shows that the deuteriated preparation generates a much higher concentration in the brain. This result is of practical importance, because the introduction of deuterium makes it possible to diminish the overall activity of the iodine-131 introduced into the organisms or to achieve a better diagnostic picture for the same dose. It is significant that the concentration of iodine-131 in the blood can be appreciably reduced under these conditions. The author put forward the hypothesis that the observed effect is attained as a result of the decrease in the rate of the enzymic oxidative deamination of the preparation.

Figure 4. Kinetics of the variation of radioactivity in the brain on introduction of the protium (line *1*) and deuterium (line *2*) forms of *p*-[^{131}I]iodoamphetamine.

Analogous studies of the ruthenocene derivatives of amphetamine labelled with ^{103}Ru established that the deuteriated derivatives are also concentrated in the brain to a greater extent than the corresponding protium forms (almost to the extent of 180%).[91,92]

A decrease in the rate of metabolism in the brain has also been observed for the deuteriated preparation of *N,N*-dimethylphenylethylamine labelled with carbon-11, which is a positron emitter.[93]

In a report delivered at the VIIth International Symposium on Radiopharmaceutical Chemistry in the Netherlands in 1988, it was demonstrated that KIE can be used successfully in the solution of an important psychopharmacological problem involving the search for different kinds of monoaminoxidase inhibitors.[94] Such inhibitors include *L*-deprenyl; *L*-deprenyl containing carbon-11 is used as a radioactive tracer for the charting of aminoxidase in human and animal brains. It was postulated that *L*-[^{11}C]deprenyl is transported into the brain, where it is oxidised by monoaminoxidase. In the study of the mechanism of this inhibition process, kinetic investigations using the following three isotopic forms of *L*-deprenyl were carried out.



(I) (II) (III)

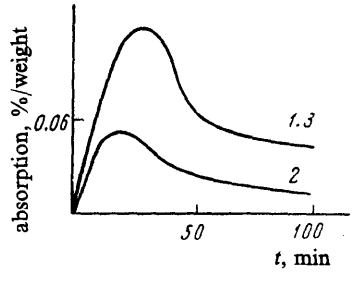


Figure 5. Kinetics of the absorption in baboon brains of the protium isotopic form of *L*-[^{11}C]deprenyl (curve *1*), the form deuteriated in the propargyl group (curve *2*), and the form deuteriated in the methyl group (curve *3*).[94]

The data for the absorption and retention of these compounds in the brains of baboons, presented in Fig. 5, were obtained by positron emission tomography.[94] An appreciably smaller absorption of ^{11}C in the brain was observed for compound (II) containing deuterium in the α-position in the propargyl group. In this case, the KIE was estimated as 3.8. The results show that monoaminoxidase

catalyses the dissociation of the C–H bond in the α-position in the propargyl group and that this is the rate-determining stage in the retention of ^{11}C in the brain.

Incubation of rat liver mitochondrial membranes in the presence of unlabelled and deuteriated serotonin showed that the activity of monoaminoxidase increases in the presence of β,β′-[$^2H_2$]serotonin, but decreases after the introduction of α,α′,β,β′-[$^2H_4$]serotonin.[85] A similar phenomenon has also been observed for dopamine. The suppression of the activity of monoaminoxidase is achieved to a greater extent in the presence of [^{2}H]phenylethylhydrazine compared with the protium form of this compound. As a consequence of this, the administration of deuteriated phenylethylhdyrazine to rats significantly increases the content of dopamine, serotonin, and *m*- and *p*-tyrosine in the brain.[95].

With the aid of fully deuteriated glucose containing simultaneously carbon-14, a significant difference was established in the distribution and metabolism of this isotopic form compared with the preparation having the usual isotopic composition.[96] This difference consists primarily in the retarded transport of deuteriated glucose into the brain, believed to be caused[96] by the isotope effects in the reaction involving glucose oxidase. The introduction of tritium instead of deuterium into glucose also alters the metabolism of this compound.[97,98] A carbon-14 KIE has been reported in the oxidation reaction of labelled *D*-glucose catalysed by glucose oxidase.[99]

There is no doubt that the examples of the use of KIE examined here do not exhaust the entire potential possibilities and that in the future kinetic differences in enzymic reactions involving labelled compounds will find new applications.

References

1. G de Hevesy *Radioactive Tracers* (Translated into Russian), Inostr. Lit., Moscow, 1950
2. E Buncel, C C Lee (Editors) *Isotopes in Organic Chemistry*, Elsevier, Amsterdam–Oxford–New York, 1984, Vol. 6, p. 266
3. L Melander, W H Saunders *Reaction Rates of Isotopic Molecules* (Translated from English into Russian), Mir, Moscow, 1983, 344 pp
4. J H Richards *The Enzymes* (Edited by P D Boyer), Academic Press, New York, 1970, Vol. 2, p. 321
5. *Isotope Effects on Enzyme-Catalyzed Reactions* (Edited by W W Cleland, M H O'Leary, D B Northrop), Univ. Park Press, Baltimore, 1977
6. J P Kinman *Adv. Enzymol.*, 1978 **46** 415
7. D B Northrop *Methods Enzymol.*, 1982, **87** 607
8. D B Northrop *Biochemistry*, 1975, **14** 2644
9. D B Northrop *Ann. Rev. Biochem.*, 1981, **50** 103
10. S M Miller, J P Klinman *Methods Enzymol.*, 1982, **87** 711
11. W W Cleland *Methods Enzymol.*, 1982, **87** 625
12. W W Cleland *CRC Crit. Rev. Biochem.*, 1982, **13** 385
13. H Simon, A Kraus *Isotopes in Organic Chemistry* (Edited by E Buncel, C C Lee), Elsevier, Amsterdam, Vol. 2, Chapter 5
14. W W Cleland *Isotopes in Organic Chemistry* (Edited by E Buncel, C C Lee), Elsevier, Amsterdam, 1987, Vol. 7, p. 61
15. W W Cleland *Bioorg. Chem.*, 1987, **15** 283
16. G P Akulov *III Vsesoyuznoe Soveshchanie po Probleme "Fiziologicheski Aktivnye Soedineniya, Mechennye Radioaktivnymi i Stabil'nymi Izotopami"* (The IIIrd All-Union Conference on the Problem of "Physiologically Active Compounds Labelled with Radioactive and Stable Isotopes"), Izd. IAE, Moscow, 1991, p. 5
17. K A H Adams, S-H Chung, A M Klibanov *J. Am. Chem. Soc.*, 1990, **112** 9418
18. J D Markham, D W Parkin, F Mentch, V L Schramm *J. Biol. Chem.*, 1987, **262** 5609
19. S Balasubramanian, C Abell, J R Coggins *J. Am. Chem. Soc.*, 1990, **112** 8581
20. G P Akulov, N A Korsakova, B K Kudelin *J. Labelled Compd. Radiopharm.*, 1989, **27** 803
21. G P Akulov, N A Patokina *Radiokhimiya*, 1990, **32** 75
22. G I Meerov *Radiometricheskie Metody Opredeleniya Aktivnosti Fermentov* (Radiometric Methods for the Determination of Enzyme Activity), Atomizdat, Moscow, 1974, 60 pp
23. E V Nikol'skaya *Radiokhimiya*, 1983, **25** 98
24. S Glasstone, K J Laidler, H Eyring *Theory of Rate Processes* (Translated into Russian), Insotr. Lit., Moscow, 1948
25. E Rosenberg *Polyhedron*, 1989, **8** 383
26. K G Oldham *J. Labelled Compd.*, 1968, **4** 127
27. G P Akulov, N A Korsakova, B K Kudelin *Radiokhimiya*, 1989, **31** 92
28. C G Swain, E C Stivers, J F Reuwer, L J Schaad *J. Am. Chem. Soc.*, 1958, **80** 5885
29. H J Bright, Q H Gibson *J. Biol. Chem.*, 1967, **242** 994
30. J G Hauge, G Foulds, R Bentley *Biochim. Biophys. Acta*, 1968, **159** 398
31. G P Akulov, E V Snetkova *Radiokhimiya*, 1990, **32** 93
32. M Dixon, E Webb *Enzymes* (Translated into Russian), Mir, Moscow, 1982
33. B E P Swoboda, V Massey *J. Biol. Chem.*, 1965, **240** 2209
34. M W Loewus *J. Biol. Chem.*, 1977, **252** 7221
35. S E Damgaard *Biochem. J.*, 1980, **191** 613
36. S E Damgaard *Biochemistry*, 1981, **20** 5662
37. C E Grimshaw, P F Cook, W W Cleland *Biochemistry*, 1981, **20** 5655
38. N Kurihara, Y Ikamoto, S Okutani, A G Clark *J. Labelled Compd. Radiopharm.*, 1989, **27** 945
39. J E Tomaszewski, D M Jerina, J W Daly *Biochemistry*, 1975, **14** 2024
40. B Belleau *Isotopes in Experimental Pharmacology* (Edited by L J Roth), University Press, Chicago, 1965, p. 469
41. R A Pascal, M W Baum, C K Wagner, et al. *J. Am. Chem. Soc.*, 1986, **108** 6477
42. S E Wu, W P Hyskey, R T Borchardt, R L Schowen *J. Am. Chem. Soc.*, 1984, **106** 5762
43. G J Martin, M L Martin, F Mabon, J Brieout *J. Am. Chem. Soc.*, 1982, **104** 2658
44. D M Grant, J Curtis, W R Croasmun, et al. *J. Am. Chem. Soc.*, 1982, **104** 4492
45. R A Rascal, M W Baum, C K Wagner, et al. *J. Am. Chem. Soc.*, 1986, **108** 6477
46. W W Cleland *The Enzymes* (Edited by P D Boyer), Academic Press, New York, 1970, Vol. 2, p. 1
47. J P Klinman, H Humphries, J G Voet *J. Biol. Chem.*, 1980, **255** 11648
48. P F Cook, W W Cleland *Biochemistry*, 1981, **20** 1790
49. J P Klinman *Biochemistry*, 1976, **15** 2018
50. P F Cook, W W Cleland *Biochemistry*, 1981, **20** 1805
51. P F Cook, N J Oppenheimer, W W Cleland *Biochemistry*, 1981, **20** 1817

52. P F Cook *Enzyme Mechanism from Isotope Effects*, CRC Press, Boca Raton, Florida, 1990
53. S L Rotenberg, D B Sprinson *J. Biol. Chem.*, 1978, **253** 2210
54. A R Brash, G D Ingram, R L Maas *Biochim. Biophys. Acta*, 1986, **875** 256
55. K G Oldham *Radiotracer Techniques and Applications* (Edited by E A Evans, M Muramatsu), Marcel Dekker, Inc., New York–Basel, 1977, Vol. 2, p. 823
56. G Hauska, O Hoffmann-Ostenhof *Hoppe-Seyler's Z. Physiol. Chem.*, 1967, **348** 1558
57. J E G Barnett, D L Corina *Biochem. J.*, 1968, **108** 125
58. F Eisenberg, A H Bolden *Fed. Proc.*, 1968, **27** 595
59. W R Sherman, M A Steward, M Zinko *J. Biol. Chem.*, 1969, **244** 5703
60. M F Higazi, R T Borchardt, R L Schowen *J. Am. Chem. Soc.*, 1979, **101** 4359
61. J S Shutzbach, D S Feingold *J. Biol. Chem.*, 1970, **245** 2476
62. J E G Barnett, D L Corina *Adv. Carbohydr. Chem. Biochem.*, 1972, **27** 127
63. G L Nelsestuen, S Kirkwood *Biochim. Biophys. Acta*, 1970, **220** 633
64. J S Blanchard, W W Cleland *Biochemistry*, 1980, **19** 4506
65. P F Cook, W W Cleland *Biochemistry*, 1981, **20** 1797
66. F A Loewis, F H Westheimer, B Vennesland *J. Am. Chem. Soc.*, 1953, **75** 5018
67. D H Bone *Biochim. Biophys. Acta*, 1963, **67** 589
68. M C Summers, R Markovic, J P Klinman *Biochemistry*, 1979, **18** 1969
69. M Farnum, M Palcic, J P Klinman *Biochemistry*, 1986, **26** 1898
70. K B Taylor, W W Cleland *Fed. Proc. Fed. Am. Soc. Exp. Biol.*, 1980, **39** 2213
71. C E Grimshaw, W W Cleland *Biochemistry*, 1980, **19** 3153
72. R K Goitein, D Chelsky, S M Parsons *J. Biol. Chem.*, 1978, **253** 2963
73. M B Thorn *Biochem. J.*, 1951, **49** 602
74. P M Weiss, P F Cook, J D Hermes, W W Cleland *Fed. Proc. Fed. Am. Soc. Exp. Biol.*, 1987, **46** 1932
75. J E Tomaszewski, D M Jerina, J W Daby *Biochemistry*, 1975, **14** 2024
76. K B Schowen, R L Schowen *Methods Enzymol.*, 1982, **87** 551
77. L Polgar *Eur. J. Biochem.*, 1979, **98** 369
78. F Ken, Y Masafumi, M Akihiro, et al. *Tetrahedron Lett.*, 1986, **27** 1179
79. D Edmondson, D Ballon, A Heuvelen, et al. *J. Biol. Chem.*, 1973, **248** 6135
80. G P Akulov, N A Patokina, B K Kudelin *III Vsesoyuznoe Soveshchanie po Probleme "Fiziologicheski Aktivnye Soedineniya, Mechennye Radioaktivnymi i Stabil'nymi Izotopami"* (The IIIrd All-Union Conference on the Problem of "Physiologically Active Compounds Labelled with Radioactive and Stable Isotopes"), Izd. IAE, Moscow, 1991, p. 44
81. M I Schimerlik, C E Grinshaw, W W Cleland *Biochemistry*, 1977, **16** 571
82. G P Akulov, N A Korsakova *Radiokhimiya* (in the Press)
83. H J M Bowen *Int. J. Appl. Rad. Isot.*, 1960, **7** 261
84. M A Kim, F Baumgartner *Radiochim. Acta*, 1991, **54** 121
85. V A Fateev, N S Titov *Khim.-Farm.Zh.*, 1986, **20** 137
86. A R Foster *Trends Pharmacol. Sci.*, 1984, **5** 524
87. A R Foster *Adv. Drug Res.*, 1985, **14** 1
88. A Laungenhove *J. Clin. Pharmacol.*, 1986, (6) 383
89. W F Trager *III Intern. Symposium on the Synthesis and Applications of Isotopically Labelled Compounds (July 17–21, 1988. Innsbruck, Austria)*, Innsbruck, 1988, p. 87
90. M Wenzel *J. Labelled Compd. Radiopharm.*, 1989, **27** 1143
91. M Wenzel, M Langstaedler, D Preiss *Appl. Radiat. Isot.*, 1988, **39** 1023
92. M Wenzel, D Preiss, G Gunther *J. Labelled Compd. Radiopharm.*, 1988, **25** 121
93. K Hashimoto, M Jojima, O Inone, et al. *Nucl. Med. Biol.*, 1986, **13** 79
94. J S Fowler, A P Wolf, R R MacGregor, et al. *J. Labelled Compd. Radiopharm.*, 1989, **26** 236
95. L E Dyck, D A Dueden, P Yu, et al. *Biochem. Pharmacol.*, 1983, **32** 1519
96. S I Gatley, M M Wess, P L Govoni, et al. *J. Nucl. Med.*, 1985, **26** 127
97. P M Bell, R G Firth, R A Rizza *J. Clin. Invest.*, 1986, (6) 1479
98. J J Katz *Am. Sci.*, 1960, **48** 544
99. L M Marschall, A Appian *J. Chromatogr.*, 1972, **73** 257

Received 16th March 1992

Translated from *Uspekhi Khimii* **61** 1839–1863 (1992) U.D.C. 547.341

Phosphorus derivatives of salicylic acid

L V Chvertkina, P S Khokhlov, V F Mironov
All Russian Phytopathology Scientific Research Institute, B Vyazemi, Moscow Region

ABSTRACT. The present state of work on the methods of synthesis, chemical properties, and practical applications of phosphorus-containing derivatives of salicylic acid has been reviewed. The characteristics of the chemical transformations of cyclic and acyclic phosphorus derivatives of salicylic acid related to the coordination state of the phosphorus atom have been examined.

The bibliography contains 158 references.

Contents

I. Introduction 1009
II. Cyclic phosphorus-containing derivatives of salicylic acid 1009
III. Acyclic phosphorus-containing derivatives of salicylic acid 1016

I. Introduction

Acyl derivatives of salicylic acid are used as drugs and microbiocides. Particular mention may be made of the use of acetylsalicylic acid as an analgesic and antipyretic.[1] Many organophosphorus compounds show a wide spectrum of biological activity.[2] The study of compounds whose molecules contain fragments of phosphorus acids and salicylic acid is of considerable interest in the search for new substances of practical importance. Although phosphorus derivatives of salicylic acid have been the subject of a large number of studies, no reviews have been published, except for selections from the literature devoted to individual aspects of the chemistry of these compounds.[3–7] Monographs on the chemistry of phosphorus compounds contain few data on phosphorus derivatives of salicylic acid.

In our opinion, phosphorus derivatives of salicylic acid deserve detailed examination not only because of their low and varied biological activity but also because of their unique reactivity, which differs sharply from that of usual acyl derivatives of phosphorus.

The aim of the present review is to summarise and where possible systematise the results of work on the methods of synthesis and reactivity of phosphorus derivatives of salicylic acid.

Salicylic acid, unlike other hydroxybenzoic acids, contains in the *ortho*-position two functional groups capable of reacting with a central phosphorus atom to give cyclic and acyclic phosphorus-containing derivatives. The chemical properties of phosphorus derivatives of salicylic acid are determined to a large extent by their cyclic or acyclic structure, and also depend on the coordination state of the phosphorus atom. These characteristics were taken as a basis for the systematisation in the compilation of the present review.

II. Cyclic phosphorus-containing derivatives of salicylic acid

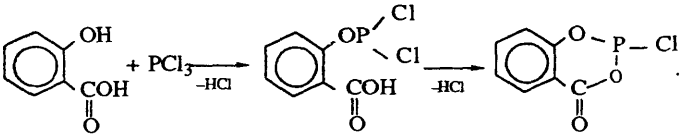
1. Cyclic phosphorus derivatives of salicylic acid containing a three-coordinate phosphorus atom

The phosphorus derivatives of salicylic acid are mixed anhydrides of phosphorus and salicylic acids. Certain features of the chemistry of these compounds are similar to those of the chemistry of acyl phosphites with an endocyclic fragment, described earlier.[8]

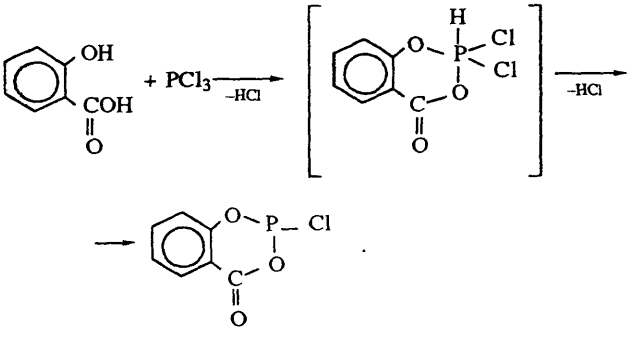
a. 4,5-Benzo-2,6-dioxaphosphorin-3-ones (BDPO)

Phosphorus derivatives of salicylic acid were first obtained by Anschütz and co-workers[9] by the reaction of salicylic acid with phosphorus trichloride. This reaction can give several products, whose structures have been studied by a number of authors.[5,6,9–16] The results of these studies have been summarised by Atherton.[4] It was established that when stoichiometric quantities of the starting materials or an excess of phosphorus trichloride are used, the chief product is 1-chloro-4,5-benzo-2,6-dioxaphosphorin-3-one (1-Cl-BDPO)—a cyclic salicyl chlorophosphite with a three-coordinate phosphorus atom in the ring. Despite the extensive practical application of phosphorylation by P^{III} chlorides in the preparation of salicyl phosphites, the mechanism of this reaction has not been studied in detail.

It has been suggested that the mechanism involves phosphorylation of the phenolic hydroxyl group, followed by ring closure:[14,15]



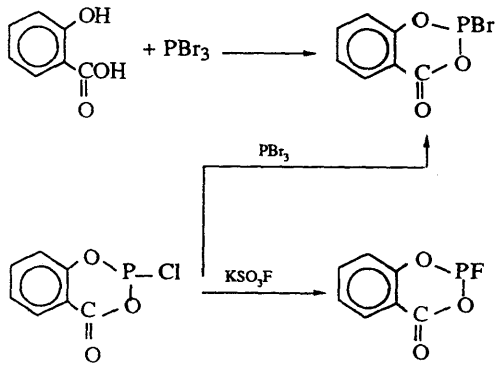
A number of authors suggest that the reaction takes place via a stage involving the formation of a phosphorane.[10,16] No spectroscopic confirmation of intermediate structures of this kind has been obtained, however.



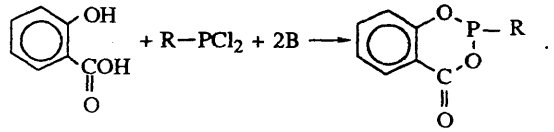
The reaction of salicylic acid with phosphorus trichloride is usually carried out by heating their mixtures in benzene, toluene, or xylene for 2–4 h,[12,14,17] or in ether with a hydrogen chloride acceptor,[15] and the product is isolated by vacuum distillation. Cooling gives a crystalline product with m.p. 36–37 °C. The ^{31}P NMR spectrum of 1-Cl-BDPO contains one signal due to the phosphorus nucleus, at 151 p.p.m.[18]

Derivatives of salicylic acid containing chlorine, bromine, iodine, methyl and nitro-groups,[11] and the hydroxyl group[19] in the benzene ring also react with phosphorus trichloride. The cyclic products were obtained in 69–90% yield.

The reaction of salicylic acid with phosphorus tribromide gives a high yield of 1-bromo-4,5-benzo-2,6-dioxaphosphorin-3-one,[14] which has also been obtained by replacing chlorine by bromine.[20] 1-F-BDPO has been synthesised by an exchange reaction.[21]



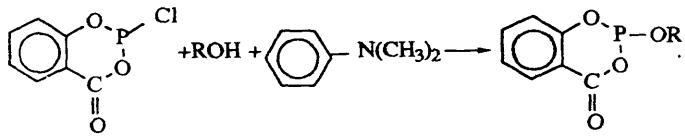
Salicylic acid undergoes a cyclisation with the dichlorides of phosphorus(III) acids in the presence of a hydrogen chloride acceptor:[15,22–24]



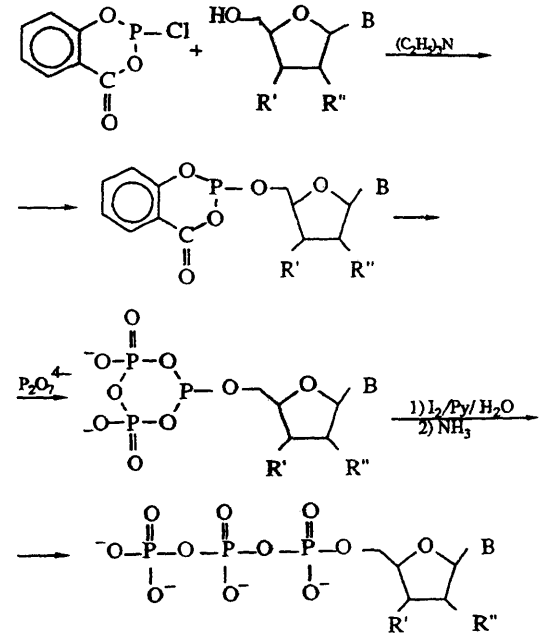
The 1-phenyl-4,5-benzo-2,6-dioxoaphosphorin-3-one formed in this reaction has been used to obtain copolymers with *ortho*- and *para*-substituted aldehydes, 4,4′-diphenoquinones, methacrylate, and acrolein.[25–27]

1-Chloro-4,5-benzo-2,6-dioxaphosphorin-3-ones react readily with electrophilic and nucleophilic reagents. These reactions can take place both with preservation and with splitting of the dioxaphosphorine ring, and with preservation or change in the coordination of the phosphorus atom. The chemical properties of these compounds have been most fully studied for 1-Cl-BDPO. As shown by Nesterov and co-workers,[28–32] this compound can serve as a key intermediate in the synthesis of various types of phosphorus derivative of salicylic acid.

The chlorine atom in position 1 of the phosphine ring has practically the same mobility as that in alkylene chlorophosphites. Thus the reaction of 1-Cl-BDPO with alcohols and phenols in the presences of a hydrogen chloride acceptor gives 1-alkoxy(aryloxy)-4,5-benzo-2,6-dioxaphosphorin-3-ones.[14,22,28–31,33,34]

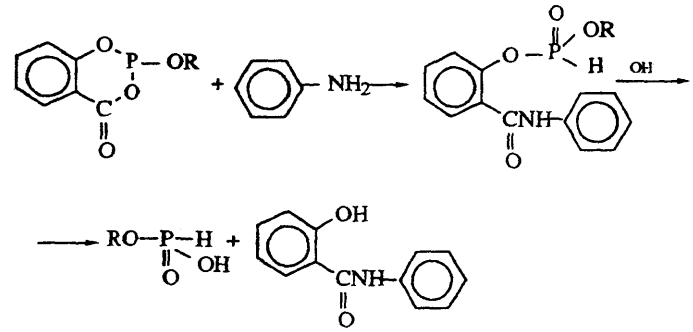


1-Alkoxy(aryloxy)-BDPO are also highly reactive, and react readily with nucleophilic reagents, with splitting of the dioxaphosphorine ring. When an excess of the alcohol or phenol is used, the chief products are salicylic acid and trialkyl(aryl) phosphites.[28,35] Carrying out this reaction in stages provided the basis for an extremely effective method for synthesising nucleoside polyphosphates.[36–39]

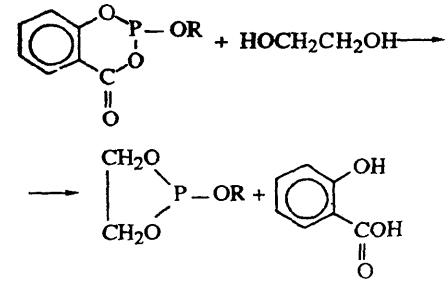


B represents nucleic bases (A^{Bz}, G^{ib}, T, C^{Bz}, U).

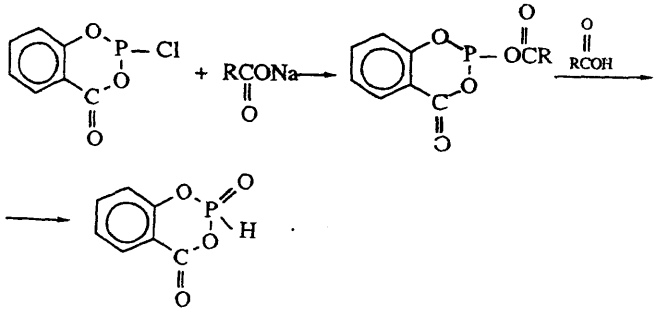
The reactions of 1-alkoxy-BDPO with amines gives monoalkyl phosphites.[40]



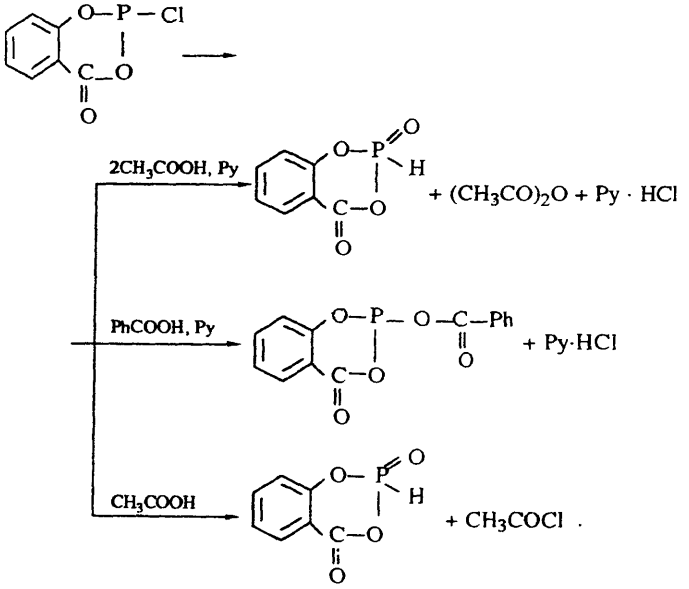
1-Alkoxy-BDPO undergo exchange reactions. With glycols, an extremely interesting reaction takes place, with recyclisation of the phosphorine ring to give a phospholane ring.[41]



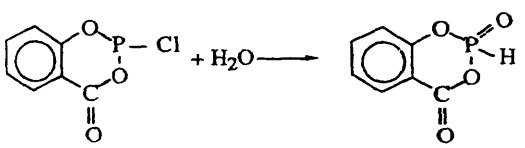
The high mobility of the chlorine atom in 1-Cl-BDPO is confirmed by the reaction with such weak nucleophilic reagents as the salts of carboxylic acids, accompanied by the replacement of the chlorine atom by the acyloxy-group[14,35] and the formation of a mixed anhydride of salicyclic, phosphorus, and carboxylic acids. With an excess of acid, the anhydride undergoes splitting, accompanied by the formation of a cyclic hydrophosphoryl compound[14,35] — 1-hydro-4,5-benzo-2,6-dioxaphosphorine-1,3-dione (1-H-BDPD):



The reaction of salicylic chlorophosphite with carboxylic acids have been studied.[14,22,35] The reaction with benzoic acid gave the acyl phosphite, but the reaction with acetic acid gave salicyl hydrogen phosphite, despite the presence of a base.

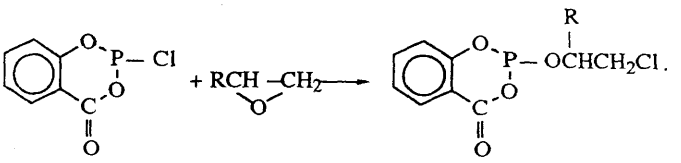


The last reaction is the most convenient preparative method for obtaining 1-H-BDPD. 1-H-BDPD can also be obtained by the reaction of 1-Cl-BDPO with water:[15,42]

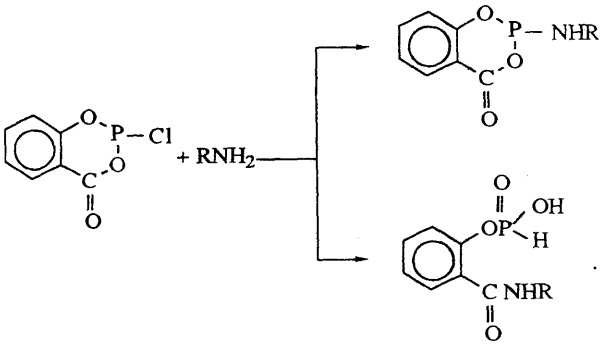


Like other hydrophosphoryl compounds, 1-H-BDPD exists in two tautomeric forms, with three-coordinate and four-coordinate phosphorus atoms, and the ^{31}P NMR spectrum correspondingly contains signals due to phosphorus nuclei at 113 p.p.m. and −4 p.p.m.[43] According to recent data,[44] however, a close structural analogue — pyrocatechol hydrogen phosphite — exists only in the oxo-form.

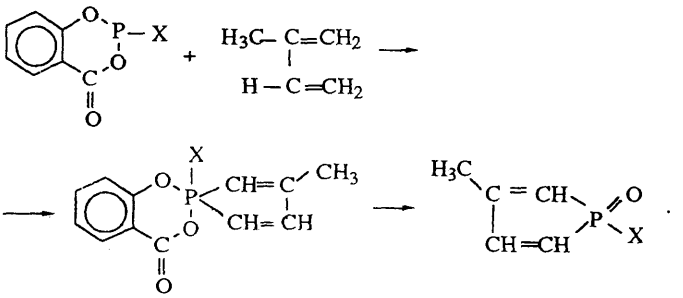
Exocyclic replacement of the chlorine atom in 1-Cl-BDPO also predominates in the reaction with alkylene oxides:[45]



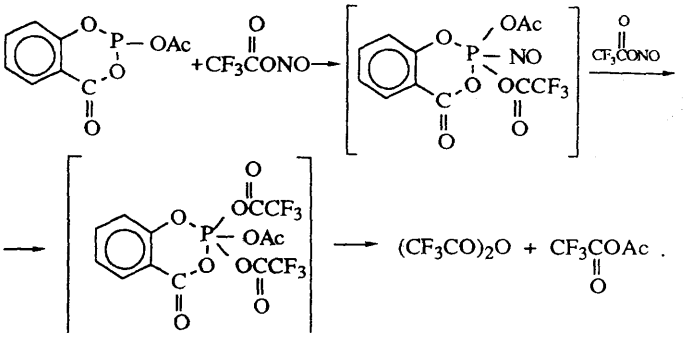
The reaction of this compound with amines is more complex. It involves not only the replacement of the chlorine atom but also splitting of the phosphorine ring:[16,46,47]



1-Chloro(ethoxy)-4,5-benzo-2,6-dioxaphosphorin-3-ones react with dienes. Their reaction with isoprene involves the intermediate formation of an unstable phosphorane, which when distilled is converted into 1-oxo-1-chloro(ethoxy)-3-methylphospholene:[48]



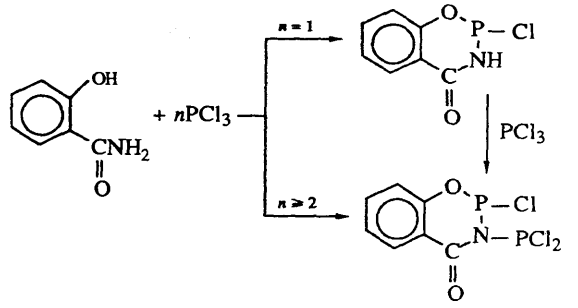
The reaction of BDPO with trifluoroacetyl nitrite gives the anhydride of trifluoroacetic acid and mixed anhydrides of trifluoroacetic acid and the acid whose residues was present on the phosphorus atom of the original phosphite:[49]



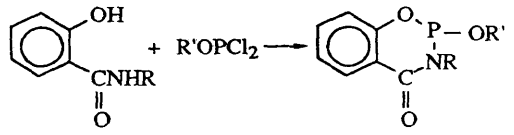
The structure of the phosphorus-containing product of this reaction has not been determined. The authors cited subsequently assigned to the organophosphorus compound formed the "general" structure $(R-COO)_3P=O$.[50]

b. 4,5-Benzo-2-aza-6-oxaphosphorin-3-ones and 4,5-benzo-6-aza-2-oxaphosphorin-3-ones

4,5-Benzo-2-aza-6-oxaphosphorin-3-ones (BAOPO) are obtained by the reaction of salicylamides with the chlorides of trivalent phosphorus acids. Salicylamides react with phosphorus trichloride in boiling benzene; the reaction is complete in several hours with the formation of a cyclic product,[51] and when there is a proton on the nitrogen atom this product can undergo further phosphorylation by an excess of phosphorus trichloride:[52]

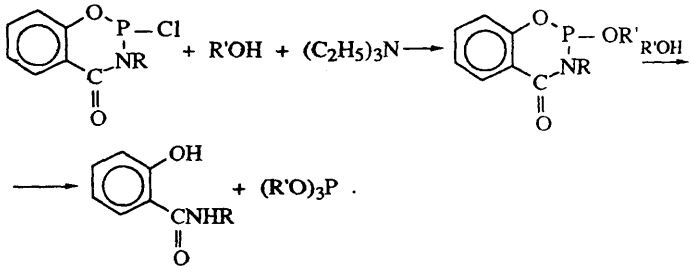


An analogous cyclisation is observed in the reaction of salicylamides with dichlorophosphites, which is complete with the formation of 1-alkoxy(phenoxy)oxa-azaphosphorin-3-ones:[51]

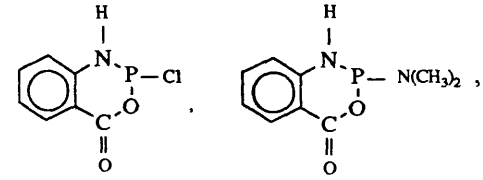


The reaction of salicylamides with amides of trivalent phosphorus acids takes place by an alternative route to give acyclic compounds[53] (see below).

1-Chloro-4,5-benzo-2-aza-6-oxaphosphorin-3-one (1-Cl-BAOPO) are highly reactive compounds. Their reactions with nucleophilic reagents can take place both with exocyclic replacement at the phosphorus atom and with splitting of the oxa-azaphosphorine ring. Thus 1-Cl-BAOPO reacts with stoichiometric quantity of an alcohol to give the 1-alkoxy-BAOPO, but in the presence of an excess of the alcohol the normal phosphite and the salicylamide are formed.[51]



Phosphorylated derivatives of anthranilic acid[54,55] with the general formula

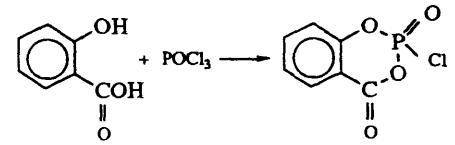


are structural isomers of 4,5-benzo-2-aza-6-oxaphosphorin-3-ones.

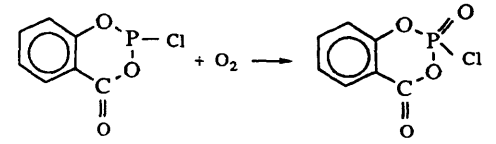
2. Cyclic phosphorus derivatives of salicylic acid containing a four-coordinate phosphorus atom

a. 4,5-Benzo-2,6-dioxaphosphorine-1,3-diones

A key intermediate in the synthesis of various 4,5-benzo-2,6-dioxaphosphorine-1,3-diones (BDPD) is 1-chloro-4,5-benzo-2,6-dioxaphosphorine-1,3-dione, for which several methods of preparation have been proposed. The simplest of these is based on the reaction of salicylic acid with phosphorus oxide chloride;[4,6,56,57]



The yield of 1-Cl-BDPD in this reaction does not exceed 50%; it can be obtained in higher yield by oxidising 1-Cl-BDPO with oxygen:[4,12]

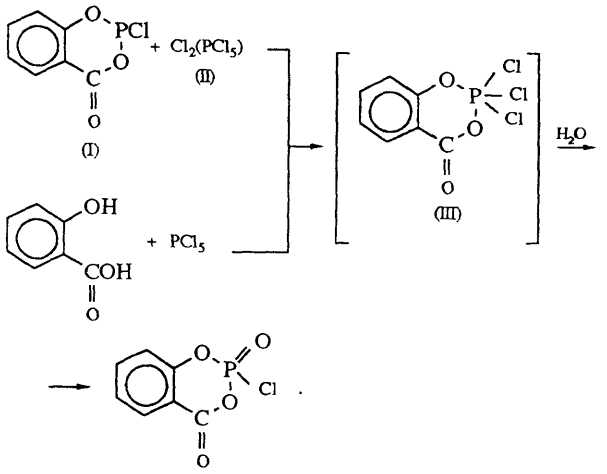


The phosphorus in 1-Cl-BDPO is only weakly nucleophilic, so that the addition of oxygen is slow, and the oxidation is not complete even on prolonged reaction.

1-Cl-BDPD, and also 1-fluoroalkoxy-derivatives of BDPD, were recently obtained in high yield (>90%) using trifluoroethyl sulphate as oxidising agent:[58]

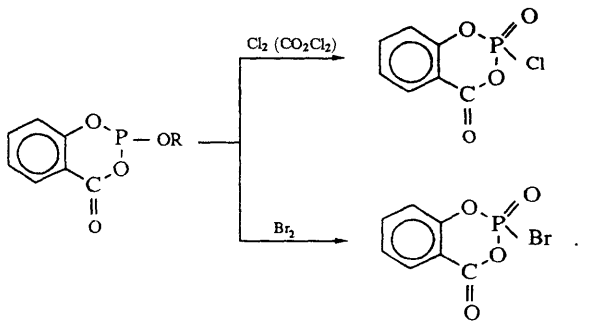
The addition of chlorine to 1-Cl-BDPO takes place more vigorously to give the trichlorophosphorane (III), controlled hydrolysis of which also gives 1-Cl-BDPO. The intermediate

phosphorane (III) can be obtained by the reaction of salicylic acid or 1-Cl-BDPO with phosphorus pentachloride:[12,59,60]



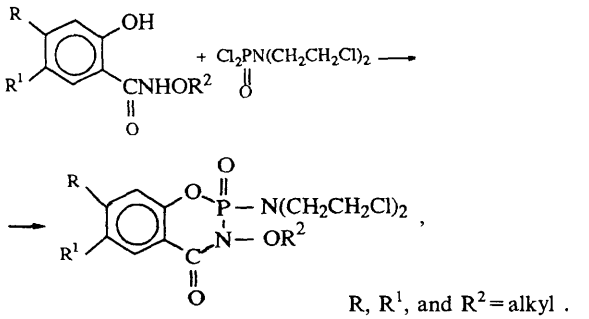
It was subsequently shown, however, that stable intermediate phosphoranes of type (III) are not formed in the reaction of the phosphite (I) with phosphorus pentachloride and chlorine.[61] The formation of stable products was observed only in the reactions of 1-chloro-4,5-benzo-2-phenylaza-6-oxaphosphorin-3-one and its 1-phenoxy analogue with chlorine.[62]

1-Cl-BDPD and 1-Br-BDPD are formed by the reaction of 1-alkoxy-BDPO with chlorine (sulphuryl chloride) or bromine respectively:[30,33]



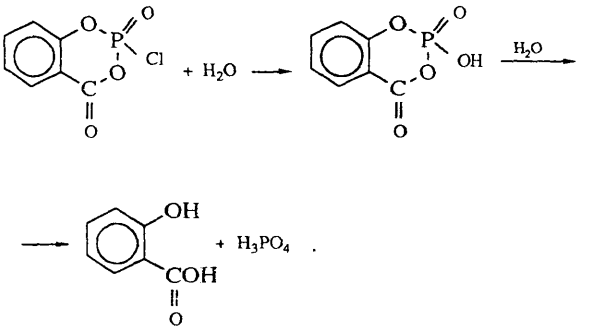
When the reaction with bromine is carried out under controlled conditions at a low temperature, ring opening takes place initially to give a product which undergoes cyclisation when the temperature is increased.[33] A similar result was obtained in a study of the reaction of 1-Cl-BDPO with halogens.[63]

Phosphorylation takes place with amidodichlorophosphates and hydroxamic derivatives of salicylic acid:[64]

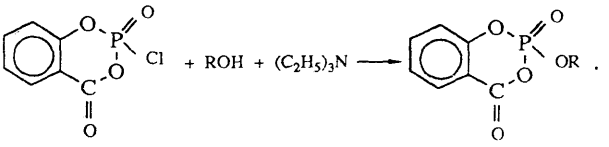


R, R^1, and R^2 = alkyl .

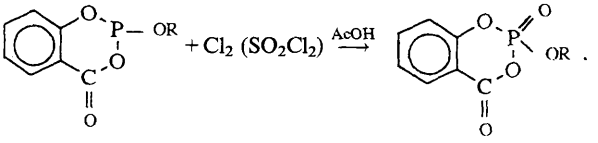
The reaction of 1-Cl-BDPD with nucleophilic reagents may involve both replacement of the chlorine atom and splitting of the phosphorine ring. On careful hydrolysis of 1-Cl-BDPD, replacement of chlorine by a hydroxyl group has been observed, but the resulting 1-hydroxy-4,5-benzo-2,6-dioxaphosphorinic acid is extremely unstable and is rapidly hydrolysed to give phosphoric and salicylic acids:[65]



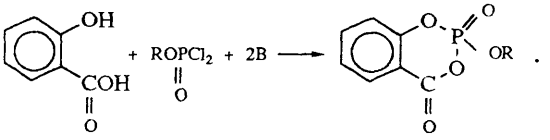
The replacement of chlorine by alkoxy and aryloxy groups takes place more selectively in the presence of hydrogen chloride acceptors to give 1-alkoxy(aryloxy)-4,5-benzo-2,6-dioxaphosphorine-1,3-diones;[6,66–68] the reaction takes place by an $S_N2(P)$ mechanism:[69]



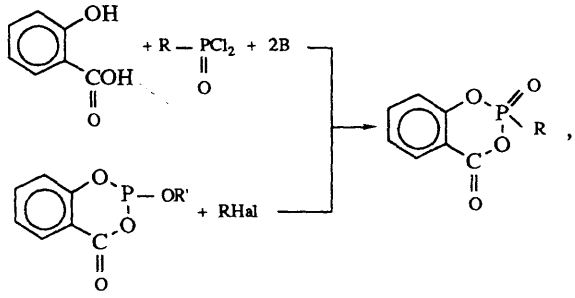
1-Chloroalkoxy(aryloxy)-BDPD have been synthesised by the reaction of 1-chloroalkoxy(aryloxy)-BDPO with chlorine or sulphuryl chloride in the presence of acetic acid:[30]

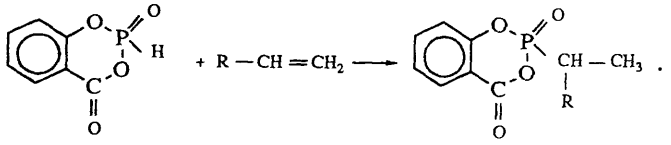


1-Alkoxy(aryloxy)BDPD have also been obtained by the counter cyclisation of the corresponding dichlorophosphates with salicylic acid:[70]



Dichlorides of phosphonic acids undergo similar cyclisation to give 1-alkyl(aryl)-BDPD, which can also be obtained by the Arbuzov[29,57,71] and Pudovik[43] reactions:



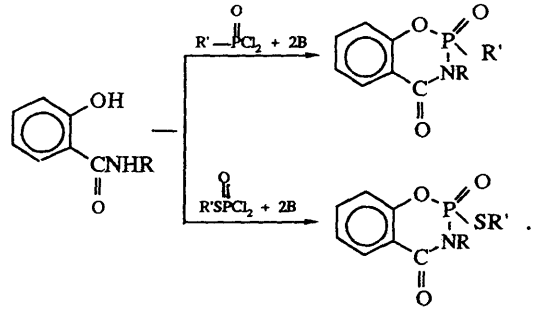


R = C_6H_5, C_2H_5, C_6H_5O, C_2H_5O

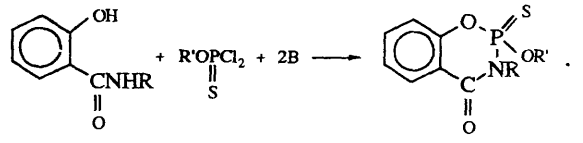
In the last case a rare non-catalysed electrophilic version of the reaction takes place.

b. **4,5-Benzo-2-aza-6-oxaphosphorine-1,3-diones and 4,5-benzo-2,6-diazaphosphorine-1,3-diones**

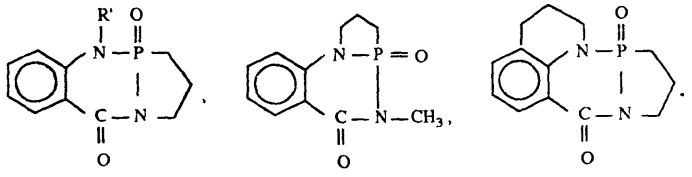
The reaction of the dichlorides of alkylphosphonic acids and alkyl dihydrogen thiophosphates with salicyliamides has been used to synthesise 1-alkyl(thioalkyl)-4,5-benzo-2-aza-6-oxaphosphorine-1,3-diones:[72–74]



The thione isomers were synthesised by the reaction of salicylamides with alkyl thiodichlorophosphates:[75]

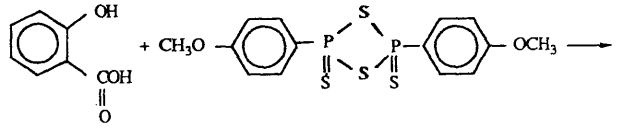


Unusual directions of the cyclisation were observed[76,77] for phosphorylated salicylamides containing a 3-chloropropyl substituent on the phosphorus or nitrogen atoms:

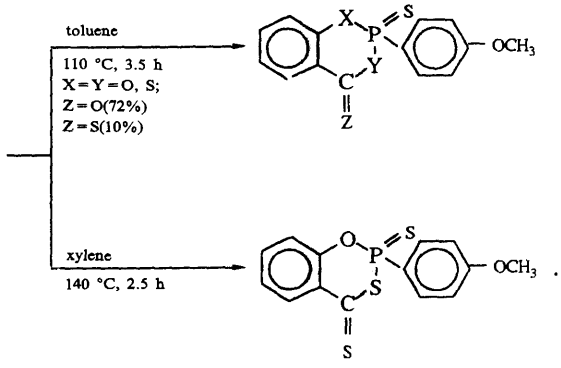


c. **1-Thio-4,5-benzo-2,6-X,Y-phosphorin-3-ones (thiones)**

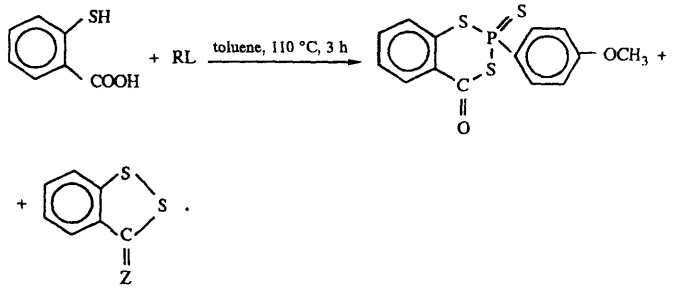
Thiophosphorus derivatives of salicylic acid have been obtained using Lawesson's reagent (RL).[78] The direction of the reaction of salicylic acid with Lawesson's reagent depends on the temperature and the solvent:



(RL)

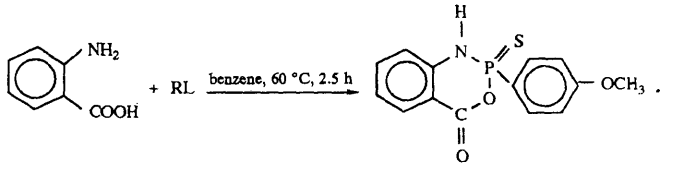


In the analogous reaction of α-mercaptobenzoic acid, phosphorylation and thionation of the original acid take place:



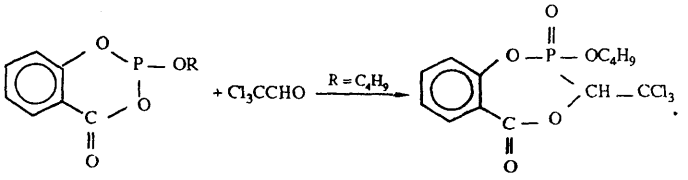
Z = O (15%); Z = S (52%) .

The reaction of anthranilic acid with Lawesson's reagent leads to only phosphorylation:

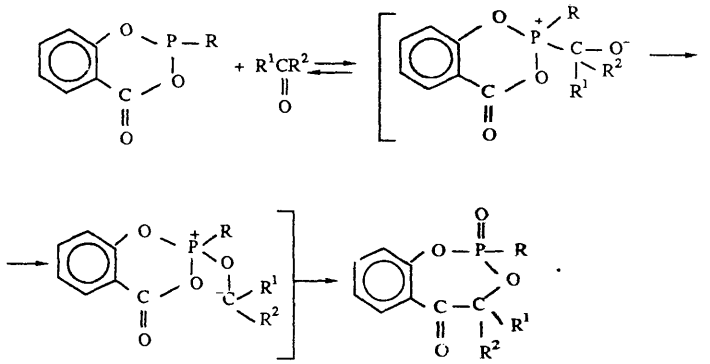


d. 5,6-Benzo-4-oxo-3,7-dioxa-1-phosphepines and 5,6-benzo-4-oxo-2,7-dioxa-1-phosphepines

An interesting feature of the reactivity of BDPO was revealed in the reactions with carbonyl compounds, in which expansion of the ring to give a phosphepine ring was observed:[79]



For R = CH_2CF_3 and $CH_2(CF_2)_2H$ the reactions were much slower, but had a high stereoselectivity, reching 95%.[80] When hexafluoroacetone and ethyl pyruvate were taken for the reaction, the expansion of the ring was accompanied by P–C → P–O–C rearrangement to give a new C–C bond:[81–83]



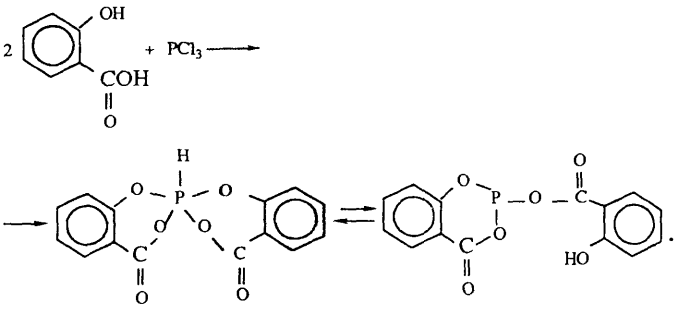
R = $N(C_2H_5)_2$, OC_2H_5, OCH_2CF_3, $OCH_2(CF_2)_2H$, $OCH_2P(O)(OC_2H_5)_2$;

$R^1, R^2 = CF_3$, CH_3, $COOC_2H_5$.

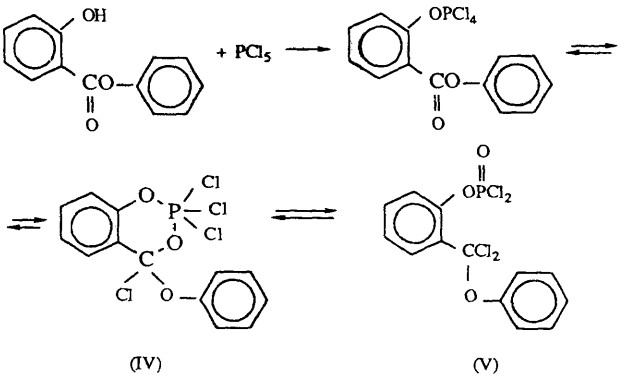
An analogous synthetic result was obtained with methyl trifluoropyruvate.[84]

3. Phosphorus derivatives of salicylic acid containing a five-coordinate phosphorus atom

The reaction of phosphorus trichloride with an excess of salicylic acid gives not 1-Cl-BDPO but a bicyclic phosphorane in equilibrium with its monocyclic form;[14,85] no ^{31}P NMR data have been published, however.



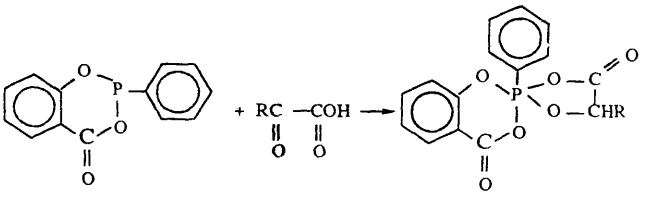
The reaction of phenyl salicylate with phosphorus pentachloride gives the monocyclic phosphorane (IV),[86] but its structure also has not been proved. The conversion of compound (V) into compound (IV) appears doubtful.



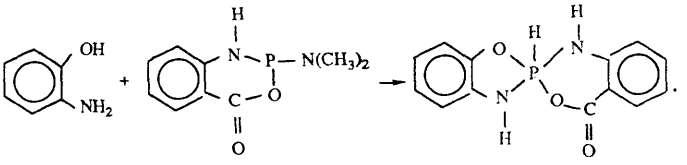
(IV) (V)

The formation of a phosphorane structure has also been assumed to take place in the careful hydrolysis of salicyl phosphate.[87] Phosphorane derivatives of salicylic acid are extremely reactive and have been little studied, and for the most part their structures have been only postulated.[60,69,87]

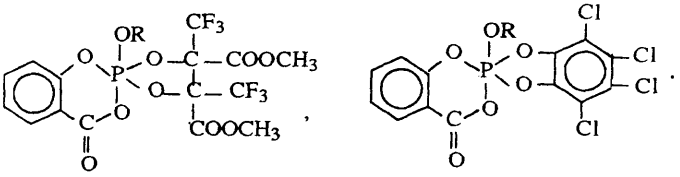
Spirodiacyloxyphosphoranes have been obtained by the reaction of 1-phenyl-BDPO with α-ketoacids, acrylic acid, and β-propiolactone, and their formation has been proved by ^{31}P NMR:[88]



A spirocyclic P–H-phosphorane based on anthranilic acid and *ortho*-aminophenol has been obtained, and its structure proved by ^{31}P NMR (δ_P 59 p.p.m., $^1J_{P-H}$ 860 Hz).[55]

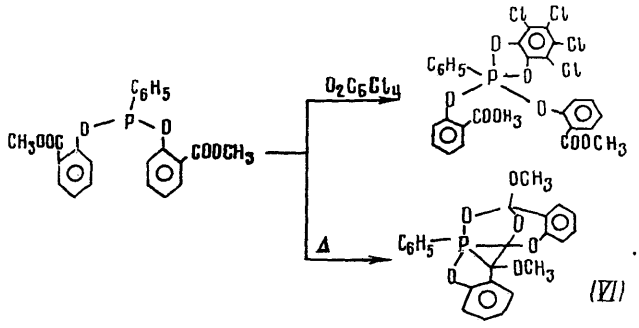


Spirobicyclic phosphoranes are also formed in the reactions with methyl trifluoropyruvate,[84] benzil, *ortho*-chloranil,[89] and phenyl azide:[83]



R = CH_2CF_3, $CH_2(CF_2)_2H$.

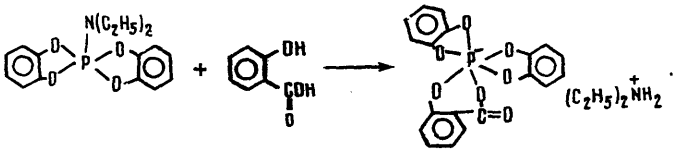
A compound of five-coordinate phosphorus has also been obtained by the reaction of an acyclic bis(2-methoxycarbonylphenyl) phosphonite with *ortho*-chloranil:[90]



(VI)

With heating, the phosphonite undergoes an unusual cyclisation to give the tricyclic phosphorane (VI).

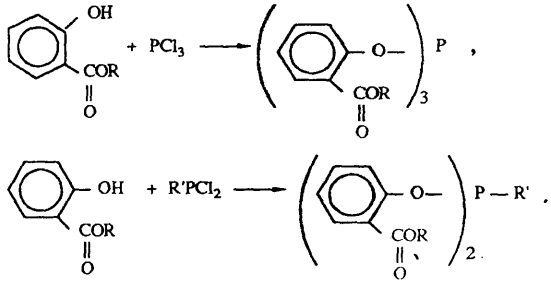
We detected the only example of a six-coordinate structure, containing a salicylate ring and obtained from diethylaminobis-(pyrocatecholato)phosphorane and salicylic acid:[91]



III. Acyclic phosphorus-containing derivatives of salicylic acid

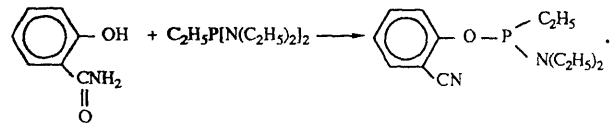
1. Acyclic phosphorus derivatives of salicylic acid containing a three-coordinate phosphorus atom

Esters of salicylic acid, like phenols, are phosphorylated at the hydroxyl group. Thus they react with phosphorus trichloride to give 2-alkoxycarbonylphenyl phosphites, and with dichlorophosphines to give the phosphonites:[92]

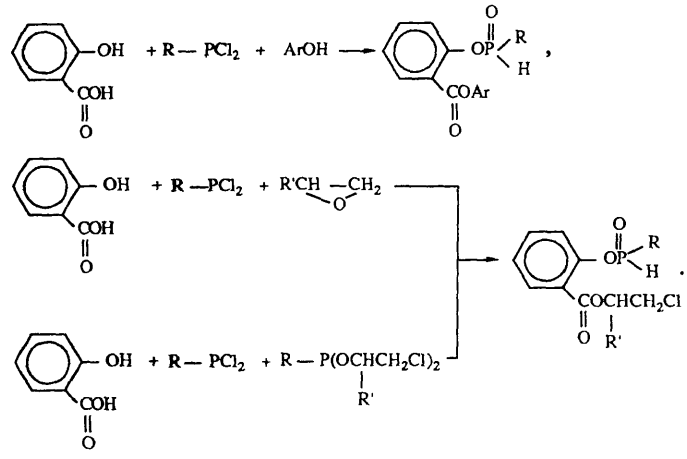


The data[92] on the synthesis of the phosphonites were later refuted[90] (see above), and it was possible to obtain these phosphonites only using bases.

Salicylamides react with phosphorus trichloride and dichlorophosphites to give mainly cyclic products,[51,52] and acyclic compounds were obtained only in the reaction with diamidophosphonites; in the opinion of the authors cited, this is due to the previous dehydration of the carbamoyl fragment of the salicylamide:[53]



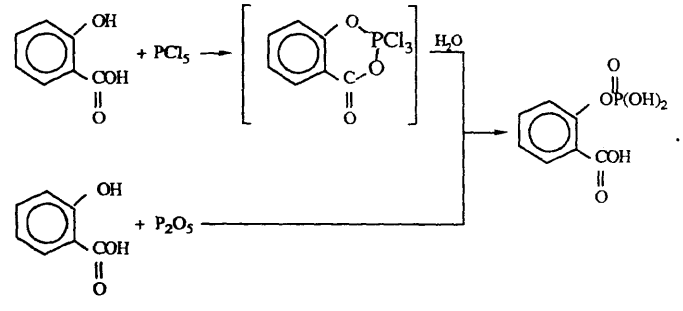
Acid esters of phosphonous acid have been synthesised by the reactions of the corresponding phosphorus chlorides with salicylic acid in the presence of phenols or alkylene oxides,[93,94] and also by an exchange reaction:[95]



2. Acyclic phosphorus derivatives of salicylic acid containing a four-coordinate phosphorus atom

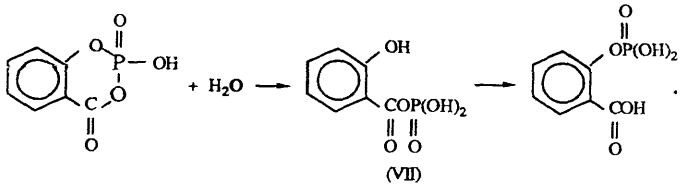
a. Phosphates and phosphonates

Phosphorylsalicylic acid is an analogue of acetylsalicylic acid, but it has not been used in medicine. Phosphorylsalicylic acid can be obtained by the direct phosphorylation of salicylic acid, and also from its cyclic phosphorus derivatives. The most convenient method of obtaining phosphorylsalicylic acid is based on the successive reactions of salicylic acid with phosphorus pentachloride and water.[59,60,61,87,96] Phosphorus pentoxide can also be used as phosphorylating agent:[97]



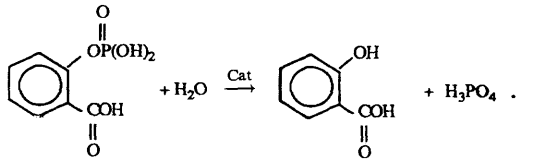
The hydrolysis of the cyclic salicylphosphoric acid to phosphoryl-salicylic acid has been said to take place via the formation of the mixed anhydride (VII),[65] but this appears doubtful, since anhydride

bonds are hydrolysed much more readily.[8] The hydrolysis of acyl phosphates, including salicyl phosphates, has been reviewed briefly.[98]



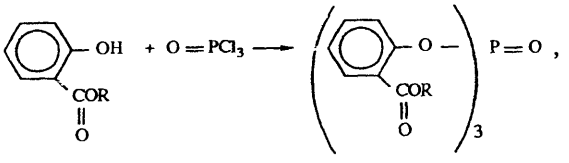
(VII)

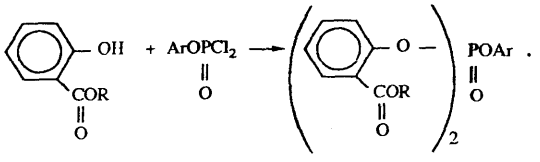
Phosphorylsalicylic acid readily undergoes further hydrolytic splitting to give phosphoric and salicylic acids.[99–104] Hydrolysis takes place more readily in a neutral medium, and is slower in strongly acidic and alkaline media.[105] The hydrolysis is catalysed by calcium ions, glyceryl phosphate, and bovine phosphatase; the hydrolysis of phosphorylsalicylic acid by bovine phosphatase is twice as rapid as that by glyceryl phosphate.[102–104]



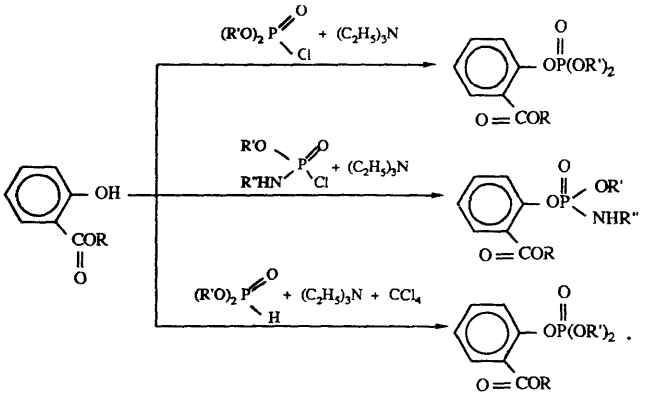
A large number of salicyl phosphates and phosphonates have been obtained in the search for biologically active substances and technically important compounds.

The reaction of salicylate esters with phosphorus oxide chloride or aryl chlorophosphates and chlorophosphonates[106,107] has been used to synthesise aromatic esters of salicylphosphoric and -phosphonic acids, proposed as polymer stabilisers:[106,107]

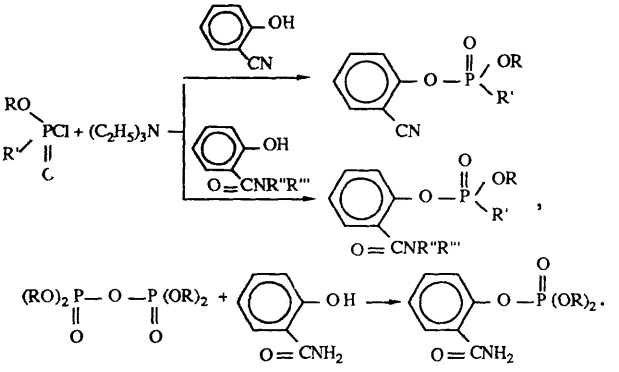




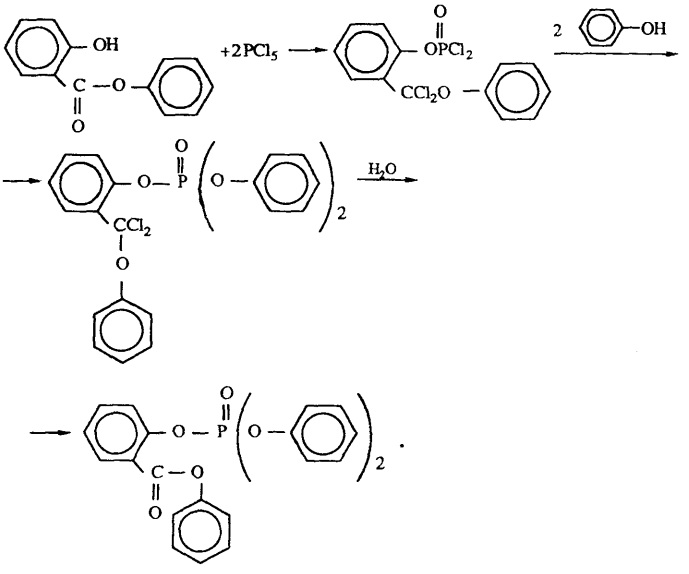
The phenolate of salicylic acid is weakly nucleophilic, and is phosphorylated by halides of phosphorus acids with difficulty.[108] Esters of salicylic acid in the presence of bases, however, are readily phosphorylated by dialkyl chlorophosphates[107–111] and amidochlorophosphates[109] to give 2-alkoxycarbonylphenyl esters of phosphorus acids, some of which are interesting insecticides and acaricides.[112] These compounds were obtained by the Todd–Atherton reaction:[113]



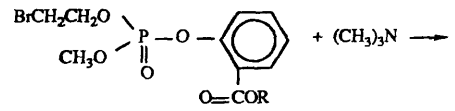
Substances with fungicidal activity have been synthesised by the reaction of salicylonitriles[114,115] and salicylamides[116] with dialkyl chlorophosphates. With salicylamides, pyrophosphates have also been used:[117]

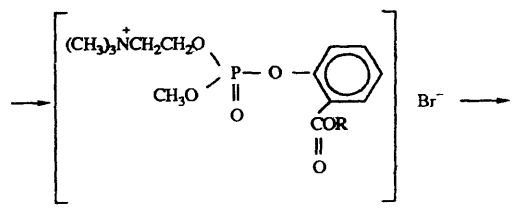


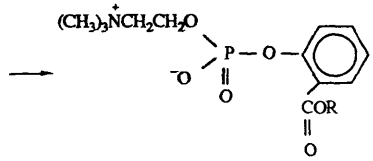
An extremely original method has been proposed for synthesising phosphorylsalicylic acid, based on the successive reactions of aryl esters of salicylic acid with phosphorus pentachloride, phenol, and water:[118]



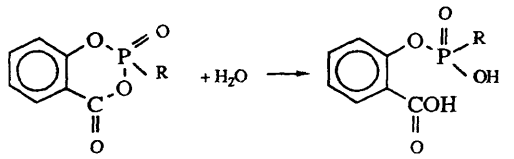
Aliphatic esters of salicylphosphoric acid can undergo dealkylation, and this has been used to synthesise salicyl phosphoxolines:[119]



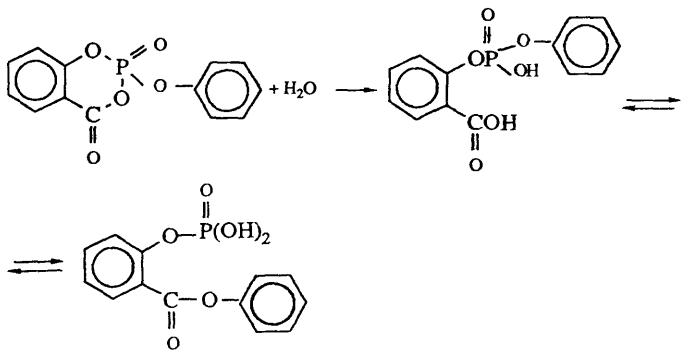




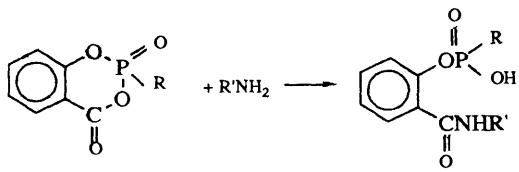
Acid esters of salicylphosphoric and -phosphonic acids are conveniently obtained by the hydrolysis of cyclic salicyl phosphates (BDPD):[68,120]



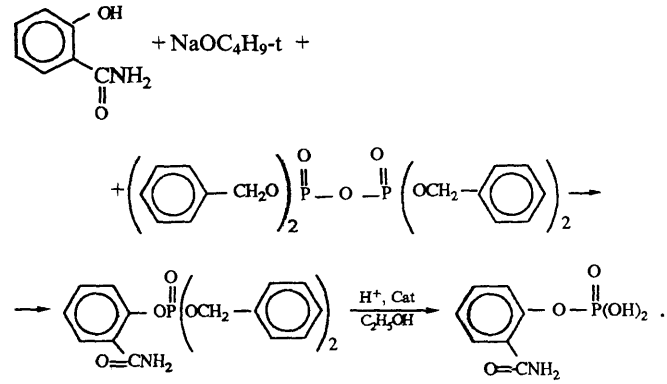
An interesting feature is that in aromatic acid esters of this type, migration of the aryloxy-group between the phosphoryl and the carboxyl groups has been observed:[65,121]



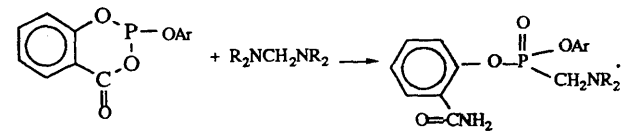
The reaction of 1-alkyl(aryl)-BDPD with amines gives 2-carbamoylphenyl esters of alkyl(aryl) hydrogen phosphates and alkyl(aryl) hydrogen phosphonates:[66,67,69,122]



Phosphorylation of salicylamide by tetrabenzyl pyrophosphate followed by hydrolysis of the dibenzyl 2-carbamoylphenyl phosphate obtained gives 2-carbamoylphenyl phosphate:[123]

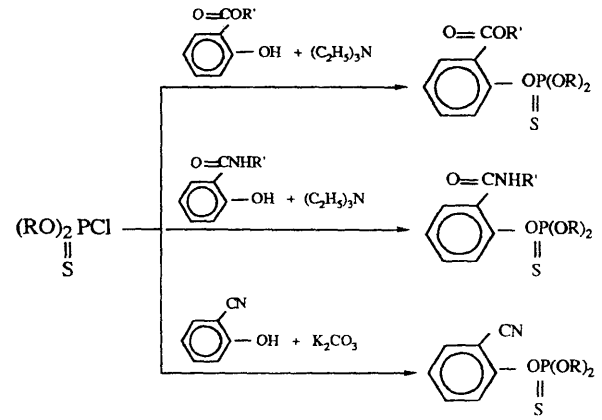


The reaction of 1-aryloxy-4,5-benzo-2,6-dioxaphosphorin-3-ones with bis(dialkylamino)methane, which gives O-aryl O-(2-carbamoyl)-phenyl aminomethylphosphonates, may be of interest:[124]



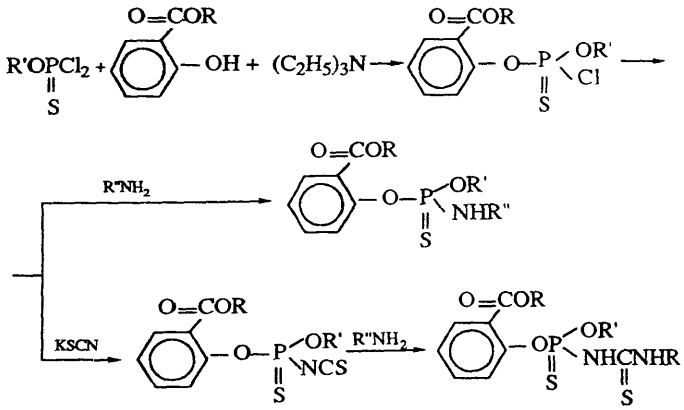
b. Derivatives of thiophosphorylsalicylic acid

The sulphur-containing phosphorus derivatives of salicylic acid include compounds with thione and thiol sulphur on the phosphorus atoms. Compounds containing sulphur in the salicylic acid fragment have not been described. The thione isomers have been synthesised mainly by the reactions of the chlorides of phosphorus thio-acids with derivatives of salicylic acid. Thus the reaction of dialkyl thiochlorophosphates with esters,[125] amides,[126,127] and nitriles[125,128–130] of salicylic acid in the presence of hydrogen chloride acceptors has been used to obtain the corresponding *ortho*-substituted phenyl esters of dialkyl hydrogen thiophosphates, which have insecticidal activity:[125–130]



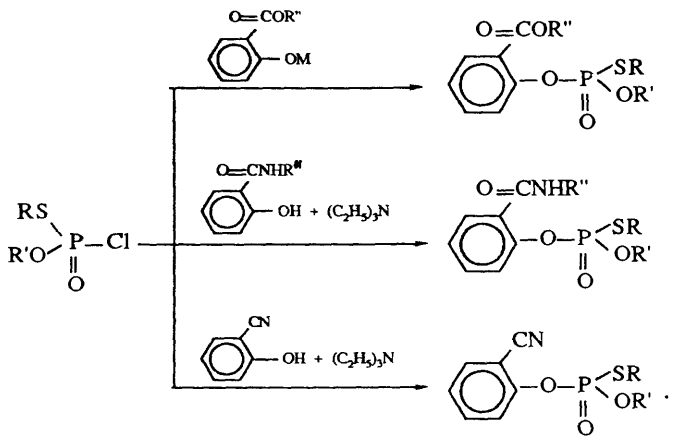
Esters,[131] amides,[126,132,133] and nitriles[134,135] of salicylic acid in the presence of hydrogen chloride acceptors also react with the ester chlorides of alkyl(aryl) hydrogen thiophosphonates to give the *ortho*-substituted phenyl esters of thiophosphonic acids, with insecticidal activity.[131–136]

An interesting feature is that in the reaction of alkyl thionodichlorophosphates with esters of salicylic acid, selective replacement of one chlorine atom by an alkoxycarbonylphenoxy-group is possible, and this has been used to synthesise amide esters[137–142] and thioureide esters[143] of thiophosphorylsalicylic acid:

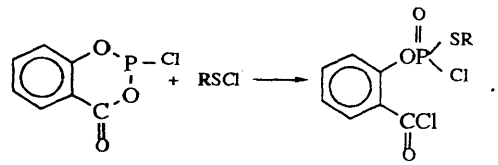


A fairly extensive group is formed by the thiol derivatives of phosphorylsalicylic acid, which are now being studied intensively in the search for pesticides with a low toxicity towards warm-blooded animals.[144–157]

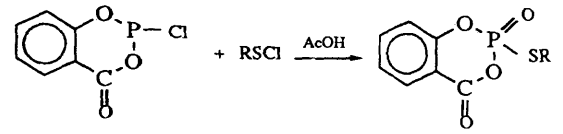
Esters,[144–151] amides,[147,152] and nitriles[153,154] of salicylic acid in the presence of hydrogen chloride acceptors react with thiolochlorophosphates to give thiol derivatives of phosphoryl-salicylic acid, many of which have been patented as insecticides and acaricides.[144–156]



An extremely interesting method of attaching a thiol group to a phosphorus atom is based on the splitting of the phosphorine ring in 1-Cl-BDPO by sulphenyl chloride to give the dichlorides of thiolo-phosphorylsalicylic acid,[158] which can be used as intermediates in the synthesis of biologically active substances:



The view that in the presence of acetic acid the reaction of 1-Cl-BDPO with sulphenyl chlorides takes place with preservation of the phosphorine ring[158] apparently requires confirmation.



* *
*

The analysis of published material shows that phosphorus-containing derivatives of salicylic acid represent an extensive group of cyclic and acyclic multidentate compounds, whose chemistry is now being intensively developed. The further development of the chemistry of acyclic phosphorus derivatives of salicylic acid is of undoubted interest in the search for new physiologically active substances.

Cyclic phosphorus derivatives of salicylic acid are highly reactive and of considerable interest as valuable synthons. The chemistry of some types of cyclic phosphorus derivative of salicylic acid has still been little studied, however. Thus there are very few data on salicyl-containing phosphoranes or proofs of their structure, although these compounds are of interest for chemical theory and as synthetic intermediates.

References

1. *Khimicheskii Entsiklopedicheski Slovar'* (Chemical Encyclopedia), Sovetskaya Entsiklopediya, Moscow, 1983, p. 63
2. G Schrader *New Organophosphorus Insecticides* (Translated into Russian), Mir, Moscow, 1965
3. R S Edmundson *Chem. Ind.*, 1962, **13** 1770
4. F R Atherton *Chem. Soc. Special Publication*, 1957, **8** 77
5. A G Pinkus, P G Waldrep, W J Collier *J. Org. Chem.*, 1961, **26** 682
6. R Cremlin, K Ruddok, O Odiseson *Phosphorus Sulfur*, 1981, **10**(3) 333
7. M B Gazizov, R A Khairullin *Itogi Nauki i Tekhniki. Organicheskaya Khimiya* (Progress in Science and Technology. Organic Chemistry), Vol. 15, Izd. VINITI, Moscow, 1990, pp 29–32
8. E E Nifant'ev, I V Fursenko *Usp. Khim.*, 1970, **39**(11) 2187 [English translation in *Russ. Chem. Rev.*, 1970(11)]
9. R Anschütz, W Emery *Ann. Chem.*, 1887, **239** 301
10. R Anschütz, H Mehring *Ann. Chem.*, 1906, **346** 311
11. R Anschütz, E Schroder, E Weber *Ann. Chem.*, 1906, **346** 341
12. R Anschütz *Chem. Ber.*, 1897, **30** 221
13. R Anschütz *Ann. Chem.*, 1924, **439** 265
14. J A Cade, W Gerrard *J. Chem. Soc.*, 1960, 1249
15. J A Cade, W Gerrard *Chem. Ind.*, 1954, **3** 402
16. R W Young *J. Am. Chem. Soc.*, 1952, **74** 1672
17. N Kh Maksudov *Sbornik Nauchnykh Trudov Tashkentskogo Politekhnicheskogo Instituta* (Collected Scientific Papers of Tashkent Polytechnical Institute), No. 221, 1977, p. 36
18. V Mark, C H Dungan, J R Van Wazer *Topics in Phosphorus Chemistry*, 1967, **5** 492

19. BRD P. 1 303 920; *Chem. Abs.*, **83** 163853h
20. B A Arbuzov, V K Krupnov, A O Vizel' *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, (5) 1193
21. R Schmutzler *Chem. Ber.*, 1963, **96** 2435
22. J A Cade, W Gerrard *J. Chem. Soc.*, 1954, 2030
23. T Saegusa, T Chow, S Kobayashi, S Kobayashi *Macromolecules*, 1979, **12**(3) 533
24. S Kobayashi *Polym. Bull.*, 1983, **9** 588
25. T Saegusa, T Kobayashi, S Kobayashi *Polym. Bull.*, 1979, **1**(4) 259
26. S Kobayashi, M Okawa, M Niwano, T Saegusa *Polym. Bull.*, 1981, **5**(6) 331
27. T Saegusa, T Kobayashi, S Kobayashi *Polym. Bull.*, 1979, **1**(8) 535
28. L V Nesterov, R A Sabirova *Zh. Obshch. Khim.*, 1961, **31**(3) 897
29. L V Nesterov, R A Sabirova *Zh. Obshch. Khim.*, 1961, **31**(7) 2358
30. L V Nesterov, R A Sabirova *Zh. Obshch. Khim.*, 1965., **35**(11) 2006
31. P A Kirpichniko, Ya A Gurvich, G P Gren *Zh. Obshch. Khim.*, 1965, **35**(4) 744
32. P A Kirpichnikov, N S Kolubakina, N A Mukmeneva, et al. *Vysokomol. Soedin., Ser. B*, 1970, **12**(3) 189
33. A P Pashinkin, T Kh Gazizov, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, (2) 437
34. B. P. 11 222 666; *Chem. Abs.*, **69**, 78110c
35. L V Nesterov, R A Sabirova *Zh. Obshch. Khim.*, 1965, **35**(11) 1976
36. USSR P. 1 397 455; *Byull. Izobret.*, 1988, (19); *Ref. Zh. Khim.*, 1988, 220211P
37. J E Marugg, M C Tromp *Tetrahedron Lett.*, 1986, **27**(23) 2662
38. A G Ven'yaminova, N I Komarova, A S Levina, M N Repkova *Bioorg. Khim.*, 1988, **14**(4) 484
39. J Ludwig, F Eckstein *J. Org. Chem.*, 1989, **54**(3) 631
40. T Tanaka *J. Pharm Soc. Jpn.*, 1959, **79** 437
41. L V Nesterov, R A Sabirova, N E Krepysheva, R I Mutalapova *Dokl. Akad. Nauk SSSR*, 1965, **148**(5) 1085
42. R S Edmundson *Chem. Ind.*, 1962, **13** 1770
43. V V Ovchinnikov, S V Cherezov, R A Cherkasov *Zh. Obshch. Khim.*, 1984, **54**(5) 1021
44. E E Nifant'ev, T S Kukhareva, I A Soldatova *Zh. Obshch. Khim.*, 1989, **59**(11) 2504
45. Dutch P. 6 514 392; *Chem. Abs.*, **65**, 15338a
46. M I Makhamatkhanov, V V Vakhidova, F A Bakhtiyarova, et al. *Tsiklicheskie Efiry Nekotorykh Fosfonovykh i Amidofosfornykh Kislot s Salitsilovoi Kislotoi* (Cyclic Esters of Various Phosphonic and Amidophosphoric Acids with Salicylic Acid), Tashkent, 1976, 4 pp., Dep. in VINITI, 14th July 1976, No. 2152-76; *Ref. Zh. Khim.*, 1976, 22Zh367
47. N Kh Maksudov *Uzb. Khim. Zh.*, 1976, (3) 39; *Chem. Abs.*, **86**, 16610k
48. B A Arbuzov, A O Vizel', V K Krupnov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, (6) 1327
49. V L Isaev, L Yu Mal'kevich, R N Sterlin, I L Knunyants *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1974, **19**(5) 586
50. L Yu Kryukova, L N Kryukov, V L Isaev, et al. *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1979, **24**(3) 298
51. R A Sabirova, L V Nesterov *Zh. Obshch. Khim.*, 1976, **37** 732
52. A K Kuliev, D A Akhmedzade, V V Moskva, et al. *Zh. Obshch. Khim.*, 1985, **55**(4) 936
53. A K Kuliev, V V Moskva, D A Akhmedzade, et al. *Zh. Obshch. Khim.*, 1987, **57**(1) 230
54. A K Kuliev, V V Moskva, D A Akhmedzade, et al. *Zh. Obshch. Khim.*, 1985, **55**(2) 457
55. A Munoz, B Garrigues, R Wolf *Phosphorus Sulfur*, 1978, **4**(1) 47
56. H A C Montgomery, J H Turnbull *J. Chem. Soc.*, 1956, 4603
57. Kh E Vakhidova, N Kh Mansurov, A Akbarov *Uzb. Khim.*, 1977, (6) 66; *Chem. Abs.*, **89** 43 604e
58. L N Mishin, R A Mavleev, V F Mironov *Sintez i Issledovanie Struktur FOS Spektral'nymi Metodami. Tezisy Dokladov Nauchnoi Shkolyseminara* (Summaries of Papers Presented at the Research School and Seminar on the Synthesis and Study of Organosphosphorus Compounds by Spectral Methods), Kazan', 1992, p.19
59. R Anschütz *Ann. Chem.*, 1885, **228** 308
60. US P. 2 810 741; *Chem. Abs.*, **52** 5909a
61. BRD P. 2 641 526; *Chem. Abs.*, **88**, 136 317
62. R A Sabirova, L V Nesterov *Zh. Obshch. Khim.*, 1967, **37** 732
63. J Hanuise, R R Smolders, N Voglet, P Wollast *Ing. Chim. (Brussels)*, 1973, **55**(267–8) 3; *Chem. Abs.*, **80**, 820005u
64. R Miller *J Med. Chem. (Chim. Ther.)*, 1974, **9** 301; *Chem. Abs.*, **81** 43371g
65. R H Bromilow, S A Khan, A J Kirby *J. Chem. Soc. B*, 1971, **6** 1091
66. B. P. 806 879; *Chem. Abs.*, **53** 14125i
67. US P. 2 944 074; *Chem. Abs.*, **54** 22692e
68. B. P. 793 722; *Chem. Abs.*, **52** 20063f
69. S A Khan, A J Kirby, M Wakselman *J. Chem. Soc. B*, 1970, 1182
70. K Sasse *Metoden der organischem Chemie* (Houben-Weyl), Stuttgart, 1964
71. M G Gazizov, L B Sultanova, L P Ostanina, et al. *Zh. Obshch. Khim.*, 1971, **41** (70) 2176
72. Jpn. P. 13 279; *Ref. Zh. Khim.*, 1968, 6N693P
73. Jpn. P. 22 360; *Ref. Zh. Khim.*, 1973, 6N698P
74. Jpn. P. 18 755; *Ref. Zh. Khim.*, 1972, 2N624P
75. Jpn. P. 16 286; *Ref. Zh. Khim.*, 1975, 120428P
76. G M Coppola *J. Heterocycl. Chem.*, 1979, **16**(5) 897
77. G M Coppola, R I Mansukhani *J. Heterocycl. Chem.*, 1978, 15(7) 1169
78. A A El-Barbary, S O Lawesson *Tetrahedron*, 1981, **37**(15) 2641
79. USSR P. 188 970; *Byull. Izobret.*, 1966, (23) 18
80. V F Mironov, R A Mavleev, E N Ofitserov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, (7) 1676
81. V F Mironov, R A Mavleev, E N Ofitserov, A N Pudovik *J. Fluorine Chem.*, 1991, **54**(1–3) 299
82. V F Mironov, I V Konovalova, R A Mavleev, et al. *Zh. Obshch. Khim.*, 1991, **61**(10) 2150
83. R A Mavleev, N F Mironov, I V Konovalova *Tezisy Dokladov III Konferentsii Molodykh Uchenykh-Khimikov* (Summaries of Papers Presented at the Third Conference of Young Research Chemists), Donetsk, 1991, p. 101
84. V F Mironov, L A Burnaeva, V M Krokhalev, et al. *Zh. Obshch. Khim.*, 1992, **62** (3)
85. D A Akhmedzade, V D Yasnopol'skii, M M Guseinova, USSR P. Application No. 2077212/23-4, 1974
86. A G Pinkus, P G Waldrep *Chem. Ind.*, 1962, 302
87. J D Chanley, E M Gindler, H H Sobotka *J. Am. Chem. Soc.*, 1952, **74** 4347
88. S Kabayashi, T Kabayashi, T Saegusa *Chem. Lett.*, 1979, **4** 393

89. Yu S Shashtina, R A Mavleev, V F Mironov *Tezisy Dokladov Nauchnoi Studencheskoi Shkoly-seminara* (Summaries of Papers Presented at the Research Students School and Seminar), Kazan', 1992, p. 17
90. S D Harper, A J Arduengo *J. Am. Chem. Soc.*, 1982, **104**(9) 2497
91. A Munoz, G Gence, M Koenig *Bull. Soc. Chim. Fr.*, 1975, (3/4), Pt. 2 909
92. M M Makhamatkhanov, V V Vakhidova, F A Bakhtiyarova, et al. *Efiry Nekotorykh Fosfonovykh Kislot s O-Metil-karboksifenolom* (Esters of Various Phosphonic Acids with O-Methylcarboxyphenol), Tashkent, 1976, 5 pp, Dep. in VINITI, 14th June 1976, No. 2153-76; *Ref. Zh. Khim.*, 1976, 22Zh359
93. USSR P. 1 549 963; *Byull. Izobret.*, 1990, (10) 107
94. USSR P. 1 583 427; *Ref. Zh. Khim.*, 1991, 2N135P
95. USSR P. 1 512 972; *Byull. Izobret.*, 1989, (37) 107; *Ref. Zh. Khim.*, 6N166P
96. B H J Hofstee *Arch. Biochem. Biophys.*, 1954, **5** 139
97. BRD P. 1 050 745; *Chem. Abs.*, **55**, 10387e
98. A J Kirby, S G Warren *The Organic Chemistry of Phosphorus* (Translated into Russian), Izd. Mir, Moscow, 1971, p. 305
99. H Brandenberger, W H Weihe *Helv. Chim. Acta*, 1955, **38** 1347
100. G N Bowers *Clin. Chem.*, 1967, **14**(7) 608
101. P G Walker, E J King *Biochem.*, 1950, **47** 93
102. B H J Hofstee *Arch. Biochem. Biophys.*, 1955, **59** 352
103. E Cherbuliez, C Gandillon *Arch. Sci.*, 1956, **9** 103
104. C A Zittle, E W Bingham *Arch. Biochem. Biophys.*, 1960, **86** 24; *Chem. Abs.*, **54** 14318g
105. V E Bel'skii *Usp. Khim.*, 1977, **46**(9) 1578 [English translation in *Russ. Chem. Rev.*, 1977(9)]
106. Jpn. P. 5891; *Chem. Abs.*, **53** 32102q
107. US P. 2 223 329; *Chem. Abs.*, **35** 1805c
108. J Epstein, R E Plapinger, H O Michel, et al. *J. Am. Chem. Soc.*, 1964, **80**(15) 3075
109. BRD P. 811 514; *Chem. Abs.*, **47** 5620h
110. BRD P. 814 512
111. USSR P. 202 138; *Byull. Izobret.*, 1967, (19)
112. USSR P. 347 976; *Byull. Izobret.*, 1972, (24) 202
113. N L Kryukov, N Yu Lebedeva, S M Kostrova *Zh. Obshch. Khim.*, 1990, **60**(5) 1066
114. BRD P. 2 101 149; *Chem. Abs.*, **75** 88303h
115. Jpn. P. 49 19859; *Ref. Zh. Khim.*, 1975, 60339P
116. BRD P. Application 2 220 907; *Ref. Zh. Khim.*, 1974, 22N638P
117. B. P. 789 563; *Chem. Abs.*, **52** 12913i
118. A G Pinkus, P G Waldrep *J. Heterocycl. Chem.*, 1965, **2**(4) 357
119. French P. 1 551 060; *Chem. Abs.*, **72** 42777c
120. USSR P. 191 554; *Byull. Izobret.*, 1967, (4)
121. J J Steffens, J J Siewers, S J Benkovic, et al. *Biochem.*, 1975, 2431; *Chem. Abs.*, **83** 39138g
122. USSR P. 191 553; *Byull. Izobret.*, 1967, (4)
123. B. P. 789 563; Chem. Abs., **52** 12913h
124. USSR P. 1 549 957; *Byull. Izobret.*, 1990, (10) 106
125. S Tamura, M Takai, S Miyamoto, et al. *Agr. Biol. Chem.*, 1961, **25** 773; *Chem. Abs.*, **56** 7748c
126. Jpn. P. 14 623; *Ref. Zh. Khim.*, 1975, 110400P
127. Jpn. P. 9010; *Chem. Abs.*, **65** 12239d
128. Jpn. P. 9983; *Chem. Abs.*, **59** 3834e
129. Belg. P. 627 817; *Chem. Abs.*, **61** 5692f
130. Jpn. P. 13 648; *Ref. Zh. Khim.*, 10N427P
131. Jpn. P. 9009; *Chem. Abs.*, **65** 12239c
132. B. P. 950 145; *Chem. Abs.*, **60** 14541e
133. Belg. P. 615 669; *Chem. Abs.*, **58** 11402c
134. Jpn. P. 15 130; *Chem. Abs.*, **59** 10123f
135. Jpn. P. 15 930; *Chem. Abs.*, **68** 105355b
136. G Schwertfeger W Vogt, M Knedel *Biomed. Mass. Spectrom.*, 1978, **5**(4) 302–311
137. BRD P. 1 668 047; *Ref. Zh. Khim.*, 1974, 4N428P
138. BRD P. 1 600 932; *Chem. Abs.*, **74** 125186z
139. USSR P. 520 014; *Byull. Izobret.*, 1976, (24) 183
140. South African P. 6 807 378; *Chem. Abs.*, **72** 23239g
141. USSR P. 321 006; *Byull. Izobret.*, 1971, (34) 204
142. M Ueji, C Tomizawa *J. Pestic. Sci.*, 1984, **9**(4) 675
143. Z Liu, H Hu, J Lhang *J. Cent. China Norm. Univ. (Natur. Sci.)*, 1987, **21**(3) 353; *Ref. Zh. Khim.*, 1988, 11Zh302
144. USSR P. 352 434; *Byull. Izobret.*, 1972, (28) 174
145. Jpn. P. 48-26221; *Ref. Zh. Khim.*, 1974, 11N412P
146. Jpn. P. 49-48946; *Ref. Zh. Khim.*, 1985, 190378P
147. US P. 3 891 728; *Ref. Zh. Khim.*, 1976, 60372P
148. US P. 3 839 511; *Ref. Zh. Khim.*, 1971, 20421P
149. US P. 3 954 919; *Ref. Zh. Khim.*, 1977, 20296P
150. Swiss P. 601 329; *Ref. Zh. Khim.*, 1979, 10114P
151. USSR P. 710 500; *Byull. Izobret.*, 1980, (2) 222
152. Swiss P. 564 307; *Ref. Zh. Khim.*, 1976, 70408P
153. US P. 3 876 782; *Chem. Abs.*, **78** 97316d
154. BRD P. 2 100 221; *Chem. Abs.*, **75**, 140525y
155. USSR P. 713 525; *Byull. Izobret.*, 1980, (4) 202
156. US P. 3 763 288; *Ref. Zh. Khim.*, 20N601P
157. E Kühle *Synthesis*, 1971, (11) 563
158. Yu G Gololobov, N I Gusar' *Sul'fenilkhloridy* (Sulphenyl Chlorides), Nauka, Moscow, 1989, 112 pp

Received 17th March 1992

Translated from *Uspekhi Khimii* 61 1864–1882 (1992) U.D.C. 541.64

The formation of linear and three-dimensional polymers by polycyclisation

Ya S Vygodskii, V A Pankratov
Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences

ABSTRACT. **The influence of the functionality of the starting materials, their isomerism, method of synthesis, process kinetics, and other factors on the structure (microstructure of copolymers), molecular weight, degree of cyclisation, and properties of polymers obtained by reactions involving the polycyclisation of polyfunctional monomers and oligomers are analysed.**

The bibliography includes 77 references.

Contents.

I.	Introduction	1022
II.	Polycondensation of polyfunctional monomers	1022
III.	Polycyclotrimerisation and other methods of polyheteroarylenes	1026
IV.	Conclusion	1031

I. Introduction

Polycyclisation (polycyclocondensation) is a method of synthesis of numerous new generation polymers, mainly highly thermostable and heat resistant.[1] A characteristic feature of polycyclisation is that the reactions leading to the formation of macromolecules (both linear and network) are accompanied by the formation of small rings—intramolecular cyclisation. Such cyclisation can follow polymer formation or can be kinetically indistinguishable from the latter. One should not think that polycyclisation is yet another method of synthesis of polymers different from polymerisation and polycondensation, because these two processes constitute the basis of the formation of polymers. The essential feature of polycyclisation is that at the beginning of polymerisation or, more frequently, polycondensation one obtains macromolecular precursors (called in a number of instances, incorrectly in our view, pre-polymers), and then (frequently simultaneously) cyclic structures are produced:

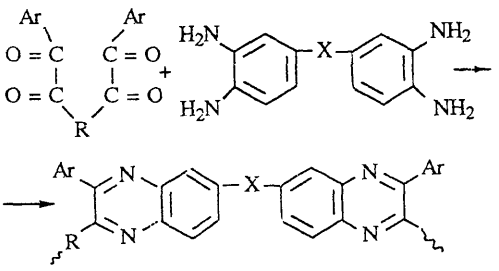
Monomer (s) ⟶	Intermediate polymer ⟶	Final polymer–
Oligomer (s)	Precursor	polyarylene,
Polymer (s)		linear or network
		polyheteroarylene

The final products, containing cyclic fragments which determine the physicochemical and operational properties of polymers, can be obtained also by the traditional procedure involving the initial synthesis of the corresponding monomers or reactive oligomers, incorporating such rings, and then the synthesis of polymers from the latter by the usual methods. This procedure is widely used for the creation of particular polyheteroarylenes, but it is important to note that these processes are no longer polycyclisation. The properties of the polymers formed can then differ markedly from those of the analogous polymers produced by polycyclisation.

Thus the simple interchange of the sequence of reaction stages ("components") alters the "sum", which is understood as the final polymer, its structure and properties. The present review is devoted to the analysis of the influence of various factors (the structure of the monomers and reaction conditions) on the formation during the polycyclisation process of polymers with a definite set of properties.

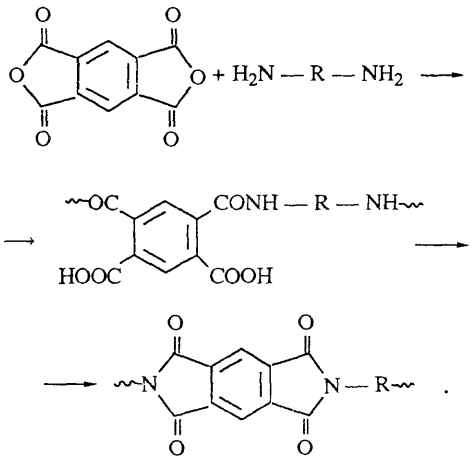
II. Polycyclocondensation of polyfunctional monomers

A series of new polymers of practical values has been obtained by polycyclisation. Here it was found essential to re-examine certain postulates of the chemistry of high-molecular-weight compounds, which have already become classical, in particular the question of the interrelation between the functionality of monomers and the structure (linear or three-dimensional) of the polymers formed.[2] If the monomers used in polycyclisation processes contain, apart from the functional group necessary for the propagation of the polymer chain, also other functional groups capable of forming cyclic fragments, linear polymers are formed also from polyfunctional polymers (trifunctional and tetrafunctional). One of the striking examples of this kind is the synthesis of polyquinoxalines from two tetrafunctional monomers: tetra-amines and tetraketones. In the presence of two amino groups in the *ortho*-positions and keto-groups in the α- positions, arranged in pairs, the six-membered quinoxaline ring is readily formed and linear high-molecular-weight polyquinoxalines are formed quantitatively under mild conditions:

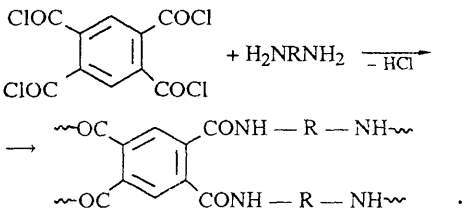


The formation of polyimides from diamines and tetracarboxylic acids is more complex and more ambiguous in this sense. When derivatives of the acids such as dianhydrides, formally regarded as bifunctional monomers, are used, linear high-molecular-weight

polyamidoacids are formed, but this entails the "appearance" of a further two functional groups—carboxy-groups, which participate in the formation of the imide ring in the next stage:



If one begins with derivatives of tetracarboxylic acids with two pairs of carboxy-groups in the *ortho*-positions, such as their acid tetrachlorides, then one obtained cross-linked network polymers instead of linear polymers:



(Naturally if the reaction centres in the polyfunctional monomers are located in positions unfavourable for ring closure, then the polymer formation reaction obeys the "classical" rules of polymer chemistry.)

Network polymers based on traditional bifunctional monomers can also be obtained by polycyclisation, for example by the polycyclotrimerisation of various monomers, which we shall consider below.

Polycyclisation processes proceed in one or several stages, frequently with formation of the corresponding intermediate polymer. As already mentioned, they are a variety of the polymerisation and polycondensation methods of synthesis of polymers and obey many of the rules governing the latter.

We shall consider certain features of linear polycyclisation occurring via the polycondensation mechanism. Thus, when the polycyclisation reactions consist of two stages, the mechanism and kinetics of the first stage hardly differ from those of the corresponding polycondensation reactions leading to the formation of linear polymers—frequently polyamides with other functional groups. Such processes can be reversible or irreversible, equilibrium or non-equilibrium, and are accompanied by the formation of low-molecular-weight products or there are no products. The methods used to carry out the reaction are also similar, although polycondensation in solution is so far usually employed for this purpose. The single stage polycyclisation reactions widely used at the present time, in which the propagation of the polymer chain and intramolecular cyclisation are kinetically indistinguishable, have much in common with the usual polycondensation processes.

The specific features of polycyclisation are manifested in the stage of the cyclisation reactions proper, which can be defined in a general form as reactions in polymer chains. Since many of the polymers formed under these conditions are infusible and insoluble, the processes are carried out on solid polymers. The main procedure involves heat treatment of the intermediate polymers over a wide temperature range. The effectiveness of the process is inferred from the degree of cyclisation of the final polymer. The "kinetic inhibition" with increase in the degree of cyclisation has been noted. It is due to the increase in the glass point of the polymer. A similar phenomenon has been observed in a number of studies in relation to the cyclisation of poly-*o*-carboxyamides, polyhydrazides, polyhydroxyamides, etc.[3–5]

At the same time, cyclisation frequently proceeds effectively in the vitreous state of the polymer and this permits the claim that the influence of the glass point of the polymer being cyclised (noted above), although significant, does not determine fully the kinetics of the cyclisation and the degree of completion of the process. The chemical structure of the cyclised group and the reactivity of the fragments which they contain are very important. The intramolecular cyclisation of polyamidoacids and their esters, which proceed effectively in the solid state, may serve as a clear example.[6–8] Although the esters are not degraded on conversion into imides, in contrast to the acids, the degree of polymerisation of the polyimides synthesised by the cyclisation of polyamidoacid esters is usually higher than that of the corresponding polyimides obtained by the thermal cyclisation of polyamidoacids. However, by virtue of the lower reactivity of the ester group compared with the carboxy-groups, the cyclisation of polyamidoacid esters is usually completed at higher temperatures in order to achieve complete conversion.

Table 1. The properties of polyimides obtained by thermal and chemical cyclisation.

Property	Ph/PM		E/PM		Ph/BP		Ph/Bphn	
	T	Ch	T	Ch	T	Ch	T	Ch
E, GPa	—	8.0	2.7	4.0	8.6	4.6	5.4	5.0
σ, MPa	—	162	112	139	321	129	154	143
ε, %	—	15	35	56	23	7	4	40
CTR, p.p.m. K^{-1}	—	5.5	31.9	22.3	31.9	8.2	18.1	25.3

Note. Ph = *p*-phenylenediamine; PM = pyromellitic dianhydrides; E = di(4-aminophenyl) ether; BP = dianhydride-3,3′,4,4′-tetracarboxylic acid; Bphn = dianhydride of benzophenone-3,3,′4,4′-tetracarboxylic acid; *E* = modulus of elasticity on extension; σ = tensile strength; ε = elongation at rupture; CTR = coefficient of thermal expansion; T = thermal cyclisation; Ch = chemical cyclisation.

Together with the degree of cyclisation, an important factor for the attainment of the optimum properties of the polymers formed on polycyclisation is their molecular weight.[9] In this sense, thermal cyclisation of the intermediate polymers, both in the solid state and,

especially, in solution, is in many instances complicated by various side reactions and leads to a decrease in molecular weight, which impairs the deformation-strength properties of the final polymeric materials. In order to eliminate or suppress the undesirable processes, the so called chemical methods, in which the aim is to carry out catalytic cyclisation under milder conditions, have been frequently used in recent years.[10–13] It is then possible to reduce to a minimum the degradative processes and to obtain polymers of a much higher quality. The improvement of the deformation-strength characteristics (Table 1) is in our view mainly a consequence of the higher molecular weight of the polymer.

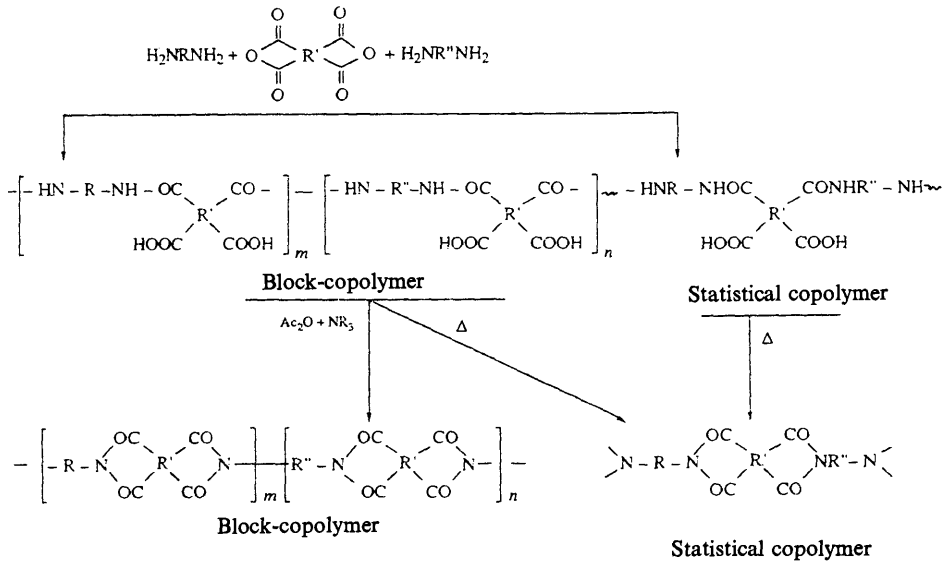
Thus in the synthesis of polymers by polycyclisation it is necessary to endeavour not only to achieve a quantitative degree of cyclisation, on which depend primarily the thermal stability, heat resistance, and other physicochemical properties of the polymers, but also it is essential to maintain a high molecular weight, which is important for the attainment of optimum deformation-strength properties of the corresponding polymeric materials. It is likewise necessary to bear in mind that the cyclisation conditions affect also the morphology of the polymers formed. Thus it has been noted that the polyimides obtained by thermal cyclisation are much less soluble in organic solvents than the corresponding polymers obtained in the presence of catalytic systems.[9] The densities of the former are lower than those of the latter.[13]

There is no doubt that the relations obtained for the cyclisation of polyamidoacids to polyimides are in general valid also for many other polymers formed as a result of the intramolecular cyclisation of intermediate polymers.

There is undoubted interest, from the standpoint of the recognition of the specific features of the polycyclisation and formation of polymers with the required set of properties, in studies directed towards the elucidation of the stereochemical and conformation characteristics of this process,[14,15] its statistics,[16] etc. However, it may be that the difficulties associated with the cyclisation processes on high-molecular-weight polymers noted above have in fact been responsible for the preferential development of single-stage polycyclisation processes, particularly in the preparation of thermoplastic and/or soluble polyheteroarylenes.

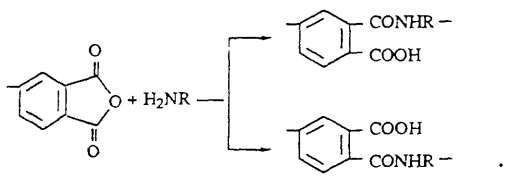
The polymers obtained by the single-state method, frequently in the presence of catalysts, are characterised by a high molecular weight and a virtually quantitative degree of cyclisation. Polycyclisation in various solvents† (high boiling organic solvents, polyphosphoric acid, etc.) have come to be most widely used. Depending on the solubility of the polymer formed, its synthesis proceeds throughout the process in solution[17,18] or is accompanied by the precipitation of the polymer at a specific stage (precipitation polyheterocyclisation), which does not prevent an increase in the molecular weight and/or degree of cyclisation of the polymer.[19–21]

Additional data concerning the specific features of polycyclisation have been obtained in the study of the formation of linear copolymers with a cyclochain structure.[22,23] In a multistage synthesis, the microstructure of such copolymers (statistical, block, or alternating) is laid down in the first stage of the reaction—the formation of the polymer chain—and is determined by factors, familiar from the polycondensation theory, namely the reversibility of the polycondensation, the ratio of the reactivities of the comonomers, the relation between the reactivities of the two reaction centres of the intermonomer, and the reaction conditions. However, by virtue of the characteristics of the second polycyclisation stage (see above), the microstructure of the copolymers can be retained or can break down. Thus in the thermal conversion into imides of copolyamidoacids with various microstructures, accompanied by their degradation, only statistical copolyimides are almost always formed. On the other hand, as a result of the catalytic cyclisation of copolyamidoacids, where there is no degradation of the polymers, the microstructures of the copolymers formed do not differ from those of the initial copolymers:



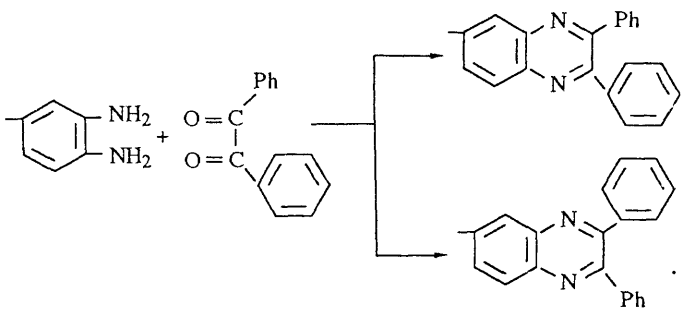
† There has been a recent growth of interest also in the synthesis of polyheteroarylenes in the melt and in the solid phase.

Proceeding now to the analysis of the relation between the physical and chemical structures and properties of polymers obtained by polycyclisation, we may note that the general laws of polymer chemistry are naturally valid for them too. The most important factor is the nature of the monomers and hence the structure of the polymers formed. The influence of various types of isomerism in polyheteroarylenes is unusual. Thus, in view of the multiplicity of the reaction centres in the monomers used in polycyclisation and a not unduly striking difference between their reactivities, the intermediate and final polymers formed contain various isomers which affect the physical structure and properties of the polymers. Striking examples are provided by the syntheses of polyamidoacids from the dianhydrides and diamines[24–26] and of polyphenylquinoxalines from bis-α-diketones and tetramines.[27–29] In the former case, the possibility of nucleophilic attack by the amine on both carbonyl carbon atoms of the anhydride ring is responsible for the formation of two isomeric fragments in the chains of the polyamidoacids:

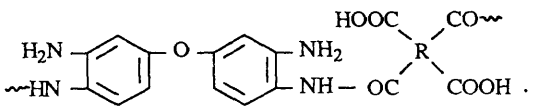


It is striking that it is not possible to obtain only one isomer by introducing different electron-donating and electron-accepting substituents even when there is a significant difference between the electrophilic properties of the above carbon atoms.[25] The heterounit structure arising in the polyamidoacids as a result of such isomerism affects their stability towards degradation.[25]

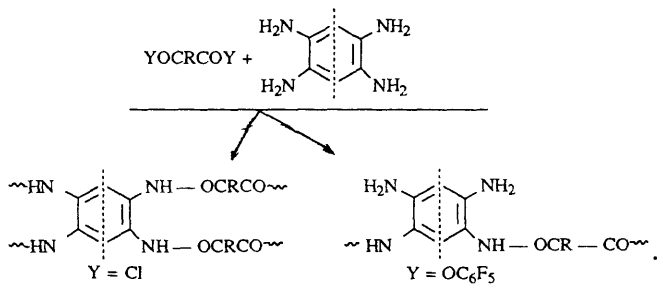
Similar factors are responsible for the appearance of isomeric fragments in the chains of polyphenylquinoxalines and hence for their amorphous structure and inadequate heat resistance, which may affect the strength parameters of the materials formed from them:



The nearly statistical distribution of different isomers in polyphenylquinoxalines as well as in many polyamidoacids is probably caused by the similar electrophilic properties of the corresponding carbonyl carbon atoms. At the same time even comparatively small differences between the basicities of the *p*- and *m*-amino-groups in tetramines (differing by approximately one order of magnitude) are found to be sufficient to ensure their selective acylation by carboxylic acid anhydrides with formation of virtually only the isomer having amide groups in the *para*-position relative to the bridging electron-donating group;[30,31]

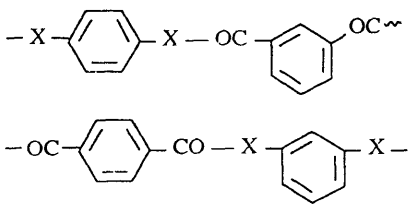


This example is also of interest because, by varying the reactivity of the acylating agent (the nature of its leaving group), it is possible to obtain both linear and network polymers. Thus, when carboxylic acid chlorides are used (as more reactive derivatives), the reaction involves all four amino-groups even under mild conditions and leads to gel formation. On the other hand, linear high-molecular weight polymers are formed on polycondensation of tetramines and activated esters (nitrophenyl, pentafluorophenyl) of dicarboxylic acids:[32]



A similar picture is observed also in acylation by tetracarboxylic acid dianhydrides. Depending on the reactivity of the latter, the mutual influence of the anhydride groups, and the nature of the bridging groups, both linear polyaminoamidoacids (reactions with relatively unreactive dianhydrides having bridging electron-donating groups—see above) and three-dimensional polymers (when the reactive pyromellitic dianhydride is used) are formed.

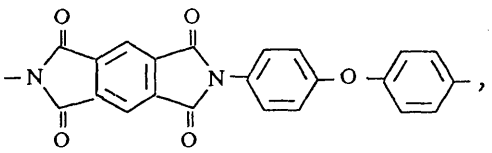
Another type of isomerism, which is manifested in an extremely unusual manner in polyheteroarylenes, is caused by the position of the bridging groups in the polymers relative to the heterocycle. In principle, this question is not new as regards heterochain polymers,[33,34] although in our view it has not been adequately considered. Thus the polyamide formed from *p*-phenylenediamine and isophthalic acid and correspondingly the polyarylate derived from hydroquinone and isophthalic acid are more crystalline than the isomeric polyamide derived from *m*-phenylenediamine and terephthalic acid and the isomeric resorcincol polyterephthalate:

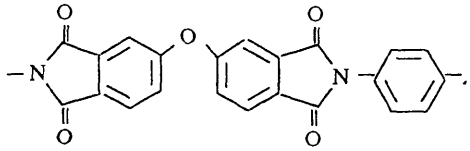


(a) X = NH
(b) X = O .

On the other hand, in the case of polyheteroarylenes the difference between the structures and properties of a series of isomeric polymers, containing bridging groups in the residues of a

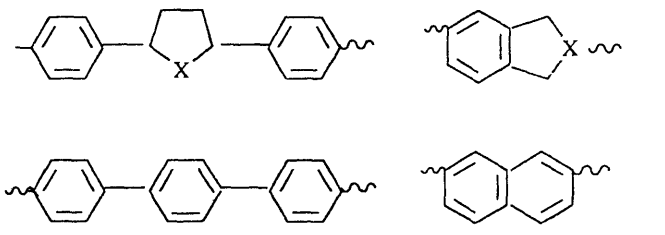
particular monomer, is in many respects associated with the different capacities for condensation of the heterocycle with fragments other than benzene rings.[35] Thus the polypyromellitimide derived from di(4-aminophenyl) ether and the polyimide obtained from *p*-phenylenediamine and di(3,4-dicarboxylphenyl) ether contain the same number of various fragments, but in the former there is a condensed system comprising three rings, while in the latter the polymer containing the phthalimide rings is a system comprising only two condensed rings:





As a result, the first polymer is significantly superior to the latter as regards heat resistance (by 50–70 °C),

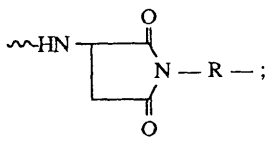
It is noteworthy that the degree of condensation of the heterocycle and other fragments of the macromolecule is a most important factor, which determines many properties of polyheteroarylenes. The latter can be arbitrarily divided into two types.[36] In the first, the heterocycles are joined by single bonds to other groups and they can be regarded as analogues of polyphenylenes. In the second, the heterocycles are condensed with other elements of the polymer chain and polynaphthalene may be regarded as their analogue. The limiting case of polymers of the second type is ladder polymers:



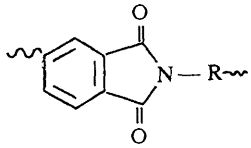
X = heteroatom

(I) (II)

Polymers of the first type (I) include poly-1,3,4-oxadiazoles, polytriazines, and polythiadiazoles, while those of the second type (II) include aromatic polyimides, polybenzimidazoles, polyphenylquinoxalines, and polybenzoxales. One may quote examples where the heterocycle enters into the composition of both types of polymers. Thus poly(asparagine imides) (A) contain isolated imide rings, in contrast to the aromatic polyimides (B), the characteristic feature of which is systems comprising two, three, and more condensed imide rings, benzene rings, and other heterocycles:



A



B

Naturally, by varying the degree of condensation of the benzene rings and the heterocycles, it is possible to vary different properties of the polymers and primarily their heat resistance.

An important factor which determines the creation of linear cyclochain polymers with the required set of properties is the size of the heterocycle in such polymers. Polyheteroarylenes with five-membered heterocycles are commonest. They include polybenzimidazoles, polybenzoxazoles, polybenzothiazoles, poly-1,3,4-oxadiazoles, and the majority of polyimides. However, representatives containing six-membered imide rings, i.e.

whose closure proceeds much more readily than that of the analogous phthalimide rings, are known for the polyimides. A specific feature of the formation of polyimides with six-membered rings is in fact that the polycyclisation cannot be arrested at the stage of the intermediate polymer — the polyamidoacid. A striking example of polymers with six-membered rings is polyphenylquinoxalines. In this case too polycyclisation proceeds in such a way that the polymer chain propagation and the closure of the six-membered quinoxaline ring occur almost simultaneously. The greater ease of closure of the six-membered ring compared with the five-membered ring (exceptions are naturally known) predetermines a series of advantages in properties, particularly the increased chemical stability. The high degree of cyclisation should have a positive effect also on the thermal stability of the polymers.

Hitherto, very many polymers have been obtained by polycrystalline reactions, polyimides being commonest among them. It is noteworthy that this is apparently due to the successful combination of thermal and mechanical properties in such polymers, the availability of the monomers, and the comparative simplicity of the synthesis. As a result of this, a vigorous development of imide-containing polymers, which already belong to the class of mass-scale polymers, can now be observed. New types of monomers for polyimides are being created and new methods of their synthesis (including catalytic methods) are being developed.

III. Polycyclotrimerisation and other methods of synthesis of polyheteroarylenes

A second important variety of polycyclisation involves the formation of linear and network poly(hetero)arylenes by the polymerisation method. This procedure has in our view a series of characteristic features, which distinguish it from both the traditional

methods of synthesis of polymers and from polycondensation. In this case polycyclic polymers are synthesised in several ways.

The first involves the polymerisation (copolymerisation) of different bi- and poly-functional compounds (monomers, oligomers, and polymers) involving the opening of multiple homo- and hetero-bonds, leading to the formation of carbocycles and heterocycles.

The second involves polycyclisation, the elementary step of which is the interaction of small (as a rule three-membered rings) with functional groups and multiple bonds, which results in the formation of new (usually five-membered) stable cyclic structures.

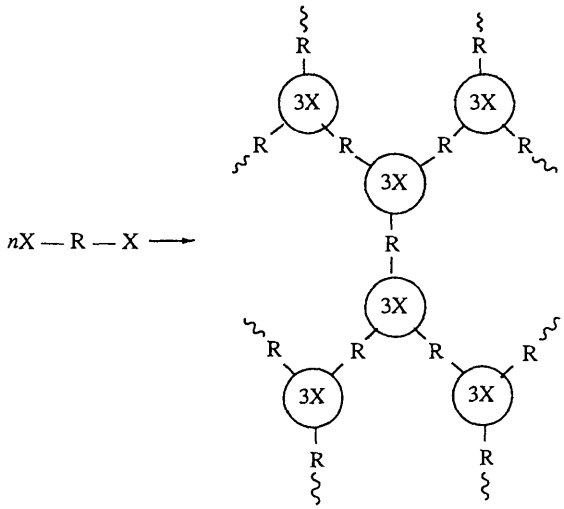
Examples of the procedures of the second type of polymerisation polycyclisation is provided by the copolymerisation of two different unsaturated rings with formation of a new cyclic structure (reactions of the Diels–Alder type), as well as the opening of unstable four-membered rings (for example, uretdione rings), with formation of stable six-membered fragments. The polycyclisation procedures listed above do not apparently exhaust the entire wide variety of the possible different versions of these reactions.

One of the most important differences between the polymerisation of different compounds with the opening of multiple bonds or strained rings and polycondensation consists in the absence of segregation of any products during the reaction. This factor determines the principal features of this polycyclisation method and makes it possible to solve the difficult problem of the processing of polycyclic polymers, which exhibit as a rule an enhanced heat resistance and thermal stability. Here not only linear cyclochain polymers but also network heat resistance structures can be made into articles directly from liquid or low-melting monomers and oligomers.

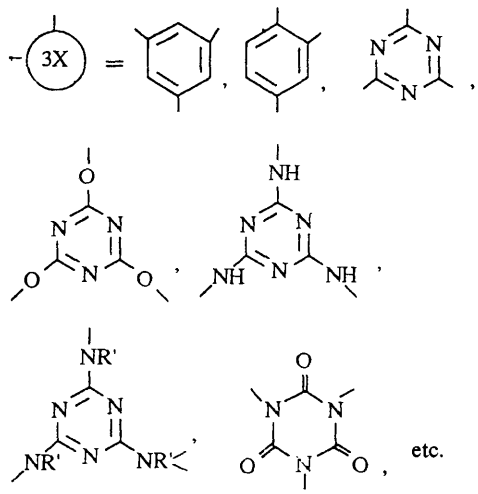
The cyclic fragments formed as a result of polycyclisation via the polymerisation mechanism may be four-, five-, and six-membered carbocycles and heterocycles, for example, polymers containing in the chain rings such as those of uretdione,[57] imino-derivatives of uretdiones,[38] 1,2,4-oxodiazole,[39] iminohydantoin,[40] oxazoline,[41], isoxazoline,[42] oxazolidinione,[43] iminooxazolidinone,[44] 1,3,5- and 1,3,4-phenylenes,[45] pyridine,[46] 2,4,6-triazine,[47] cyanurate,[48] isocyanurate,[47] etc.

Our aim was not to consider in a short review the numerous studies in this field and only certain most characteristic examples of such reactions will be surveyed with emphasis of their specific features. Polycyclotrimerisation is one of the reactions investigated in greatest detail.[47]

The polycyclotrimerisation of monomers (or oligomers and polymers) containing two and more functional groups with multiple bonds between homo- and hetero-atoms should lead to the formation of hypothetical network polymer structures with the same internodal fragments and stable six-membered aromatic carbocycles and heterocycles as network nodes:



where X = $-C\equiv CH$, $-C\equiv N$, $-O-C\equiv N$, $-NH-C\equiv N$, $-NH-C\equiv N$, $-N\equiv C=O$, $-N=C=N-$, etc,

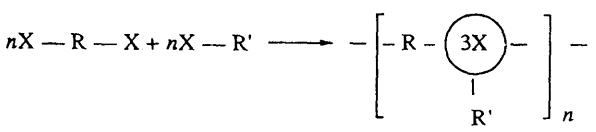


In the presence of thermostable aromatic or organoelement groups as internodal fragments in such polymers, one may expect a high thermal stability of these blends. In the case of small intermodal fragments (M_c), the thermal stability of such dense network structures should also be high.

It is noteworthy that the advantages of the polycyclotrimerisation reaction can be utilised provided that a number of conditions are fulfilled. For example, the reaction must take place stereoselectively with virtually complete conversion of the functional groups, since only in this case does the polymer structure remain undisturbed by the fragments formed as a result of side reactions of some kind or by residual non-cyclised functional groups.

There are literature data[47] on polymers obtained by the polycyclotrimerisation of compounds such as ethynyl derivatives (−R−C≡CH), nitriles (−R−C≡N), cyanates (−R−O−C≡N), isocyanates (−R−N=C=O), unsubstituted cyanamides (−R−NH−C≡N), *N*-substituted cyanamides (−R−NR′−C≡N), and carbodiimides (−R−N=C=N−R−). Other types of compounds containing multiple bonds between different atoms may be achieved in the future.

Polycyclotrimerisation is one of the examples confirming the necessity for the revision of certain classical postulates in the chemistry of high-molecular-weight compounds. Thus, whereas bifunctional monomers, for example diisocyanates form linear polyureas or polyurethanes on reaction with bifunctional amines or diols, the polycyclotrimerisation of the same diisocyanates affords dense network polymers with a regular chemical structure, illustrated in the polycyclotrimerisation scheme presented above. In "classical" polycondensation, the introduction of a monofunctional monomer leads to chain termination and the restriction (regulation) of the molecular weight of the polymer.[2] On the other hand, in polycyclotrimerisation the introduction of a monofunctional monomer can yield a linear polymer in accordance with the following scheme:



The similarity of a series of fundamental features of gel formation in the polycyclotrimerisation of dicyanates and diisocyanates, i.e. polymers of different classes, as well as the study of the molecular weight characteristics in the course of the reaction up to the gel point and of the sol fraction beyond the gel point made it possible to formulate general ideas concerning the formation of the topological gel structure in this method of synthesis of network polymers.[49−52] In a number of instances, the experimental data are close to the theoretical postulates[53] developed for the gel formation process in polycyclotrimerisation reactions. The existing differences can be explained by the failure of the theory to take into account the macrocyclisation associated with the appreciable branching of the macromolecules.[49,53]

The traditional methods of synthesis of network polymers from monomers, oligomers, or polyfunctional polymers are complicated by factors such as the differences between the reactivities of the functional groups which do not lead to branching, the proportions of the initial oligomers and polymers having different molecular weights and different types of functional groups, which are difficult to regulate, and many others. All this hinders the synthesis of network polymers with a chemically regular structure.

In the synthesis of polymers by the polycyclotrimerisation reaction, it is possible to overcome most of these difficulties and to obtain regularly cross-linked (at the molecular level) polymers. In this method of synthesis, the reaction of each functional group is accompanied by the branching of the macromolecule with the exception of the "losses" of the functional groups in macrocyclisation.

Detailed study of the gel formation process and of the molecular weight characteristics has shown[49−53] that the macrocyclisation reaction may be regulated by varying the conditions in the synthesis of the polymers. This determines in its turn the change of their topological structure. The possibility of influencing the topology (i.e. a higher level of structural organisation than the molecular level) of the networks leads to greater prospects for the directed regulation of the physical properties of network polymers.

An interesting feature discovered for a number of polymers obtained by polycyclotrimerisation is their capacity for crystallisation.[54−56] In the known[57−61] crystalline network polymers, the internodal segments are flexible aliphatic and siloxane fragments with M_c not below 2100.[57−59] The crystal structures of the cross-linked polymers is similar to that of the initial crystalline oligomers and is in essence determined by the latter.

Rigid-chain dense network polymers with a crystal structure completely different from that of the initial crystalline monomer, have been obtained in the case of polycyanurates. In other words, the crystal structure of the network polymer is formed in the course of its synthesis. In the study of the polycyanurate based on 1,4-dicyanatobenzene (M_c = 108), it was shown by X-ray diffraction that, by regulating the conditions in the synthesis, it is possible to obtain polymers with the same chemical structure but a different physical structure.[54]

A tendency towards crystallisation has been observed also in other polycyanurates based on aromatic dicyanates[47,55,56] and also in certain dense network polymers with a different chemical structure, obtained by the cyclotrimerisation of monomers with C−N multiple bonds.[47] By an appropriate selection of the initial monomers and the cyclisation conditions, similar structures can apparently be obtained in a highly crystalline state.

The capacity for crystallisation of network polyheteroarylenes obtained by polymerisation polycyclisation as well as many other unusual properties of these polymers are a consequence of their regular structure achieved as a result of the highly selective cyclisation of the functional groups of the initial monomers and its virtually quantitative completion.

When a series of polycyanurates based on dinuclear aromatic dicyanates differing in the nature of the bridging group between the phenyl groups are studied systematically, the most striking feature is that the polymers of dicyanates having a flexible bridging group and small substituents at the central carbon atom have anomalously high specific impact strengths (up to 30 kJ m^{-1}), in contrast to all the known dense network aromatic polymers. Furthermore, block specimens of aromatic and many organoelement polycyanurates have a high bending strength, a Brinell hardness of 100−170 MPa, a tensile strength of 100 MPa, a modulus of elasticity in the range 3000−5000 MPa, and a relative elongation on rupture of 3−6%. These polymers retain effective physicomechanical properties also at elevated temperatures.[47,48,63]

In order to elucidate the causes of the unusual mechanical properties of polycyanurates, a study was made of the formation of the super molecular structures of these polymers at different stages of their synthesis, starting with the initial monomer 2,2-bis-(4-cyanatophenyl)propane and ending with a regular network system and a virtually quantitative conversion of the functional groups.[64] It was found that, in the course of polycyclotrimerisation, the formation of a material with a globular structure is observed initially against the background of the characteristic cryptocrystalline structure of the monomer. The size of the globules did not remain constant in the course of the polymerisation and gradually diminished—from ~500 to 100−200 Å. The aggregation of globules, leading to fibrille-like formations in the final stage of the polymerisation (for a conversion of the N≡C−O group of ~98%) was subsequently observed under these conditions.

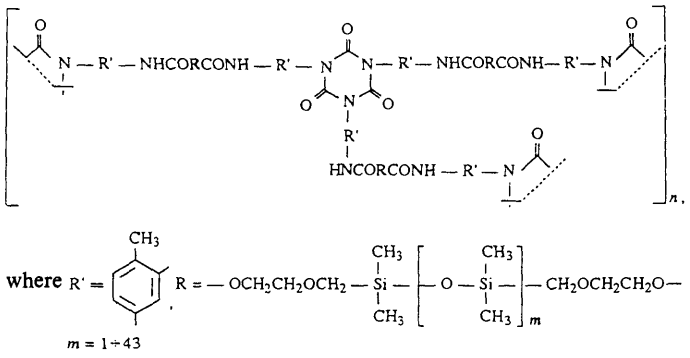
Simultaneously with the formation of the supermolecular structure of polycyanurates, the relaxation properties of the solid networks formed in different stages of the conversion of the NCO groups of the initial monomer were investigated. With increase in the degree of conversion, the relaxation curves initially shift towards higher stresses and then, beyond a ~90% conversion of the monomer, they begin to be displaced to the region of lower stresses.

The parameters of the Kohlrausch equation for different stages of the process were calculated. The data obtained show that, as the polycyclotrimerisation of aryl dicyanates advances and with the consequent increase in the regularity of the network formed, the nature of the supermolecular structure of the polymer changes, which leads in its turn to a steady variation of the mechanical properties of the network system—a decrease in brittleness and an increase in elasticity.[64] It may be that, if it becomes possible to obtain a regular defect-free network also in the case of the usual thermoreactive systems, then it will be possible to obtain also polymeric materials with increased resistance to impact influences and increased elasticity.

By introducing various organic and organoelement groups (containing B, F, and Si) into the internodal fragment in polycyanates, highly thermostable rubbers with T_g = −120 °C and highly heat-resistant systems with T_g = ~400 °C were synthesised. Carbaborane-containing polycyanates retain a large amount (~100%) of coke residues up to 900–1000 °C.[47,48,63]

Heat-resistant network polymers based on dicyanates can be designed not only by altering the structure of the initial dicyanate but also by their copolymerisation with diisocyanates, bismaleimides, oligoepoxides, and other compounds.[47,63,65–67]

The synthesis of telechelic oligomers with flexible (aliphatic and siloxane) fragments between the isocyanate functional groups has been achieved. The polycyclotrimerisation of these oligmers yielded transparent network polymers with different specifically regulated lengths between the network nodes:[68]



The combination of rigid network nodes with an aromatic framework and of flexible siloxane chains of different lengths leads to the observation of two transition temperatures. The devitrification of the siloxane and subsequently of the rigid isocyanurate fragments is reflected in the temperature variation of the tangent of the mechanism losses angle (Fig. 1).

A phase separation takes place in this system, which has been confirmed by electron microscopy and X-ray photoelectron spectroscopy data. These results show that the contents of silicon and nitrogen on the surface and within the bulk of the glass specimen differ appreciably. This shows that the siloxane phase is forced out onto the surface of the glass.[68]

Whereas the usual organic glasses have a modulus of elasticity of the order of 10^3 MPa, in this instance monomers were obtained with a wide set of moduli of elasticity, ranging from 3×10^3 to 3 MPa depending on the value of n. On the other hand, these polymers behave similarly to vitreous (elastic) polymers. This factor opens the way to new possibilities in the photoeleasticity method and in other branches of engineering.[68,69]

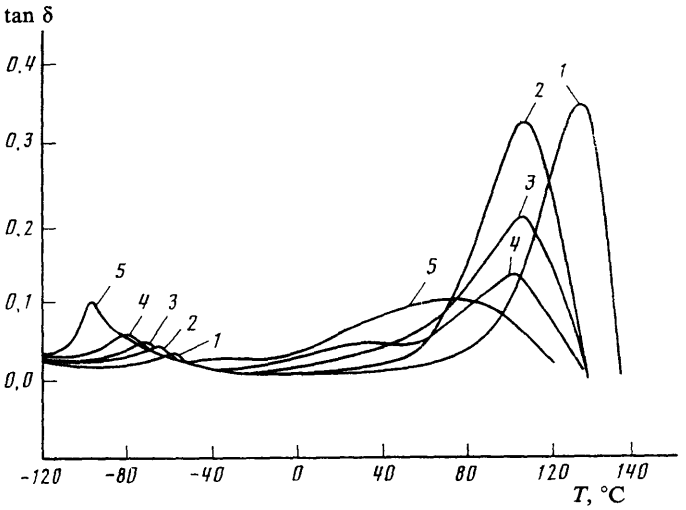


Figure 1. Temperature variation of tan δ for block specimens of polyisocyanurates with different lengths of the internodal organosilicon fragments m: *1*, 1.2; *2*, 2.1; *3*, 3.2; *4*, 5.4; *5*, 9.2.

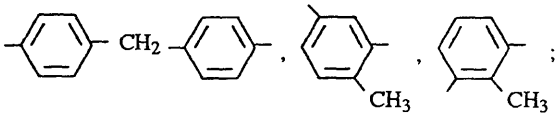
The synthesis of linear polymers and oligomers containing in the chain regularly alternating functional groups capable of entering into the polycyclisation reaction, namely ... −X−R−X−R−X−R−..., where X is the functional group and R are aromatic, aliphatic, or organoelement substituents, constitutes a promising way of designing new polymeric structures with interesting properties.

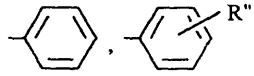
Polycarbodiimides are representatives of polymers of this type.[47,70,71] A series of infusible (T_{soft} = 50–150 °C) oligocarbodiimides, based on bis(4-isocyanatophenyl)methane and 2,4-tolylene

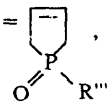
diisocyanate and soluble in organic solvents, have been synthesised:[47,70,71]

$$n\mathrm{O{=}C{=}N{-}R{-}N{=}C{=}O + 2R'{-}N{=}C{=}O \xrightarrow{\text{Cat.}}$$

$$\rightarrow R'{-}N{=}C{=}N{-}[{-}R{-}N{=}C{=}N{-}]_n{-}R' + (n+1)CO_2,$$

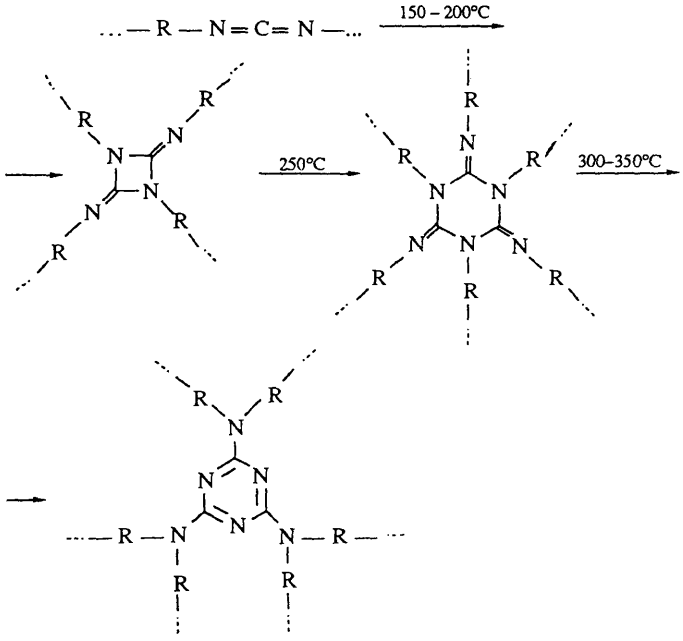
where R = 

R' = 

Cat. = 

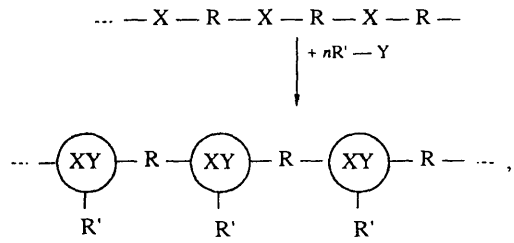
R''' = — CH_3, Ph.

Their polymerisation at elevated temperatures yields polycyclic network structures with temperatures for the onset of decomposition of 420–450 °C and temperatures for the onset of deformation of 350–450 °C:[47,72–75]



Polycarbodiimides (polyfunctional linear polymers), used as polymer matrices for high-strength heat-resistant composite materials, combine the advantages of thermoplastics and reactoplastics.[76] Oligocarbodiimides are multipurpose thermoreactive oligomers capable of being processed into various heat resistant and thermostable composite materials for use in modern branches of engineering (Table 2).[76]

Oligomers and polymers containing functional groups of the type of carbodiimide groups alternating in the chain are capable not only of homopolymerising with formation of network polyheteroarylenes but also of entering into copolymerisation reactions with various compounds to form linear cyclochain polymers in accordance with the scheme



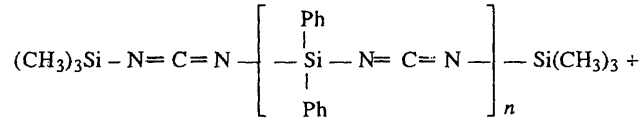
where X and Y are functional groups.

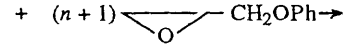
Table 2. Properties of composite materials based on oligocarbodiimides.

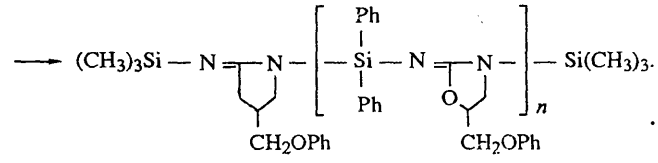
Property	T, °C	Carboplastic	Glass plastics	Adhesive
σ_{bend}, MPa	20	962	440	—
	300	466 (after 200 h)	390	—
	350	765	—	—
	400	452	—	—
σ_{comp}, MPa	20	900	400	—
ε	20	—	3.8—4.2	—
	300	—	3.9—4.7	—
tan δ	20	—	0.009—0.01	—
	300	—	0.020—0.025	—
τ_{sh}, MPa	20	—	—	15—18
	250	—	—	12—13

Note. ε = dielectric constant.

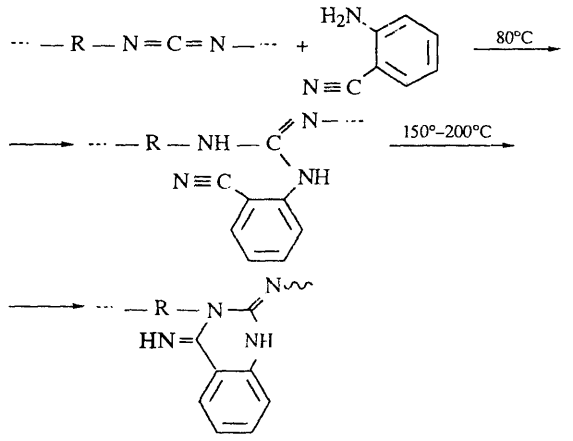
Thus polysilylcarbodiimides react with glycidyl phenyl ether to form polymers with iminooxazolidine fragments in the chain:[77]



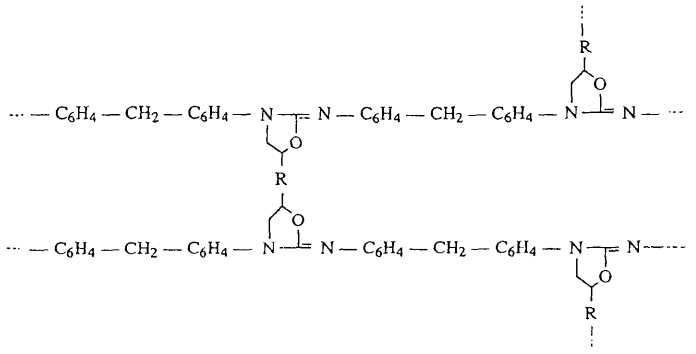




Linear polyheteroarylenes with iminoquinazoline rings in the chain have been obtained by the reaction of aromatic polycarbodiimides with anthranilic acid nitrile:



The reaction of di- and poly-epoxides with polycarbodiimides results in the formation of network polyaminooxazolidines:[44]



It has been shown[44] that, together with iminooxazolidine fragments, other heterocyclic fragments (isomelamine, uret diimine) are also obtained as a result of the homopolymerisation of the carbodiimide groups. By altering the ratio of the carbodiimine and epoxide groups in the initial mixture of oligomers, the contents of different heterocyclic fragments in the final products were regulated.[44] In the presence of an excess of oligocarbodiimides, the uret diimine rings predominate in the polymer structure, being converted into isomelamine units at high hardening temperatures (250 °C). With increase in the content of the epoxide component in the initial mixture, reactions involving the formation of iminooxazolidine rings predominate.[44]

IV. Conclusion

Since the appearance of the first publications on polyheteroarylenes, whose synthesis is based on polycyclisation reactions, more than 30 years have elapsed, but the possibilities of this interesting aspect of polymer chemistry are far from being exhausted. New monomers are being synthesised for the preparation of polymers with a specified set of properties and new methods of their synthesis, primarily catalytic methods, are being developed. Polycrystallisation processes involving parallel-consecutive reactions proceeding via the polymerisation and polycondensation mechanisms are of interest. Processes of the monomers (oligomer)–finished article and of the RIM-technological type have attracted particular attention. Finally, recent years have been marked by the appearance of data on the synthesis of polymers of the type of polycatenanes and polyrotaxanes, which are again based on polycyclisation processes.

References

1. *Entsiklopediya Polimerov* (Encyclopedia of Polymers), Izd. Sov. Entsiklopediya, Moscow, 1977, Vol. 3, p. 85
2. V V Korshak, S V Vinogradova *Neravnovesnaya Polikondensatsiya* (Non-Equilibrium Polycondensation), Nauka, Moscow, 1972, 96 pp
3. N A Adrova, M I Bessonov, I A Laius, A P Rudakov *Poliimidy—Novy Klass Termostoikikh Polimerov* (Polyimides—A New Class of Thermostable Polymers), Nauka, Leningrad, 1968, p. 36
4. V V Korshak, G L Berestneva, I P Bragina *Vysokomol. Soedin., Ser. A*, 1972, **14** 1036
5. A N Pravednikov, I B Kardash, E N Teleshov *Vysokomol. Soedin., Ser. A*, 1971, **13** 425
6. G K Slonimskii, Ya S Vygodskii, Z V Gerashchenko, et al. *Vysokomol. Soedin., Ser. A*, 1974, **16** 2449
7. J B Lando *Polymer Preprints*, 1964, **5** 579
8. V V Korshak, G L Berestneva, A N Lomteva, Yu B Zimin *Dokl. Akad. Nauk SSSR*, 1977, **233** 598
9. P P Nechaev, Ya S Vygodskii, G E Zaikov, S V Vinogradova *Vysokomol. Soedin., Ser. A*, 1976, **18** 1667
10. S V Vinogradov, Ya S Vygodskii, V D Vorob'ev, et al. *Vysokomol. Soedin. Ser. A*, 1974, **16** 506
11. M M Koton, T K Meleshko, G I Kudryavtsev, et al. *Vysokomol. Soedin., Ser. A*, 1982, **24** 715
12. E B Sviridov, E V Lamskaya, N A Vasilenko, B V Kotov *Dokl. Akad. Nauk SSSR*, 1988, **300** 404
13. Y Yamamoto, M Kitahashi, S Etoh *Polymer Preprints Jpn.*, 1990, **37** E400
14. I S Milevskaya, N V Lukasheva, A M El'yashevich *Vysokomol. Soedin., Ser. A*, 1979, **21** 1302
15. V A Zubkov *Quantum-Chemical Analysis of the Synthetic Reactions and Structures of Polyimides*, Doctoral Thesis in Chemical Sciences, Institute of Macromolecular Compounds, USSR Academy of Sciences, Leningrad, 1988, 275 pp
16. V V Korshak, Ya G Urman, Ya S Vygodskii *Makromolek. Chem., Rapid Commun.*, 1984, **5** 695
17. S V Vinogradova, Ya S Vygodskii, V V Korshak *Vysokomol. Soedin., Ser. A*, 1970, **12** 1987
18. V V Korshak, S V Vinogradova, Ya S Vygodskii *Acta Polymerica*, 1977, **28** 439
19. V V Korshak, S V Vinogradova, Ya S Vygodskii, B N Yudin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 1405
20. A L Rusanov, A M Berlin, S Kh Fidler, et al. *Tezisy Dokladov XXII Konferentsii po Vysokomolekulyarnym Soediniyam, Alma-Ata* (Abstracts of Reports at the XXIInd Conference on Macromolecular Compounds, Alma-Ata), Alma-Ata, 1985, p. 79
21. V V Korshak, A L Rusanov, A Ya Chernikhov, et al. *Dokl. Akad. Nauk SSSR*, 1985, **282** 375
22. S T Alekseeva, S V Vinogradova, V D Vorob'eva, et al. *Vysokomol. Soedin., Ser. B*, 1979, **21** 883

23. V V Korshak, S V Vinogradova, Ya S Vygodskii, et al. *Makomolek. Chem.*, 1983, **184** 235
24. S G Alekseeva, S V Vinogradova, V D Vorob'eva, et al. *Vysokomol. Soedin., Ser. B*, 1976, **18** 803
25. S G Alekseeva, S V Vinogradova, V D Vorob'eva, et al. *Vysokomol. Soedin., Ser. A*, 1979, **21** 2207
26. V M Denisov, V M Svetlichnyi, V A Gindin, et al. *Vysokomol. Soedin., Ser. A*, 1979, **21** 1498
27. H M Relles, C M Orlando, D R Heath, et al. *J. Polym. Sci., Polym. Chem. Ed.*, 1977, **15**
28. Ya G Urman, N S Zabel'nikov, S G Alekseev, et al. *Vysokomol. Soedin., Ser. A*, 1978, **20** 2236
29. E Gründemann, H Raubach *Acta Polymerica*, 1979, **30** 83
30. E A Kagantseva, B I Zapadinskii, Ya G Urman, B I Liogon'kii *Tezisy Dokladov XXII Konferentsii po Vysokomolekulyarnym Soediniyam, Alma-Ata* (Abstracts of Reports at the XXIInd Conference on Macromolecular Compounds, Alma-Ata), Alma-Ata, 1985, p. 73
31. N G Matvelashvili, A L Rusanov, I I Ponomarev, Ya G Urman *Tezisy Dokladov Mezhdunarodnogo Shkoly-Seminara "Netraditsionye Metody Sinteza Polimerov", Alma-Ata* (Abstracts of Reports at the International School-Seminar on "Non-traditional Methods of Synthesis of Polymers", Alma-Ata), Alma-Ata, 1990, p. 118
32. R D Katsarava *Vysokomol. Soedin., Ser. A*, 1989, **31** 1555
33. V A Vasnev, Ya S Vygodskii *Novye Polikondensatsiony Polimery* (New Polymercondensation Polymers), Mir, Moscow, 1969
34. S M Salazkin *Studies in the Field of Card Polymers*, Doctoral Thesis in Chemical Sciences, Institute of Organoelement Compounds, USSR Academy of Sciences, Moscow, 1979, 571 pp
35. Ya S Vygodskii, S V Vinogradova *Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii. Itogi Nauki i Tekhniki* (The Chemistry and Technology of Macromolecular Compounds. Advances in Science and Engineering), Izd. VINITI, Moscow, 1975, Vol. 7, p. 14
36. K-U Bühler *Heat Resistant and Thermostable Polymers* (Translated into Russian), Khimiya, Moscow, 1984, 998 pp
37. H Hess, G Grögler, R Kopp, BRD P. 3 232 736
38. V A Pankratov, V M Laktionov, A I Akhmedov, et al. *Vysokomol. Soedin., Ser. A*, 1984, **26** 79
39. D A Klein *Macromolecules*, 1968, 1 318
40. A V Yanshevskii, A N Flerova, E N Teleshov, A N Pravednikov *Dokl. Akad. Nauk SSSR*, 1983, **271** 133
41. K Kurita, N Hirakawa *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17** 2567
42. N A Krivosheev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2279
43. V A Pankratov, Ts M Frenkel;, A M Fainlieb *Usp. Khim.*, 1983, **52**(6) 1018 [English translation in *Russ. Chem. Rev.*, 1983(6)]
44. V A Pankratov, Ts M Frenkel, A M Fainleib, V V Korshak *Crosslinked Epoxides*, Berlin, 1987
45. V A Sergeev, V K Shitikov, V A Pankratov *Usp. Khim.*, 1979, **48**(1) 148 [English translation in *Russ. Chem. Rev.*, 1979(1)]
46. V A Sergeev, V K Shitikov, V A Pankratov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1629
47. G M Pogosyan, V A Pankratov, V N Zaplishnyi, S G Matsoyan *Politriaziny* (Polytriazines), Erevan, 1987, 615 pp
48. V A Pankratov, S V Vinogradova, V V Korshak *Usp. Khim.*, 1977, **46**(3) 530 [English translation in *Russ. Chem. Rev.*, 1977(3)]
49. V A Pankratov *Kompozitsionnye Polimernye Materialy* (Composite Polymeric Materials), Naukova Dumka, Kiev, 1984, No. 26, p. 70
50. V V Korshak, V A Pankratov, A A Ladovskaya *J. Polym. Sci., Polym. Chem. Ed.*, 1978, **16**
51. V A Pankratov, A A Ladovskaya, V V Korshak, S V Vinogradova *Vysokomol. Soedin., Ser. A*, 1979, **21** 1014
52. A M Gupta *Macromolecules*, 1991, **24** 3459
53. V A Pankratov, A A Ladovskaya, S A Pavlova *Vysokomol. Soedin., Ser. A*, 1978, **20** 1074
54. V V Korshak, V A Pankratov, D Ya Tsvankin *Vysokomol. Soedin., Ser. B*, 1974, **16** 324
55. V A Pankratov, V V Korshak, S V Vinogradova *Plaste und Kautschuk*, 1973, **20** 481
56. V V Korshak, V A Pankratov, A A Askadskii *Vysokomol. Soedin., Ser. A*, 1974, **16** 981
57. G N Matveeva, E S Papkova, O G Sel'skaya *Dokl. Akad. Nauk SSSR*, 1967, **173** 364
58. A A Berlin *Eur. Polym. J.*, 1969, **5** 15
59. K A Andrianov et al. *Dokl. Akad. Nauk SSSR*, 1976, **226** 85
60. K J Smith *Polymer Eng. Sci.*, 1976, **16** 168
61. W Wu *Polymer Preprints*, 1978, **19** 294
62. V A Pankratov, A E Chesnokova *Usp. Khim.*, 1989, **58**(9) 1528 [English translation in *Russ. Chem. Rev.*, 1989(9)]
63. V A Pankratov, A E Chesnokova *Plast. Massy*, 1990, (9) 5
64. V V Korshak, G L Slonimskii, V A Pankratov *Dokl. Akad. Nauk SSSR*, 1975, **221** 621
65. Yu E Doroshenko, A V Samoryadov, V V Korshak *Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii. Itogi Nauki i Tekhniki* (The Chemistry and Technology of Macromolecular Compounds. Advances in Science and Engineering), Izd. VINITI, Moscow, 1981, Vol. 15, p. 72
66. M Bauer, W Tänzer, H Much, R Ruchmann *Acta Polymerica*, 1989, **40** 335
67. J Bauer, M Bauer *J. Macromol. Sci.*, 1990, **27** 97
68. A A Askadskii et al. *Vysokomol. Soedin., Ser. A*, 1990, **32** 1517
69. A A Askadskii, G V Surov, A S Marshalkovich, et al. *Mekhanika Kompozitnykh Materialov*, 1991, (1) 3
70. A Williams, I T Ibrahim *Chem. Rev.*, 1981, **81** 589
71. K Wagner, K Findeisen, S Schafer, W Dietrich *Angew. Chem., Int. Ed. Engl.*, 1981, **20** 819
72. S V Lindeman, V E Shklover, Yu T Struchkov, et al. *Kristallografiya*, 1982, **27**(1)
73. V A Pankratov, V M Laktionov, A I Akhmedov, et al. *Vysokomol. Soedin., Ser. A*, 1984, **26** 79
74. V A Pankratov, P N Gribkova, V M Laktionov, et al. *Vysokomol. Soedin., Ser. A*, 1984, **26** 129
75. V A Pankratov, Y M Laktionov, A I Achmedov, et al. *Acta Polymerica*, 1986, **37** 39
76. V A Pankratov *Zh. Vses. Khim. Ova. im D I Mendeleeva*, 1989, **34** 459
77. V A Pankratov *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Khimii Fizikokhimii Oligomerov, Nal'chik* (Abstracts of Reports at the IVth All-Union Conference on the Chemistry and Physical Chemistry of Oligomers, Nalchik), Nalchik, 1990, p. 5

Received 10th June 1992

Translated from *Uspekhi Khimii* **61** 1883–1931 (1992) U.D.C. 547,92;542.98;579.61

Microbiological hydroxylation of 5α-*H*-steroids

A M Turuta, N E Voishvillo, A V Kamernitskii
Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow

ABSTRACT. The literature data on the use of microrganisms for the hydroxylation of 5α-*H*-steroids of the 5α-*H*-androstane and 5α-*H*-pregnane series and also 5α-*H*-sapogenins are surveyed. A systematic description of the influence of substitution in the steroid molecule on the specificity of the hydroxylation and the activity of the microbial enzymes is given within the framework of the enzyme–substrate interaction model.

The bibliography includes 124 references.

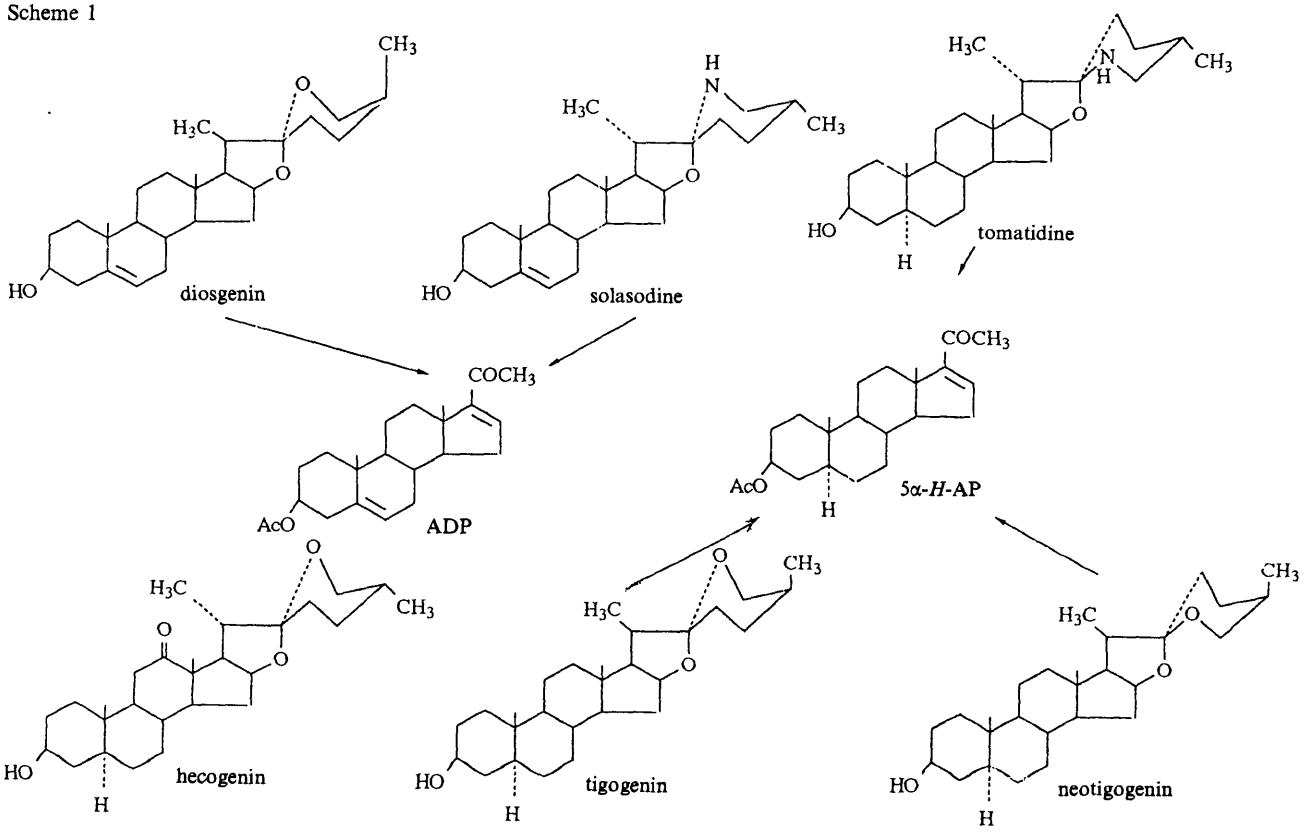
Contents

I.	Introduction	1033
II.	Hydroxylation of 5α-*H*-sapogenins	1035
III.	Hydroxylation of 5α-*H*-androstanes	1035
IV.	Transformations of halo-5α-*H*-androstanes	1047
V.	Hydroxylation of 5α-*H*-D-homoandrostanes	1048
VI.	Hydroxylation of 5α-*H*-pregnanes	1051

I. Introduction

The industrial manufacture of corticosteroids is based nowadays mainly on diosgen, solasodin, and their cleavage reaction intermediate 16-dehydropregnenolone 3β-acetate (DPA). The expansion of the manufacture of steroids has become a significantly more difficult in view of the sharp increase in the cost of these raw materials which are purchased in countries with a tropical climate. The only local industrial source of the steroid raw material is solasodine, the requirement for which in the CIS countries is not satisfied. For this reason 5α-*H*-steroids—hecogenin, tigogenin, neotigogenin,[1] and 3β-acetoxy-5α-*H*-Δ^{16}-pregn-20-enone (5α-*H*-AP) obtained from them—are used with increasing frequency as promising alternative sources. So far they cannot compete with their Δ^5-analogues because the *A* and *B* rings are saturated and it is difficult to transform them by chemical means into the Δ^4- and $\Delta^{1,4}$-3-oxo-substituted steroid preparations which are of practical value (Scheme 1).

Scheme 1



Data have now been accumulated concerning the possibility of microbiological methods for the effective transformation (hydroxylation and dehydrogenation) of 5α-*H*-steroids. However, they have never been treated systematically and are therefore unavailable for deliberate practical application. Furthermore, most of them refer to the 5α-*H*-androstane series and an appreciably smaller number to the 5α-*H*-pregnane series, the practical value of which is incomparably greater. Nevertheless, close examination shows that there is a close analogy between these series, which makes it possible to compare the results and permits their *a priori* transfer from the androstane to the pregnane series. The principal aim of the review is to present a systematic picture reflecting the influence of substituents in various positions in the steroid nucleus on the microbiological hydroxylation of 5α-*H*-steroids; the examination of the transformations of the *A* ring in 5α-*H*-steroids with the aid of microbiological dehydrogenation and subsequent 9α-hydroxylation effected by bacteria remains outside its framework. We believe that it is also undesirable to include in the review and to consider data on the transformation of 5β-*H*-steroids, which are not only less available but are also factually non-comparable. Thus it is known that the geometrical isomerism at the C(5) atom, which controls the junction between the *A* and *B* rings, is one of the most important factors influencing the interaction of steroid substrates with steroid hydroxylases.[2] We shall illustrate this using as an example androsterone and its 3β-hydroxy-isomer, which is hydroxylated by the mould *Penicillium* sp. in the 1α- and 12β-positions respectively. Their *A/B-cis*-analogues are hydroxylated only in the 7β-position regardless of the configuration of the 3-hydroxy-group.[3] The mould *Aspergillus tamarii* hydroxylase androsterone and its 3β-hydroxy-isomer in the 11β- and 11α-positions, whereas their *A/B-cis*-analogues are hydroxylated in the 7β-position.[4] Yet another example of compounds of the pregnane series is 16α,17α-epoxy-5α-*H*-pregnan-3-one, which is transformed with the aid of *Rhizopus nigricans* into the 11α-hydroxy-derivative (60), while its 5β-*H*-isomer is also transformed in the same way but with much difficulty.[5] The critical change in the stereochemistry of the substrate (from *A/B-trans*- to *A/B-cis*-) undoubtedly affects the steric structure of the enzyme – substrate complex; as can be seen from the foregoing, this factor becomes decisive and requires independent consideration.

Studies on the microbiological transformations of steroids refer mainly to compounds with Δ^4-3-oxo or Δ^5-3β-hydroxy-groups and have been surveyed in a number of communications.[2,6–11] The efforts of many investigators have been directed in this connection to the study of the mechanisms of the microbiological transformations and to the specificity of the action of microorganisms as a function of their positions in the classification system and on the stereochemical features of the steroid substrates. In contrast to dehydrogenation, the study of the mechanism of the hydroxylation reaction is complicated by the considerable lability of the steroid hydroxylases.[12] The question why the same culture changes the mode of hydroxylation when the steroid substrate is altered remains unelucidated. The question arises whether it is a consequence of the functioning of different enzymes in the cell. The causes of the microbiological hydroxylation of steroids have not been finally established. According to the existing hypotheses, the microbiological transformation of steroids is induced in certain cases by the need for their detoxication, while in others it occurs as a stage in the assimilation of steroids as a source of carbon. The latter has been confirmed in relation to bacterial hydroxylation. Bacteria begin to cleave the steroid molecule with hydroxylation of the 9α-, 22-, and 26-positions. However, there are no data concerning the causes of the hydroxylation in the 16α-position characteristic of streptomycetes.[6–11] With the exception of the examples of the hydroxylation by schizomycetes described, in the vast majority of cases steroids have been hydroxylated with the aid of representatives of all classes of fungi in the 1α-, 1β-, 2α-, 2β-, 3β-, 4β-, 5β, 6α-, 6β-, 7α-, 7β-, 8β-, 9α-, 10β-, 11α-, 11β-, 12α-, 12β-, 14α-, 15α-, 15β-, 16α-, 16β-, 17α-, 18-, and 21-positions.[6–11] This review, which constitutes a first attempt at a systematic treatment and analysis of the scattered data concerning the transformation of 5α-*H*-steroids, including the results published in 1992, deals with examples of the hydroxylation by fungal cultures only. All the species of fungi used for the transformation of 5α-*H*-steroids are presented in Table 1.

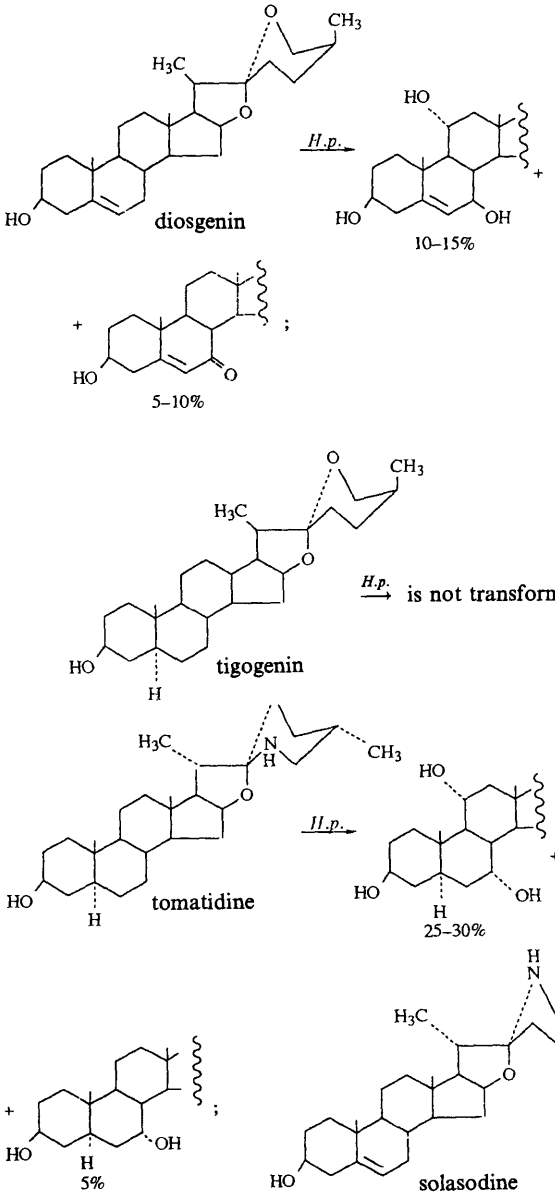
Table 1. The taxonomy of the fungi hydroxylating 5α-*H*-steroids.

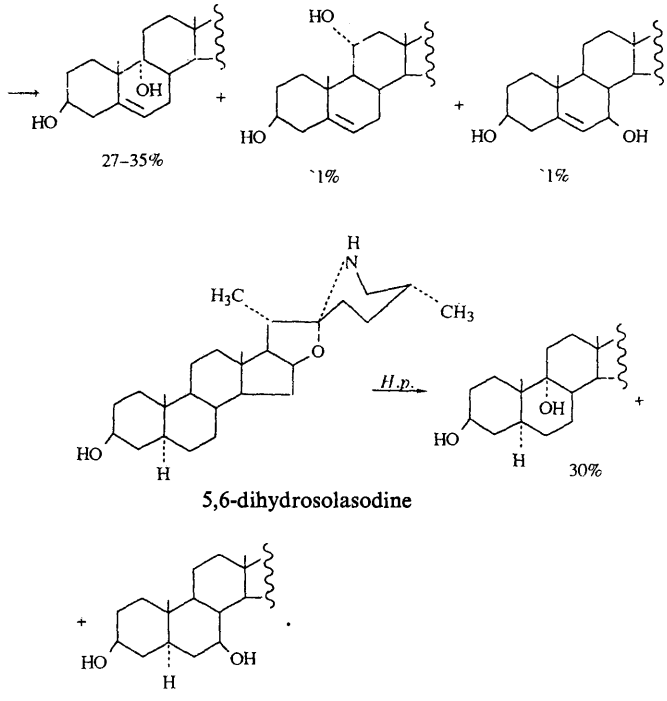
Class	Genus	Species	Abbreviated designation	Refs.
Ascomycetes	*Calonectria*	*decora*	*C.d.*	[13, 16, 19, 20, 30, 34–36, 100–103]
	Diaporthe	*celastrina*	*D.c.*	[31]
	Didymella	*vodakii*	*D.v.*	[64]
	Glomerella	*cingulata*	*Gl.c.*	[58]
		fusaroides	*Gl.f.*	[58]
		lagenarium	*Gl.l.*	[58]
	Gymnoascus	*reesii*	*G.r.*	[97]
	Ophiobolus	*herpotrichus*	*O.h.*	[27]
Basidiomycetes	*Corticium*	*praticola*	*C.pr.*	[38]
	Daedalea	*rufescens*	*D.r.*	[28, 35]
	Hypholoma	*sublateritium*	*H.s.*	[99]
	Leptoporus	*fissilis*	*L.f.*	[37]
	Polystictus	*sanguineus*	*P.s.*	[38]
Deuteromycetes	*Aspergillus*	*nidulans*	*A.n.*	[38]
		ochraceus	*A.o.*	[17, 18, 21, 25, 26, 29, 34, 36, 38, 68, 80, 93, 98, 111]
		tamarii	*A.t.*	[4]
	Beauveria	sp.	*B.sp*	[62]
	Chaetomella	*oblonga*	*Ch.o.*	[113]
		raphigera	*Ch.r.*	[113]
	Curvularia	*clavata*	*C.cl.*	[82, 87, 88, 117]
		lunata	*C.l.*	[59, 61, 65, 68, 105–107]
	Epicoccum	*humicola*	*E.h.*	[114]
		neglectum	*E.n.*	[114]
		oryzae	*E.o.*	[114]
		yuccae	*E.u.*	[114]
	Fusarium	*graminearum*	*F.g.*	[71]
		sulfureum	*F.s.*	[57]
	Gliocladium	*roseum*	*G.r.*	[116]
	Phoma	sp.	*Ph.sp.*	[60]
	Penicillium	sp.	*P.sp.*	[3, 70, 77]
		urticae	*P.u.*	[18]
	Pestalotia	*funerea*	*P.f.*	[64, 110]
	Spondylocladium	*australe*	*Sp.a.*	[66]
		xylogenum	*Sp.x.*	[66]
	Sporotrichum	*epigaeum*	*S.e.*	[63]
		sulfurescens	*S.s.*	[55, 63]
	Wojnowicia	*graminis*	*W.g.*	[27]
Phycomycetes	*Absidia*	*regnieri*	*A.r.*	[33]
	Circinella	sp.	*C.sp.*	[67]
	Cokeromyces	*recurvatus*	*C.r.*	[115]
	Cunninghamella	*blakesleeana*	*C.bl.*	[107]
		bainieri	*C.b.*	[124]
		elegans	*C.el.*	[47, 89–96]
	Helicostylum	*piriforme*	*H.p.*	[41–46, 84, 86, 87]
	Mucor	*griseo-cyanus*	*M.g.-c.*	[56]
	Thieghemella	*orchidis*	*T.o.*	[107]
	Rhizopus	*arrhizus*	*R.a.*	[24, 35, 38, 54, 69]
	Rhizopus	*circinans*	*R.c.*	[24, 35]
		nigricans	*R.n.*	[5, 14, 22, 23, 26, 29, 34–36, 54, 79, 81, 111, 112]
	Syncephalastrum	*racemosum*	*S.r.*	[33, 85]

II. Hydroxylation of 5α-*H*-sapogenins

After the discovery of the ability of lower fungi to hydroxylate progesterone,[39] a number of attempts were made to obtain microbiologically hydroxylated steroid sapogenins, because they were regarded as promising initial substrates in the synthesis of steroid hormones (Scheme 1). The first result of such transformations were negative despite the fact that fairly wide ranging microorganisms and conditions in their cultivation were employed for this purpose.[40] However, later Japanese workers obtained with the aid of phycomycetes *H.p.* the hydroxy-derivatives of both Δ^5- and 5α-*H*-sapogenins (diosgenin, tomatidine solasodine, and 5,6-dihydrosolasodine.[41–46] The fact that diosgenin and tomatidine, a 5α-*H*-steroid alkaloid, undergo the same type of transformation and the complete absence of a microbiological transformation of tigogenin compared with diosgenin (Scheme 2) merits attention.[44]

Scheme 2





The principal site of hydroxylation is determined by the structure of the substrate. Diosgenin and tomatidine are transformed predominantly with formation of 11α-hydroxy-derivatives, while solasodine and 5,6-dihydrosolasodine are converted into 9α-hydroxy-derivatives.[41,46] It must be emphasised that in the transformation of tomatidine by the *H.p.* culture the nitrogen atom in the *F* ring does not hinder the 11α-hydroxylation.

A repeated attempt to obtain the hydroxy-derivatives from 5α-spirostanols was undertaken 20 years after the studies mentioned above. 1β,7β-Dihydroxy-derivatives of hecogenin were obtained with the aid of *C. el.*[47] In contrast to *H.p.* and *C. el.*, the cultures of the *Gymnoascus, Scopulariopsis, Fusarium, Dendrostibella,* and *Hypomyces* fungi do not hydroxylate 5α-*H*- and Δ^5-sapogenins, but, like bacteria, transform the *A* ring and cleave the side chain.[48–53]

III. Hydroxylation of 5α-*H*-androstanes

The hydroxylation by fungi of 5α-*H*-androstanes has been most widely investigated. Analysis of the results of the transformations of different 5α-*H*-androstanes (monoketones, diketones, ketoalcohols), chosen as the simplest model compounds for the interpretation of the behaviour of the microorganisms, permitted the main conclusions concerning the mechanism of the microbiological hydroxylation of the steroids. The hydroxylating activity in relation to 5α-*H*-androstanes has been investigated for fungi belonging to different classes of ascomycetes, basidiomycetes, deuteromycetes, and phycomycetes, which are known to be capable of hydroxylating Δ^4-3-oxosteroids in the 11α-positions (*A.o., R.n.*), the 11β-position (*C.cl.*), the 12β- and 15α-position (*C.d., P.u., P.*sp.), and the 21-position (*W.g., O.h.*).[2,6,7] Cultures of *A.t.*,[4] *D.r.*,[28] *A.r.*,[33] *L.f.*,[37] *D.c.*,[31] and *R.c.*,[24] which had not been investigated previously, were also tested. The results of these tests are presented in Tables 2 and 3.

Table 2. Hydroxylation of 5α-*H*-androstanes by fungi.

Substituents in substrate	Micro-organism	Initial compound, %	Principal hydroxylation sites	Yield, %	Secondary hydroxylation sites	Yield[a], %	Refs.
1	2	3	4	5	6	7	8
2,7-$(CO)_2$	*L.f.*	15	16β	22	16β, 18	6	[37]
2,7-$(CO)_2$	*W.g.*	15	2β, 17β	19	17β	9	[27]
					2β,18	10	
3-CO	*A.o.*	56	6β, 11α	51	11α	11	[21]
3-CO	*A.r.*	55	9α, 15β	8	9α	4	[33]
3-CO	*W.g.*	72	9α, 17β	13	–	–	[27]
3-CO	*D.r.*	90	not transformed		–	–	[28]
17-CO	*A.o.*	65	7β, 11α	27	–	–	[21]
3,6-$(CO)_2$	*D.r.*	9	3β, 16β	39	3β, 15β	12	[28]
					3β, 6α, 16β	25	
3,6-$(CO)_2$	*L.f.*	21	16β	12	3β, 16β	8	[37]
3,7-$(CO)_2$	*W.g.*	32	3β, 17β	41	3α, 17β	27	[27]
3,7-$(CO)_2$	*L.f.*	4	16β, 18	7	3β, 18	5	[37]
3,7-$(CO)_2$	*O.h.*	12	3β, 17β	62	–	–	[27]
3,7-$(CO)_2$	*A.r.*	0	3β, 11α	6	Δ^1-17-CO	3	[33]
					11α	1	
3,7-$(CO)_2$	*S.r.*	3	3β, 12α	13	7α, 9α	5	[33]
		3	3β, 12β	6	1β	3	
					11α	2	
					12α	2	
					7α, 9α, 11α	2	
3,7-$(CO)_2$	*D.c.*	7	3β, 16α	48	3β, 16β	11	[31]
3,7-$(CO)_2$	*R.a.*	3	16β	15	16α	3	[24]
			3β, 16β	31	11α, 16β	3	
					17α	2	
3,7-$(CO)_2$	*R.c.*	7	3β, 11α	22	11α, 16β	5	[24]
			16β	10	3β, 16β	6	
3,7-$(CO)_2$	*D.r.*	3	3β, 7α, 16β	33	3β, 7α, 16-CO	3	[28]
					3β, 7β, 16β	13	
3,11-$(CO)_2$	*A.r.*	0	17β, ($\Delta^{1,4}$)	6	16β ($\Delta^{1,4}$)	4	[33]
					17-CO($\Delta^{1,4}$)	2	
					16-CO	2	
3,11-$(CO)_2$	*S.r.*	–	16β($\Delta^{1,4}$)	18	17β($\Delta^{1,4}$)	9	[33]
					17-CO($\Delta^{1,4}$)	9	
3,11-$(CO)_2$	*D.c.*	0	3β, 16α	55	16α	18	[31]
					3β, 11, 16-$(CO)_2$	10	
3,11-$(CO)_2$	*R.c.*	17	6α	20	3β, 7β	3	[24]
			16β	15	9α, 16β	2	
			7β	10			
3,11-$(CO)_2$	*D.r.*	5	3β, 16β	28	3β, 15β	15	[28]
3,11-$(CO)_2$	*L.f.*	11	16β	13	16β, 18	5	[37]
3,11-$(CO)_2$	*R.a.*	16	3β, 16β	22	16β	7	[24]
			9α, 16β	23	9α, 16α	7	
3,11-$(CO)_2$	*O.h.*	46	16β	11	16-CO	38	[27]
			17β	11	16-CO, 3β	21	
3,11-$(CO)_2$	*W.g.*	24	17β	28	3α, 17β	8	[27]
					3β, 17β	13	
					3β, 16β	6	
3,11-$(CO)_2$	*P.u.*	—	15α	31	—	—	[18]
			3β, 15α	15	–	–	
3,16-$(CO)_2$	*L.f.*	15	18	16	—	—	[37]
3,17-$(CO)_2$	*W.g.*	7	1α, 17β	7	1α, 3α, 9α, 7β	1	[27]
			1α, 3β	6	7α	1	

Table 2 (cont'd).

1	2	3	4	5	6	7	8
3,17-$(CO)_2$	*S.s.*	–	11α	22	3β	7	[55]
3,17-$(CO)_2$	*A.r.*	0	9α	14	3β, 9α	5	[33]
			7α, 9α	13	7α	10	
3,17-$(CO)_2$	*A.r*	–	9α	11	7α	2.4	[33]
					1β, 9α	0.7	
3,17-$(CO)_2$	*C.cl.*	–	11β	–	7α	–	[82]
3,17-$(CO)_2$	*D.c.*	6	3β, 9α	6	9α	3	[31]
3,17-$(CO)_2$	*S.r.*	0	3β, 7α	7	3β	7	[33]
			3β, 7α, 17β	3	3β, 9α	2	
3,17-$(CO)_2$	*D.r.*	0	3β, 7β, 17β	24	3β, 11α, 17β	13	[28]
					3β, 6α, 17β	11	
3,17-$(CO)_2$	*A.o.*	–	11α	66	–		[21, 93]
3,17-$(CO)_2$	*A.t.*	–	6β	25[b]	–	–	[4]
			11β	30[b]	–	–	
3,17-$(CO)_2$	*P.sp.*	–	1α	17	–	–	[70]
6-CO	*D.r.*	21	3β, 6α, 16β	16	3β, 6α, 16-CO	5	[28]
					3β, 16β	4	
					3β, 15β	2	
6,17-$(CO)_2$	*L.f.*	17	2β	13	–	–	[37]
7-CO	*D.r.*		3β, 7α, 16β	41	–	–	[28]
			3β, 7β, 16β	16	–	–	
7,11-$(CO)_2$	*D.r.*	0	3β, 7α, 16β	42	–	–	[28]
7,16-$(CO)_2$	*D.r.*	0	3β, 7α	39	–	–	[28]
7,17-$(CO)_2$	*D.r.*	0	3β, 7α, 17β	32	3-CO, 7β, 17β	5	[28]
			3β, 7β, 17β	16			
7,17-$(CO)_2$	*A.r.*	33	5α	6	–	–	[33]
7,17-$(CO)_2$	*S.r.*	4	1α, 17β	23	12β, 17β	7	[33]
					11α, 17β	11	
					5α, 17β	4	
7,17-$(CO)_2$	*W.g.*	13	2α	34	3β	11	[27]
			2α, 17β	30	3β, 17β	5	
7,17-$(CO)_2$	*L.f.*	12	2β	24	–	–	[37]
7,17-$(CO)_2$	*O.h.*	38	3β, 17β	43	3β	32	[27]
7,17-$(CO)_2$	*R.c.*	38	3β	15	11α, 17β	8	[24]
			11α	18	4α	6	
					3β, 17β	5	
7,17-$(CO)_2$	*R.a.*	11	3α	31	3β	6	[24]
					3β, 17β	6	
					3α, 17β	2	
					3α, 11α	6	
					3β, 11α	2	
					11α	3	
7,17-$(CO)_2$	*D.c.*	0	3α	52	1α	4	[31]
					17β	7	
11-CO	*D.r.*	10	3β, 14α, 16β	12	3β, 16-CO	7	[28]
					3β, 16α	5	
11-CO	*O.h., W.g.*	50—58	not isolated	–	–	–	[27]
11,17-$(CO)_2$	*A.r.*	34	–	–	17β	28	[33]
11,17-$(CO)_2$	*S.r.*	37	7α, 17β	27	5α, 17β	9	[33]
					7α	5	
11,17-$(CO)_2$	*D.c.*	32	7α, 17β	11	7α	10	[31]
11,17-$(CO)_2$	*L.f.*	39	not isolated	–	–	–	[37]
11,17-$(CO)_2$	*O.h.*	63	3α	45	17β	44	[27]

Table 2 (cont'd).

1	2	3	4	5	6	7	8
11,17-$(CO)_2$	*R.a.*	11	4α, 17β	27	7β, 17β	8	[24]
			3α, 17β	20			
11,17-$(CO)_2$	*R.c.*	19	4α, 17β	54	7β, 17β	18	[24]
16-CO	*D.r.*	58	not transformed	–	–	–	[28]
17-CO	*D.r.*	50	not transformed	–	–	–	[28]
17-CO	*H.p.*	–	not transformed	–	–	–	[86]
17-CO	*O.h., W.g.*	74—87	not transformed	–	–	–	[27]
17-CO	*C.el.*	50	1β, 7α	14	1β, 7-CO	6	[92]
3α-OH, 6-CO	*L.f.*	0	16β, 18	39	16β	31	[37]
3β-OH, 6-CO	*L.f.*	–	17β	40	17-CO	3	[37]
			16β	27	16-CO	3	
3β-OH, 6-CO	*A.r.*	5	9α	23	14α	9	[33]
					11α	5	
3β-OH, 7-CO	*L.f.*	0	16β	24	16β, 18	6	[37]
3α-OH, 7-CO	*W.g.*	6	17β	55	–	–	[27]
3β-OH, 7-CO	*W.g.*	4	17β	63	3-CO, 17β	3	[27]
					17-CO	5	
					7α, 17β	2	
3β-OH, 7-CO	*S.r.*	0	12α	51	9α	19	[33]
					12β	8	
3β-OH, 11-CO	*D.r.*	0	16β	17	15β	8	[28]
					14α, 16β	5	
					16-CO	3.5	
3β-OH, 11-CO	*L.f.*	5	16β, 18	24	–	–	[37]
3β-OH, 11-CO	*W.g.*	48	6β	48	17β	22	[27]
3β-OH, 11-CO	*D.r.*	0	16β	17	15β	8	[28]
					14α, 16β	5	
					16-CO	3.5	
3β-OH, 16-CO	*L.f.*	22	18	21	–	–	[37]
3α-OH, 17-CO	*R.a.*	0	11α	30	7β	8	[24]
3α-OH, 17-CO	*P.sp.*	–	12β	12[b]	–	–	[3]
3β-OH, 17-CO	*P.sp.*	–	7α	11.8[b]	–	–	[3]
3α-OH, 17-CO	*A.t.*	–	11β	30[b]	11α	5	[4]
3α-OH, 17-CO	*A.o.*	–	11α	82	–	–	[18]
3α-OH, 17-CO	*C.el.*	0	7β	43	7α	10	[92]
3β-OH, 17-CO	*R.a.*	–	7β	57	7-CO	1	[24]
			7α	20	6α	8	
3β-OH, 17-CO	*W.g.*	5	1α	22	14α	13	[27]
					9α	7	
					5α	7	
3β-OH, 17-CO	*F.g.*	–	15α	–	–	–	[71]
3β-OH, 17-CO	*A.t.*	–	11β	45[b]	–	–	[4]
3β-OH, 17-CO	*D.c.*	0	9α	40	3-CO, 9α	15	[31]
					7α	12	
3β-OH, 17-CO	*M.g.-c.*	–	7α	–	7α, 14α	–	[56]
3β-OH, 17-CO	*R.c.*	7	7β	43	6α	25	[24]
3β-OH, 17-CO	*A.r.*	4	9α	19	9α, 14α	2	[33]
					7β	12	
					7α, 14α	4	
3β-OH, 17-CO	*S.r.*	0	7β	27	7-CO	10	[33]
			7β, 17β	24			
3α-OAc, 17-CO	*C.el.*	15	6β, 11β	22	1β	8,0	[92]

Table 2 (cont'd).

1	2	3	4	5	6	7	8
3β-OAc, 17-CO	*C.el.*	0	7β	31	7α	3	[92]
					7-CO	3	
6β-OH, 3-CO	*L.f.*	0	10β, 18	34	–	–	[37]
6α-OH, 17-CO	*R.c.*	37	11α	56	3β	5	[24]
6α-OH, 17-CO	*R.a.*	4	11α	72	11α, 17β	5	[24]
7α-OH, 3-CO	*D.r.*	28	16β	53	3β, 16β	28	[28]
7β-OH, 3-CO	*D.r.*	33	3β	18	–	–	[28]
7β-OH, 11-CO	*A.r., S.r.*	22—63	–	–	17-CO	15—25	[33]
9α-OH, 3-CO	*D.c.*	3	3β, 16α	47	16α	15	[31]
9α-OH, 3-CO	*A.r.*	82	not isolated				[33]
9α-OH, 3-CO	*S.r.*	10	3β, 12α	12	–	–	[33]
11α-OH, 3-CO	*A.r.*	49	not isolated				[33]
11α-OH, 3-CO	*S.r.*	25	3β, 7β	27	7β	17	[33]
					3β	4	
11α-OH, 3-CO	D.c.	28	16α	9	–	–	[31]
12α-OH, 3-CO	D.c.	0	3β, 16α	48	16β	19	[31]
12α-OH, 3-CO	S.r., *A.r.*	53—65	–	–	3β	6—10	[33]
17β-OH, 3-CO	*A.t.*	–	11β	20[b]	–	–	[4]
17β-OH, 3-CO	*D.c.*	54	3β, 9α, 17-CO	18	3β, 9α	9	[31]
17β-OH, 3-CO	*A.r.*	5	9α	14	7α, 9α, 17-CO	7	[33]
					9α, 14α	2	
17β-OH, 3-CO	*L.f.*	67	not isolated				[37]
17β-OH, 3-CO	*A.o.*	7	11α	79	6α, 11α	2	[26]
17β-OH, 3-CO	*R.a.*	21	11α	23	3β, 7β	5	[24]
			6α	12	3β, 6α	4	
					3β, 11α	4	
					5α	4	
17β-OH, 3-CO	*D.c.*	54	3β, 9α, 17-CO	18	9α, 17-CO	4	[31]
					3β, 9α	9	
17β-OH, 3-CO	*R.c.*	19	6α	33	–	–	[24]
			11α	26	–	–	
17β-OH, 3-CO	*R.sp.*	–	1α	–	–	–	[70]
17β-OH, 3-CO	*C.el.*	–	7α	18	9α	0.5	[93]
					6α	3	
					12α	0.8	
17β-OH, 3-CO	*D.r., O.h.*	81	not isolated				[27]
17β-OH, 3-CO	*W.g.*	7	1α	5	3β	2	[27]
			1α, 3α, 9α	2			
17β-OH, 3-CO	*S.r.*	0	3β, 7α	27	7β	9	[33]
					9α	7	
17β-OH, 6-CO	*S.r.*	19	11α, 17-CO	23	–	–	[33]
17β-OH, 7-CO	*W.g.*	14	2α	58	3β, 7α	5	[27]
			2α, 7α	15			
			3β	11			
17β-OH, 7-CO	*D.c.*	0	3β	26	3α, 17-CO	16	[31]
					3α	7	
17β-OH, 7-CO	*A.r.*	18	3β	24	3α, 17-CO	6	[33]
17β-OH, 7-CO	*S.r.*	0	3β, 12β	23	3β	17	[33]
					12β	1	
					1β	7	
17β-OH, 11-CO	*W.g.*	39	3β	35	3α	11	[27]
17β-OH, 11-CO	*A.r., S.r.*	22—63	–	–	17-CO	15—25	[33]
17β-OH, 11-CO	*D.c.*	8	7α	18	7,17-$(CO)_2$	5	[31]

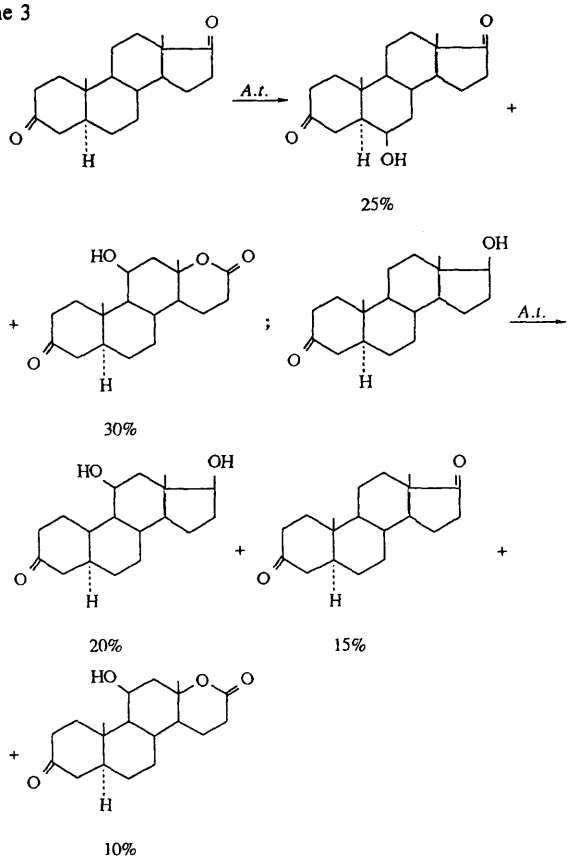
Table 2 (cont'd).

1	2	3	4	5	6	7	8
3β, 7α-$(OH)_2$-17-CO	*D.c.*	70	3-CO	56	–	–	[31]
3β, 7β-$(OH)_2$-17-CO	*A.o.*	16	7β, 11α	78	–	–	[26]

[a] Here and in the subsequent tables, the yields are quoted relative to the converted substrate.
[b] The yields of the product isolated relative to the substrate introduced into the reaction.

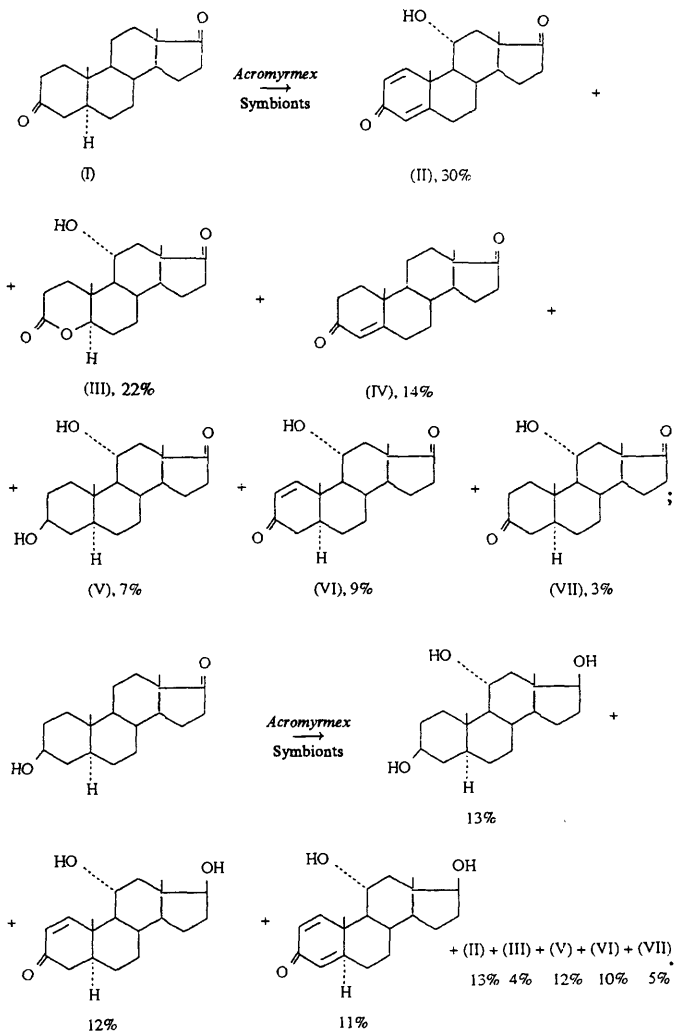
In assessing the data in Table 2, attention should be drawn to what we believe to be two important factors. Strange as it may seem, among all the species investigated, only the strain *A.t.* forms 11β-monohydroxylated compounds in the series of 5α-*H*-androstanes in a sufficiently high yield. However, the lactonisation of the *D* ring is characteristic of the culture and unfortunately this process competes with the main 11β-hydroxylation reaction. The presence of 3-oxo-group in the substrate activates the cleavage of the *D* ring with formation of the lactone, whilst in the incubation of *A.t.* with 3-hydroxy-5α-*H*-androstane *D*-homoisomerisation does not occur* (Scheme 3).

Scheme 3



The second phenomenon which merits attention refers to unidentified fungi—symbionts of ants, which have not been investigated either before the study mentioned above[32] or after it. It follows from Scheme 4 that the symbiont fungi catalyse three processes in the series of 5α-*H*-androstanes: (a) the hydroxylation of the sites specified by the directing influence of the existing substituents in the molecule; (b) the Baeyer–Villiger oxidation; (c) dehydrogenation of the *A* ring. The last two processes occur only in the presence of an oxygen-containing substituent in the 11-position. Examples comprising 5α-*H*-androstanes with oxygen-containing functional groups in the 3- and 17-positions confirm the constancy of the overall mode of the process as the nature of the oxygen-containing substituent at C(3) is varied (Scheme 4).

Scheme 4



It is regrettable that similar studies have not been made with compounds of the 5α-*H*-pregnane series, because the simultaneous activation of the *A* and *C* rings in the pregnane series appears to be an urgent task. The rare combination of the hydroxylating and dehydrogenating activities in the *Acromyrmex* fungi can be

explained, in our view, by the fact that the fungi constitute a microbial consortium whose members perform different transformations of the steroid molecule. The ability of fungi of the genus *Septomyxa* to transform 5α-*H*-steroids into the $\Delta^{1,4}$-3-oxo-compound is known in principle, but this does not entail hydroxylation.[72–74]

Table 3. Hydroxylation by *Calonetria decora* and *Rhizopus nigricans* cultures of 5α-androstanes monosubstituted and disubstituted by oxygen-containing groups.

Substituents in substrate	*Calonetria decora* (Refs. 13, 19, 20, 30)					*Rhizopus nigricans* (Refs. 14, 22, 23)				
	recovered substrate, %	principal hydroxylation sites	Yield, %[a]	Secondary hydroxylation sites	Yield, %[a]	recovered substrate, %	principal hydroxylation sites	Yield, %[a]	secondary hydroxylation sites	Yield, %[a]
1-CO	75	complex mixture	–	–	–					
2-CO	13	6α,12β	26	6α, 11α	11	51	6α, 16α	10	6α,16α(2-CO → 2α-OH)	2.5
3-CO(EtOH)	23	12β, 15α	40—52	12β, 15α(3-CO → 3β-OH)	13	46	11α, 16β	18	6β, 11α	4
3-CO(ДМСО)	0	6α, 12β, 15α	28			–	11α, 16β	33	6β, 11α	4
									11α	1
3β-OH(EtOH)	33	12β, 15α	18	–	–					
4-CO	0	12β,15α	41	–	–	40	11α, 16β	9	11α, 16β(4-CO → 4β-OH)	7
		11α, 15α	40	–	–					
6-CO	90	does not react				90	does not react			
7-CO	72			12β, 15α	4	90	3α, 16β	34	4β,16β	16
11-CO	40	1β, 6α	11	6α	3	62	4α, 16β	7	3α,16β	5
									3β, 16β	3
15-CO	4	14β, 6α, 12β	21	2α, 12β	8	59	not isolated			
16-CO	31	6α, 11α	26—33	1β, 6α	7	34	3β, 7α	46		
17-CO	32—75	1β, 6α	15—47	1-CO, 6α, 19	38	59	3α, 11α	10	3α, 6α	8
12-CO	8	6α, 15α	15	1β, 6α, 15α	12	–	3β, 7β	9	3β,11β	2.5
							6α, 11α	9		
							3β, 7β	29		
17β-OH	41	1β, 6β	18	6α, 11α	7					
15α-OH-2-CO	0	6α	13	–	–					
17β-OH-2-CO	4	6α	31	–	–	17	6α	15	–	
6α-OH-3-CO	–	–	–	–	–	0	16α	30	17α	7
6β-OH-3-CO							16β	27	11α,16β	4
							11α	14		
						0	16β	39	16β(3-CO → 3β-OH)	2
							11α, 16β	30		
							11α	14		
7α-OH-3-CO						0	16β	33		
							16β(3-CO → 3β-OH)	24		
7β-OH-3-CO						31	16β	52		
11α-OH-3-CO	4	12β, 15α	24	–	–	5	16β	45—30	16β(3-CO → 3β-OH)	11
							16α	14	7β,17α, 16-CO	4
							16β(3-CO → 3β-OH)	11—50		
11β-OH-3-CO						27	9α, 16β(11β-OH → 11-CO)	13	16β(3-CO → 3β-OH)	4
							16β	11	6α(3-CO → 3β-OH), 11β-OH → 11-CO)	2
							16β(11β-OH → 11-CO)	9	16α-(3-CO → 3β-OH, 11β-OH → 11-CO)	1
							16β-(3-CO → 3β-OH, 11β-OH → 11-CO)	9		

Table 3 (cont'd).

Substituents in substrate	*Calonetria decora* (Refs. 13, 19, 20, 30)					*Rhizopus nigricans* (Refs. 14, 22, 23)				
	recovered substrate, %	principal hydroxylation sites	Yield, %[a]	Secondary hydroxylation sites	Yield, %[a]	recovered substrate, %	principal hydroxylation sites	Yield, %[a]	secondary hydroxylation sites	Yield, %[a]
16β-OH-3-CO						0	11α	61—80	11α(3-CO → 3β-OH)	23—27
17β-OH-3-CO						8	11α	34	7β(3-CO → 3β-OH)	7
							6α	30	5α	6
17β-OMe-3-CO	16	12β, 15α(3-CO → 3β-OH)	8	–	–					
3β-OH-6-CO						0	16α	43	16β	18
17β-OH-6-CO						0	3β	23	5α,11α	7
							3α	21	3α,11α	7
							11α	11		
3β-OH-7-CO						0	16β	77		
17β-OH-7-CO						0	3α	52	4α	3
									3β	12
3β-OH-11-CO						0	16β	34	7β,16β	8
							16α	11	17β, 16-CO	7
							6α	9	16-CO	6
									5α, 16β	5
									7β, 17α	4
17β-OH-11-CO						26	3α	47	–	–
15α-OH-12-CO	0	6α	13	–	–	–	4α	25	–	–
14β-OH-15-CO	23	7β, 12β	34	7β, 12β	–					
12β, 14β(OH)$_2$-15-CO	0	7β	21							
3β-OH-16-CO						0	7α	90	–	–
3α-OH-17-CO		1β, 15α	25	–	–	7	7β	24		
		1β, 6α	37	–	–	–	11α	23	6α	5
3α-OMe-17-CO	3	1β, 6α	60	–	–					
3β-OH-17-CO	6	12β, 15α(3β-OH → 3-CO)	32			0	7β	48	7α	15
		12β, 15α	21						6α	12
6α-OH-17-CO						16	11α	58	3β	10
7α-OH-17-CO						10	3β	77		
17β-OH-17-CO						25	3β	57		
2,16-(CO)$_2$	–	12β-6-CO	27	6α,12β	12	0	7α(2-CO → 2α-OH)	55	7α	7
									6α(2-CO → 2α-OH)	5
1,17-(CO)$_2$	15	6α	33	6α, 19	25					
2,17-(CO)$_2$	15	6α	13			0	7α(2-CO → 2α-OH)	20	7β(2-CO → 2α-OH)	6
									6α(2-CO → 2α-OH)	2
3,6-(CO)$_2$						6	16β(3-CO → 3β-OH)	26	16β	9
							16α(3-CO → 3β-OH)	23		
							16α	23		
3,7-(CO)$_2$	26	12β(3-CO → 3β-OH)	19			4	16β	32	16β(3-CO → 3β-OH)	9
3,11-(CO)$_2$	27	15α(3-CO → 3β-OH)	23			4—19	16β	55—20	9α,16β	6
		15α	18				16β(3-CO → 3β-OH)	20	9α,16α	5
									16α(3-CO → 3β-OH)	4
									16α	2

Table 3 (cont'd).

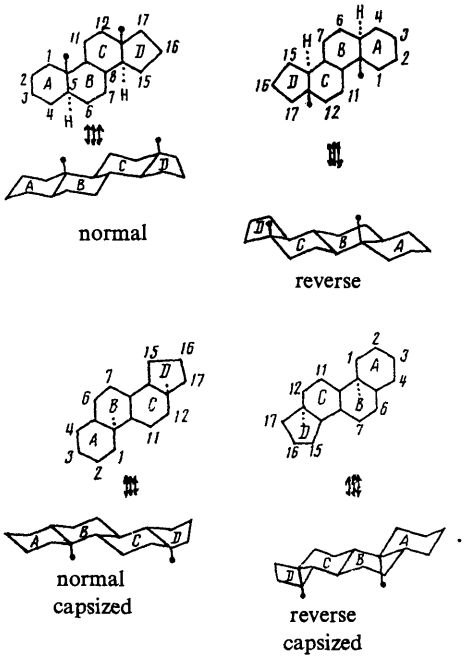
Substituents in substrate	*Calonetria decora* (Refs. 13, 19, 20, 30)					*Rhizopus nigricans* (Refs. 14, 22, 23)				
	recovered substrate, %	principal hydroxylation sites	Yield, %[a]	Secondary hydroxylation sites	Yield, %[a]	recovered substrate, %	principal hydroxylation sites	Yield, %[a]	secondary hydroxylation sites	Yield, %[a]
3,12-$(CO)_2$	10	15α	14							
3,16-$(CO)_2$	69	15α(3-CO → 3β-OH)	26	12β, 15α	11	0	7α(3-CO → 3β-OH)	50	-	-
3,17-$(CO)_2$	23	12β, 15α	5			32	11α	23	6α(3-CO → 3β-OH)	3
							6α	15	7β(3-CO → 3β-OH)	4
6,17-$(CO)_2$	27	1β	64—56							
7,17-$(CO)_2$	25	1β	55	-	-	0	3α	37	3α, 11α	5
							3β	7	3β(17-CO → 17β-OH)	4
									3α-(17-CO → 17β-OH)	6
11,16-$(CO)_2$						22	3β, 7β	24	3β	5
(EtOH, 6 j)							3α	10		
11,17-$(CO)_2$	4	6α	32	-	-	21	3α(17-CO → 17β-OH)	36	4α(17-CO → 17β-OH)	15
1,17-$(CO)_2$-6α-OH	6—40	19	26—29	-	-					
								-	3α	14
3β, 6α-$(OH)_2$						6	16α	37	16β	17
3β, 6β-$(OH)_2$						17	16β	38	15α	17

Considerable progess in the understanding of the mechanism of the hydroxylation of steroids has been achieved as a result of studies by workers at Oxford University. They investigated the influence of the functional groups of the substrate on the type of hydroxylation by different fungal cultures. In an attempt to depart from the uniformity which had arisen in connection with the use of substrates of the pregnane series with oxygen-containing substituents at C(3) (mainly CO) and to find a general model of hydroxylation, the research group led by Jones[32] investigated a very wide set of 5α-*H*-steroids (more than 300) in which the position, nature, and number of the oxygen-containing substituents were varied systematically and additional structural factors (double bonds, ring junction, the presence of a heteroatom) were excluded beforehand. This giant study, in which more than 800 hydroxysteroids were obtained and whose importance it is difficult to overestimate, was carried out in 1969—1980.[13—38] Initially the familiar microorganisms characterised by both substrate specificity and substrate independence were included in the research and were then followed by new microorganisms, not investigated previously as steroid hydroxylating biocatalysts, up to the fungi mentioned above—the *Acromyrmex octospinosus* symbionts.[32]

The data in Tables 2 and 3 show that these studies replaced the occasional and few investigations of the transformations of 3,17-disubstituted 5α-*H*-androstanes by individual cultures.[54—56,64,70,77] The workers at Oxford University investigated the influence of a wide range of substituents in 5α-*H*-androstane on the hydroxylating capacity of *A.r.*, *P.u.*, *R.a.*, *R.c.*, *W.g.*, and *O.h.* with emphasis on *C.d.*, *R.n.*, *and A.o.* The results confirmed in most cases Brannon's hypothesis[4] that the hydroxylation of the steroid molecule in different positions is catalysed by the same non-specific enzyme. The enzyme—substrate interaction model, determining the mode of hydroxylation, which was constructed on the basis of the interpretation of the results of the hydroxylation of various substrates by *R.n.*,[22,23] does not conflict with this hypothesis either. The general interpretation of the hydroxylation mechanism proposed by Jones[78] not only explained satisfactorily the results of the oxidation of steroids by the cultures listed above but was also recognised and developed by other groups of investigators.[79—96]

The proposed model of the hydroxylation reaction postulates the existence on the surface of the enzyme globule of three active centres designed for two purposes, i.e. each centre-site can perform two functions—the function involving the binding of the enzyme to the substrate and the hydroxylation function (Fig. 1). According to this model, the sites have a triangular location, corresponding approximately to that occupied by the C(3), C(11), and C(17) atoms of the steroid ring. The way in which the enzyme—substrate complex is formed and hence the result of the hydroxylation depend on whether these centres of the steroid ring carry oxygen-containing substituents (how many and what kind); the binding of the steroid to the substrate can then take place in one of the possible orientations. It is believed that four orientations of the steroid in relation to the enzyme are theoretically possible: (a) normal; (b) reverse; (c) normal capsized; (d) reverse capsized. The last two are obtained by the rotation of the steroid molecule about the C(3)—C(17) axis by 180°. The normal and reverse orientations are preferable and virtually only these are considered in Jones's hydroxylation model (Scheme 5).

Scheme 5



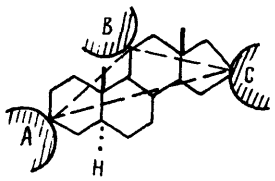


Figure 1. Jones's model of the enzyme–substrate interaction.[78]

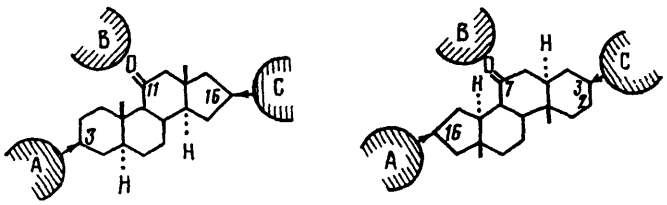
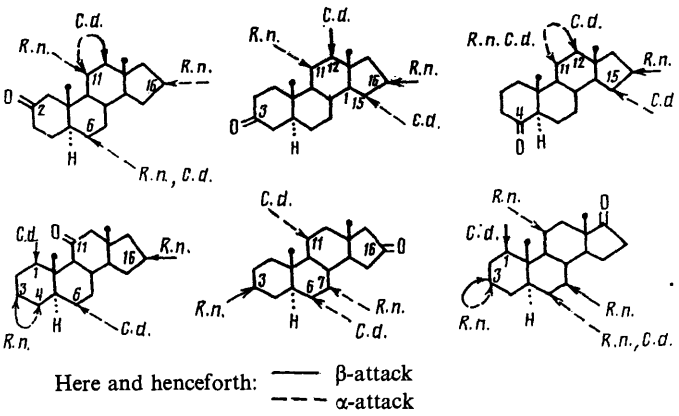


Figure 2. Site of hydroxylation of 11-oxo- and 7-oxo-5α-*H*-androstanes by a *D. r.* culture.[28]

According to this model, the binding of the enzyme to the steroid substrate occurs at two oxygen centres, which is satisfactorily confirmed by data for the transformation of the monoketones of the 5α-*H*-androstane series by different cultures. Virtually all the monoketones (1-, 2-, 3-, 4-, 6-, 7-, 11-, 12-, 15-, 16-, and 17-CO) are transformed either with much difficulty—with recovery of up to 90% of the unreacted substrate—or are not transformed at all. When transformation does occur, a considerable non-uniformity of the reaction products is observed. The high percentage of the recovery can be attributed to the low solubility of the monoketones compared with other steroids and hence with the greater difficulty of their permeation into the cell. However, the main explanation of the low reactivity the monoketones and the non-uniformity of the products obtained from them is apparently that the substrate molecule, fixed on the surface of the enzyme at only one site, rotates or oscillates about the binding centre, subjecting not all the predicted positions to the action of the enzyme. The monoketones are then as a rule dihydroxylated. Fig. 2 shows how this occurs for *D.r.*

The same model explains the principle of the dihydroxylation of the monoketones by the *C.d.* and *R.n.* fungi in the following way: the keto-group of the substrate in one (or several) of its orientations is bound to one of the binding centres of the enzyme, while the other two sites perform the function of hydroxylating those C–H bonds which are in vicinal positions in relation to them. For example, the 3- and 16-ketones are dehydroxylated by *R.n.* in the 11,16- and 3,7-positions as a consequence of the binding of the keto-groups to the enzyme at the centre A in the normal and reverse ways respectively (Fig. 3). The authors explain the formation of a multicomponent mixture of the 6,11-, 3,7-, and 3,11-dihydroxy-derivatives on transformation of 17-oxo-5α-*H*-androstane by the non-uniform binding in both ways. In this case, the formation of 6,11-dihydroxy-derivatives and also of 6α,16α- and 6α,11α-dihydroxy-products rather than the 11,16-dihydroxy-derivatives on transformation of 2-oxo-5α-*H*-androstane with the aid of *R.n.* cannot be readily explained.[22]

Scheme 6



One cannot rule out the possibility that the above variants of the dihydroxylation are a consequence of the successive monohydroxylation initially in the 11α- or 16α-position and then in the 6α-position; at any rate, it is known that 6-hydroxylase can be induced in *R.n.* by 11α-hydroxysteroids on incubation with Δ^4-3-oxosteroids.[2] It may be that the 16α-hydroxy-derivatives of 5α-*H*-steroids also induce the synthesis of a second enzyme. It is noteworthy that the high percentage of the recovery of the initial substrate (17-CO and 2-CO) shows that none of the available binding methods creates a situation favourable for hydroxylation (Scheme 7).

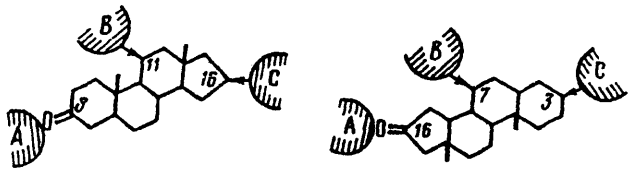
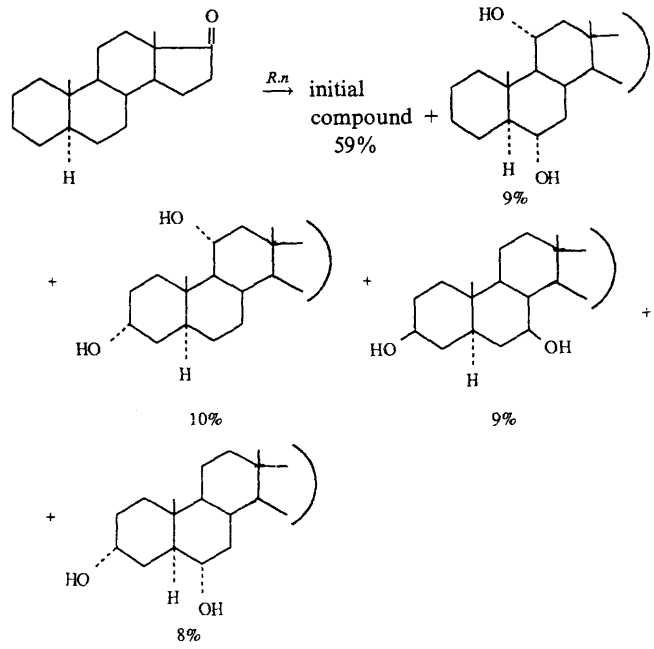


Figure 3. The site of hydroxylation of 3-oxo- and 16-oxo-5α-*H*-androstanes by the *C.d.* and *R.n.* fungi.[20,22,30]

Scheme 7



We shall compare these data (Scheme 6) with the results of the oxidation of the monoketone derivatives of 5α-*H*-androstanes by a *C.d.* culture. As a result, the *C.d.* culture introduces both equatorial groups at virtually the same distances from the oxygen atom of the substrate and the distance between the attacked carbon atoms is also approximately the same (1−6 = 3.9 Å; 6−11 = 4.4 Å; 11−15 = 4.5 Å). Evidently the oxidation of the monoketones by *R.n.* is not quite so specific because, together with equatorial substitution, there is also axial substitution and the distance between the attacked centres is not quite so uniform although it is in most cases approximately 5 Å (11−16, 3−17). Appreciable conversion of the monoketones into the main product on incubation with *C.d.* takes place only when the substituent is in the terminal rings. An interesting feature of *R.n.* in relation to steroids of the 5α-*H*-androstane series is the intense hydroxylation in the 16β-position (see Table 3 above), which is never manifested in the pregnane series.[35] *R.n.* is also distinguished by a low capacity for the oxidation of monoalcohols (1α-, 3β-, 6α-, 11α-, 17β-). After incubation with the above microorganism, 75−95% of the initial substrate remains,[22] whereas *C.d.* hydroxylates at least the 3β- and 17β-alcohols (the others have not been investigated) (Table 3). The most characteristic feature of the *C.d.* species, known as the 12β,15α-dihydroxylating culture for Δ^4-3-oxosteroids,[104] is also the 12β-,15α-dihydroxylation of 5α-*H*-androstanes with 3-CO, 3β-OH, and 3α-OH substituents as well as compounds with the 3β-OH-Δ^1-, 3-CO-Δ^1, or 17-acetate groups.[13,19,29] In contrast to *C.d.*, the *R.n.* and *A.o.* moulds do not hydroxylate 3- and 17-monoacetates of 5α-*H*-androstane.[29]

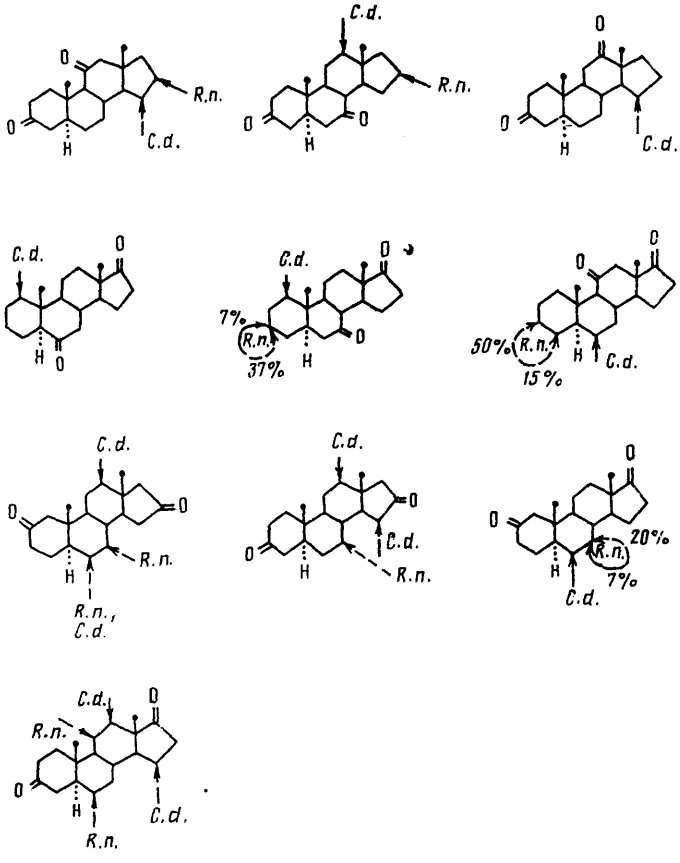
In the transformation of the monoketones with the aid of *D.r.*, the enzyme is bound to the substrate mainly with participation of the substituent at the centre of the molecule [C(7) and C(11)] with formation of 3β-,16β-dihydroxylated products (Table 2, Fig. 2). When androstanes with substituents in the terminal rings (in the 3-, 16-, and 17-positions) are used as the substrates, the recovery of the unreacted steroid is 50−90% and a complex mixture of unidentified products is formed.[28] The *W.g.*, *O.h.*, *D.c.*, *D.r.*, and *S.r.* cultures are inert in relation to the majority of monosubstituted (mainly CO-substituted) 5α-*H*-androstanes,[27] which agrees with the hypothesis of the involvement of two enzyme centres in the binding discussed here.

The *A.o.* culture does not transform the majority of monoketones. Exceptions are the 3- and 17-oxoandrostanes transformed respectively into 6β,11α-dihydroxy-derivatives with 44 and 35% conversions, 7β,11α-dihydroxy-derivatives (51 and 27%), and 11α-dihydroxy-derivatives (11 and 5%).[21] However, the formation of the dihydroxylated derivatives by the *A.o.* culture is due to the action of not just one enzyme, as for *C.d.*, but two steroid hydroxylases, the existence of which has been demonstrated in experiments with a cell-free extract.[75,76] It has been suggested that the second hydroxylase system in the *A.o.* cells is induced by the reaction product of the first enzyme, which is also the 11α-hydroxy-derivative. This leads to the formation of 6β,11α-dihydroxy-derivatives and sometimes the 6β-monohydroxy-derivatives.[28] The presence of the second oxygen-containing group (CO or OH) in the molecule in different positions facilitates the hydroxylation of 5α-*H*-androstanes with the aid of *A.o.*, but always in the 11α-position. Furthermore, whereas on incubation with monoketones the *A.o.* microorganism catalyses predominantly dihydroxylation, disubstituted androstanes are converted by this culture exclusively into 11α-monohydroxy-derivatives in 66−82% yield (Table 2). However, the functioning of two steroid hydroxylases in the *A.o.* cells and the site-specificity characteristic of this microorganism justify the assumption that it is unsuitable for the solution of the problem formulated. The research group therefore concentrated attention on *C.d.* and *R.n.*, which are capable of hydroxylating steroids in different positions depending on the structure of the substrate (Table 3), using the cultures indicated in Table 2.

Analysis of the results of the conversion of the monosubstituted 5α-*H*-androstanes has shown that the driving force determining the mode of hydroxylation is the specificity of the microorganism and the directing effect of the keto-group. The use of ketones and diketones substituted in different ways as substrates makes it possible, having increased the rate and efficiency of the transformation (by changing the hydrophilicity of the substrate, the solvent to be added to the reaction mixture, and the incubation time), to follow the competitive effect of the substituents (having restricted the monohydroxylation process as a result of the blocking effect of the second substituent) and, what is most important to discover the factors responsible for the mode of hydroxylation. It has been noted that polar groups in the terminal rings have a dominant effect on the hydroxylation process catalysed by the *C.d.* culture, as observed for monosubstituted androstanes. For example, the 3-oxo-group in 3,11-, 3,12-, and 3,7-diketones, which is common to these substrates, directs the hydroxylation to the *C* and *D* rings, while the 17-oxo-group in the 6,17-, 7,17-, and 11,17-diketones,

common to these substrates, directs the hydroxylation by the above microorganism to the *A* and *B* rings. The keto-groups in the middle *B* and *C* rings have a weak directing effect, blocking the hydroxylation in its own position and stimulating that in the neighbouring position or in a position close to it in space (Table 3, Scheme 8).

Scheme 8



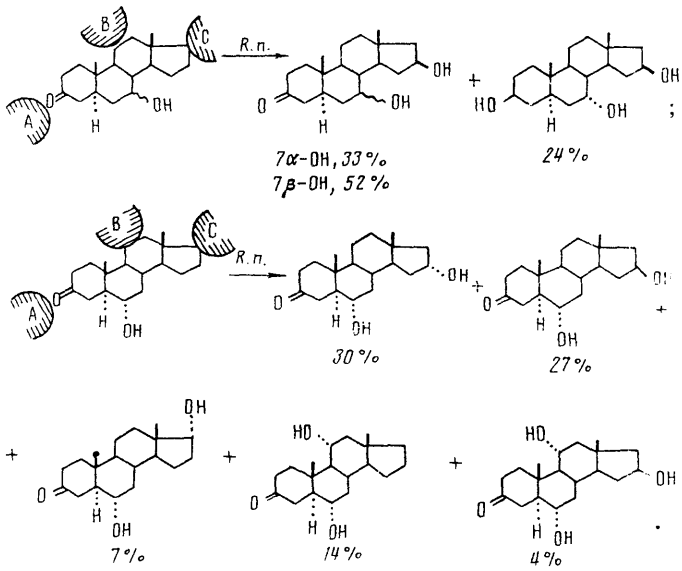
Naturally the competition between the keto-groups located in the terminal rings (the last four examples in Scheme 8) is reflected in the dihydroxylation, the mode of which is determined by the directing effect of both keto-groups. The hydroxy-groups in the main products formed as a rule assume the equatorial orientation and are at a distance of 3.5–4.5 Å from the nearest oxygen-carrying carbon atom and at a distance of 6.3–8 Å from either C(3) (substrate with a substituent in the *A* ring) or from C(17) (substrate substituted in the *D* ring). The directing force of the principal directing substituents has been estimated as follows in the analysis of the results of the oxidation reaction: 3-CO-Δ^4 (and less distinctly 5α- and 3β-OR, R = H, Me) > 17-CO > 3α-OR (R = H, Me); 3-CO-Δ^4 > 17β-OH, etc., i.e. the nature of the oxygen group is less important than its steric orientation relative to the steroid nucleus as a whole. This is an extremely important conclusion, which makes it possible to eliminate the established view, which is apparently false as shown using the *A.o.* culture, that the presence of the Δ^4-3-oxo-group, for example, in the steroid molecule is necessary for its successful microbiological hydroxylation.

According to the hydroxylation model discussed, the substrates with two oxygen-containing groups are oriented at the enzyme molecule in such a way that the maximum possible hydrophobic binding between both substituents and the corresponding enzyme centres is ensured. In this case the third catalytic centre is responsible for the hydroxylation of the nearest carbon atom.

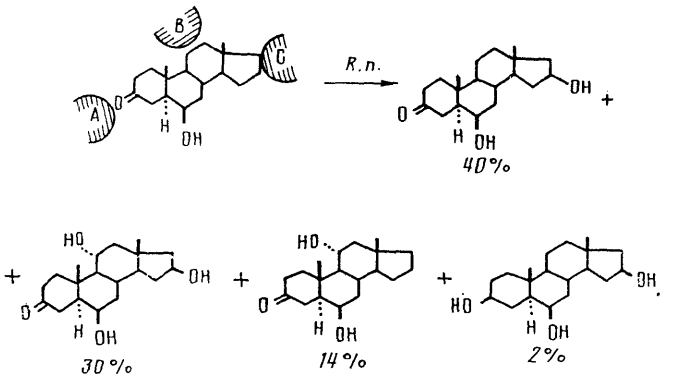
The *R.n.* enzymes hydroxylate terminally substituted substrates oriented in the normal manner in the 11-position, while those oriented in the reverse manner are hydroxylated in the 6- or 7-position. Thus, among the four terminally substituted diketones subjected to oxidation, three substrates (2,16-, 2,17-, and 3,16-) are hydroxylated only in the reverse manner (Table 3, Scheme 8).[23] The models described show that, for the first two steroids, binding in the normal manner does not permit contact between the steroid and the enzyme site B, while in the 3,16-diketone the geometrical disposition of the centres is favourable for both types of binding. The reverse type of hydroxylation observed for the 3,16-diketone indicates the preferential binding of the 16-oxo-group to the site A. Although the 3,17-diketone is in fact hydroxylated in the normal manner, the degree of conversion (32% of the starting material) and the yield of the 11α-hydroxy-derivative (23%) are low and the 6α-hydroxy-derivative is formed. It is thus legitimate to extend what has been stated above for the 17-monoketone to the 3,17-diketone. A striking result is the quantitative 11α-hydroxylation (~100%) of the 16β-hydroxy-3-ketone and the 7α-hydroxylation (90%) of the 3β-hydroxy-16-ketone bearing in mind that the corresponding monoalcohols are not transformed by the *R.n.*[23] In combination with the 3-oxo- and 16-oxo-groups, these alcohols probably constitute the optimum model for the normal and reverse hydroxylation respectively. The 17-oxo-group combined with the 3β-hydroxy group exhibits preferential hydroxylation in one particular (reverse) way (48% 7β-OH and 15% 7α-OH); on the other hand, the presence of the 3α-hydroxy-group promotes the formation of products of hydroxylation in both ways (23% of 11α-OH and 5% of 6α-OH). The presence of the 17β-hydroxy-group in 17β-hydroxy-5α-androstan-3-one not only facilitates the hydroxylation by *R.n.*, but also makes it selective. The asymmetric disposition of the substituents at C(17) probably interferes with the optimum binding of the substrate to the enzyme in this case also.

The results of the oxidation, catalysed by *R.n.*, of virtually all the ketones and ketols investigated, in which one oxygen atom is in the terminal ring and the other is in the middle ring, can be interpreted satisfactorily from the standpoint of the hypothesis of three two-target sites. As a rule, substrates with the substituent in the *A* ring are hydroxylated preferentially in the *D* ring and conversely the substrate substituted in the *D* ring is hydroxylated in the *A* ring, i.e. here too, as in the case where *C.d.* is used, the dominant influence of the terminal substituents is observed. These substituents are bound to the site A of the enzyme usually in the normal or reverse manner and are hydroxylated at the site C. On the other hand, the substituents in the central rings exert only an auxiliary influence, discussed above for *C.d.* (Scheme 9). The minor hydroxylation products can probably arise when a hydroxy-group enters positions adjoining the main hydroxylation site (for example the 4- or 17-position). One cannot fail to notice that monohydroxylation is more characteristic of disubstituted compounds even if the type of binding of the substrate molecule favours the entry of a second group. Thus in the examples presented in Scheme 10, the epimeric 7-hydroxy-3-ketones are not hydroxylated at the site *B* at all, while the epimeric 6-hydroxy-3-ketones are only partly hydroxylated at this site (Table 3).

Scheme 9

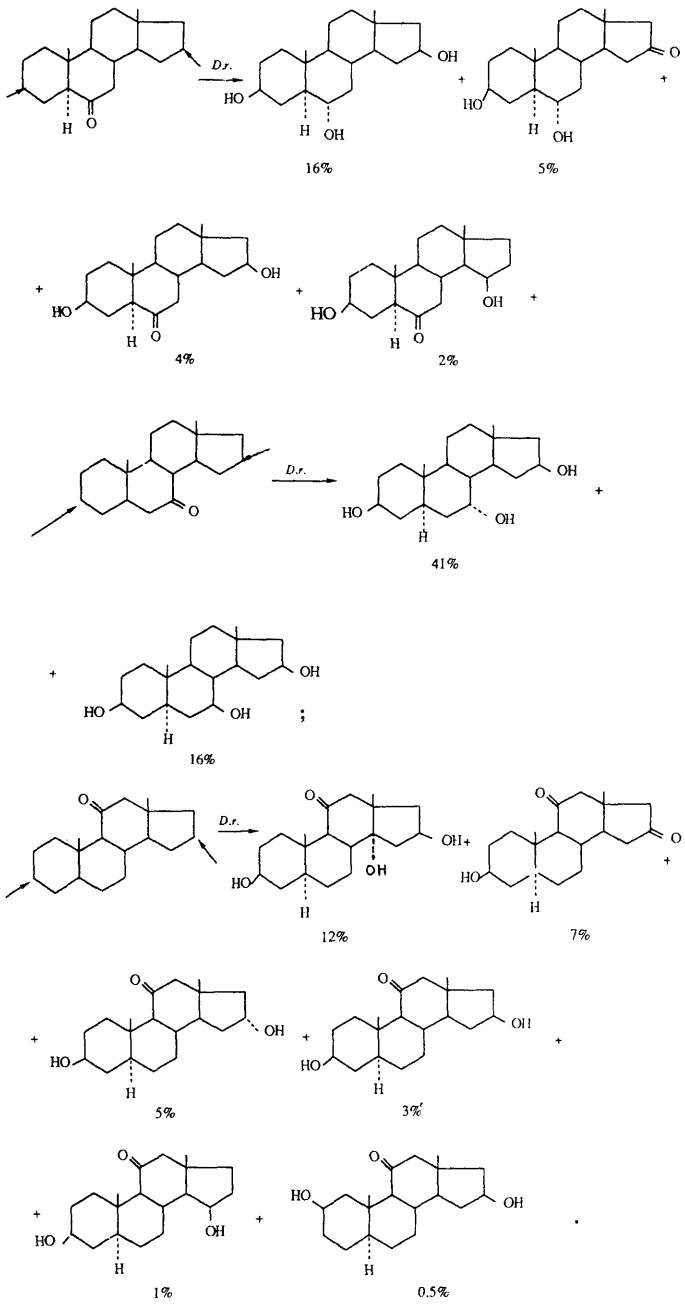


Scheme 10



In the authors' version, the proposed dehydroxylation model concentrates attention on the regiospecificity of the reactions but completely ignores their stereochemical aspects: the stereospecificity of the reactions or its absence and the influence of the stereochemistry of the substituent in the substrate. After two years, McCrindle et al.,[79] who analysed the hydroxylation of norcaranes catalysed by *R.n.* from the standpoint of Jones's hypothesis of the formation of a temporary enzyme–substrate complex, proposed a modification, which takes into account the three-dimensional nature of the steroid molecule and the protein globule. Their idea was to draw an imaginary plane through the steroid substrate molecule in such a way that the sites A and B are below it (or are coplanar with it), while the site C is above it. It is assumed that the site A binds preferentially the oxygen atoms below this plane and that hydroxylation takes place in the α-region. The site B imposes a similar requirement on the binding to the enzyme, but hydroxylation can occur both in the α-region (axial or equatorial) or in the β-region (only equatorial). The site C is bound preferentially to the enzyme above this plane and directs hydroxylation preferentially to the β-position. From the author's point of view, all the results for the stereochemistry of the hydroxylation of steroids catalysed by *R.n.* and their own data on the hydroxylation of norcaranes fit satisfactorily within the framework of this hypothesis.[79]

Scheme 11

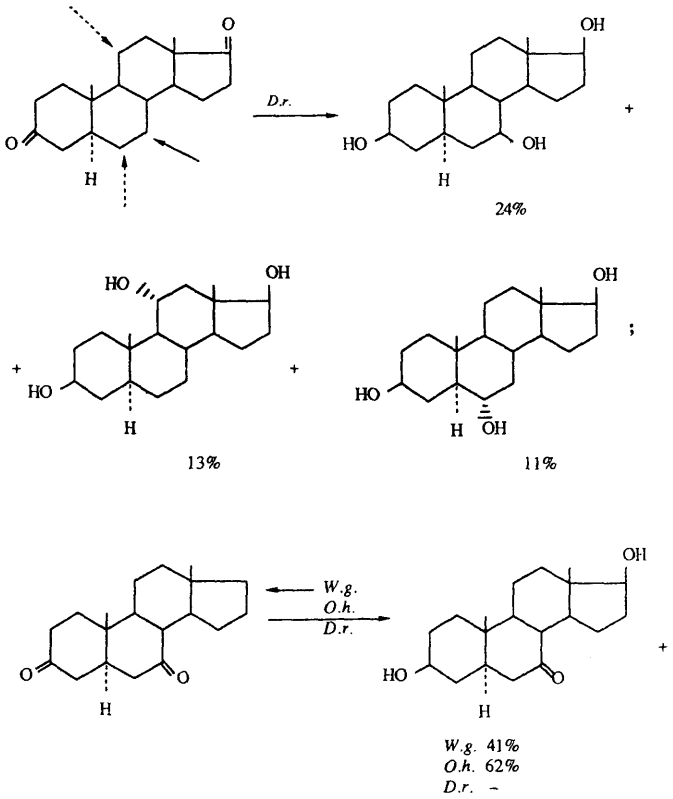


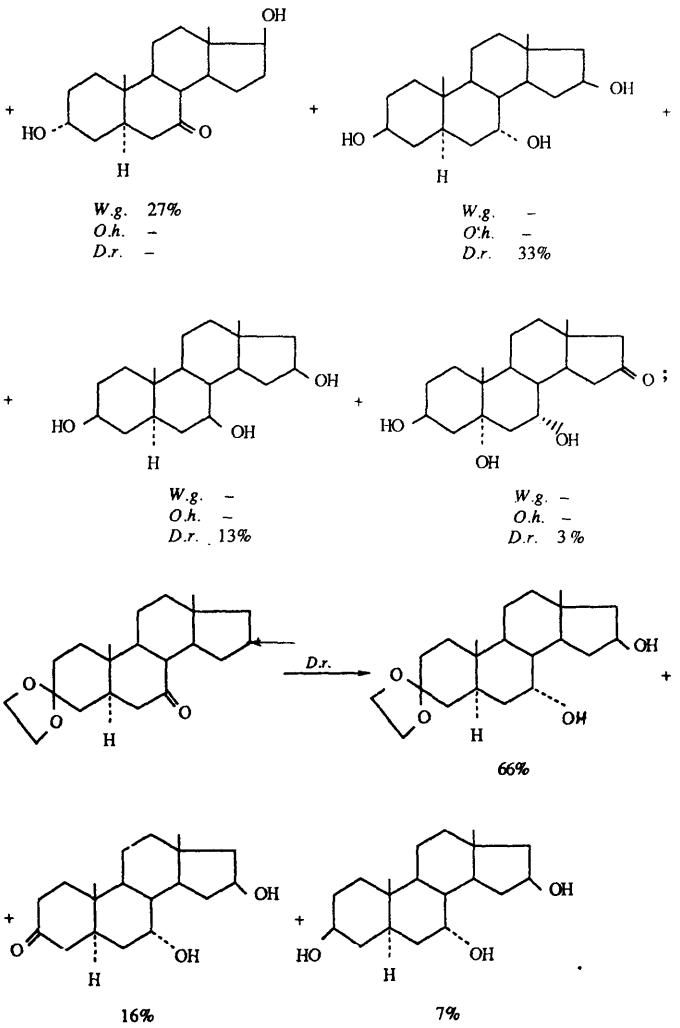
The results of the transformation of 5α-androstanes by *W.g.*, *O.h.*, and *D.r.* cultures, where the majority of monosubstituted, mainly with CO, 5α-androstanes are inert in the presence of *W.g.* and *O.h.*, are satisfactorily consistent with the proposed hypothesis. The *D.r.* enzyme system exhibits a surprising contrast between the slow hydroxylation of substrates having a carbonyl group in the terminal ring and the higher rates of conversion of substrates having this

group in the central ring. Thus 5α-androstanes with 3-CO, 16-CO, and 17-CO groups are transformed by *D.r.* only to the extent of 10–40%, forming a complex mixture of unidentified products, while their 6-CO, 7-CO, and 11-CO analogues are oxidised with 80–90% conversion at the terminal rings. The hydroxylation reactions of the 11- and 7-ketones catalysed by the *D.r.* culture are distinguished by their specificity: the former afford several hydroxylation products, while the 7-ketones are hydroxylated more unambiguously (Scheme 11, Table 2).

We shall consider in relation to these cultures (*W.g.*, *D.r.*, *O.h.*) how the results obtained with their aid fit within the framework of Jones's model. The *O.h.* enzyme system proved to be inert in relation to the terminally substituted androstanes with two oxygen-containing groups. On the other hand, the *W.g.* and *D.r.* cultures effectively hydroxylate these substrates (Table 2).[27,28] 5α-Androstanes in which one keto-group is in the terminal ring (2-, 3-, or 17-) and the other is in the middle ring (7- or 11-) are hydroxylated readily and always in the terminal ring regardless of the microorganism used, the replacement of the keto-group by a hydroxy-group having an insignificant influence on the hydroxylation reaction. The clear tendency towards preferential attack on specific positions in the steroid nucleus (usually 3-, 7-, and 16- or neighbouring positions) is characteristic of all three cultures (Scheme 12).

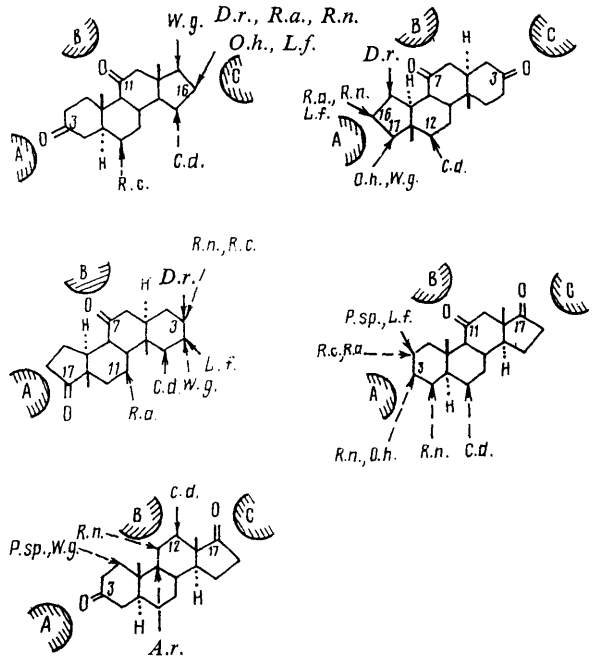
Scheme 12





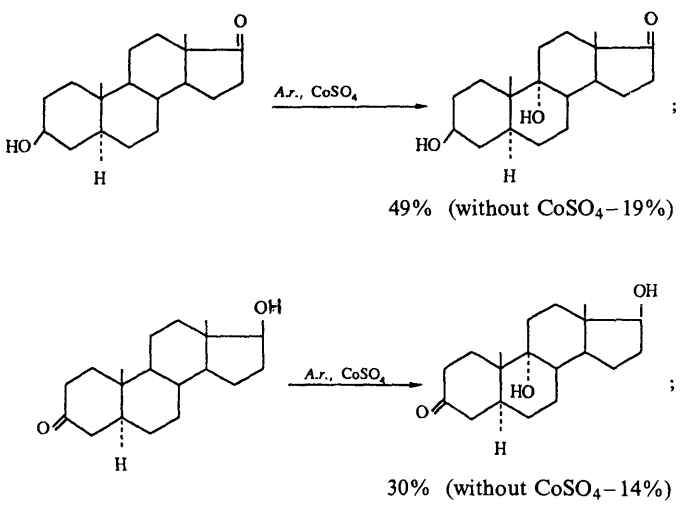
The data discussed above concerning the oxidation of 5α-androstanes and included in Tables 2 and 3 (the results of transformations catalysed by fungi of unidentified genus are not considered) are summarised in Scheme 13. In most cases, these results fit within the framework of the Jones–McCrindle model of enzyme–substrate specificity. Thus, on binding to the sites A and B or B and C, hydroxylation takes place at the sites C and A respectively [the 3,11-$(CO)_2$, 3,7-$(CO)_2$, 7,17-$(CO)_2$, and 11,17-$(CO)_2$ structures], while on binding to the sites A and C, all fungi (it must be emphasised that these represent different classes), introduce an axial hydroxy-group (with the exception of *C.d.*) in the positions within the molecule oriented towards the site B. At the same time, one of the binding sites can effect hydroxylation and in such a case dihydroxylated products are formed. On the other hand, if this does not occur, then monohydroxylated products are formed, which is observed on transformation of disubstituted androstanes in the vast majority of cases. The reactions of androstane substrates take place similarly when keto-groups are replaced by hydroxy-groups and also for 3- and 17-monoacetals and 3,17-diacetals and 2α,3α-epoxides, but not 2β,3β-, 16α,17α-, and 16β,17β-epoxides.

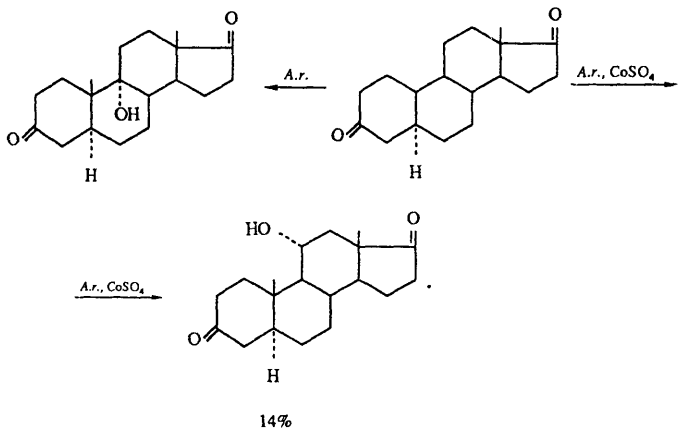
Scheme 13



The results of hydroxylation catalysed by the *A.r.* microorganism, which introduces an 11α- or 9α-hydroxy-group into the 3,17-diketone depending on the presence of divalent cobalt in the medium, are not susceptible to explanation.[33] If the substrates are 3β- or 17β-keto-alcohols, then the hydroxy-group is introduced in the 9α-position regardless of the presence of cobalt. However, in its absence the yield of the 9α-hydroxy-products is smaller by a factor of 2. The exceptional nature of these data consists also in the fact that heavy metal salts, including cobalt salts, fully inhibit the activity of 9α-hydroxylases of bacterial origin[2] (Scheme 14).

Scheme 14

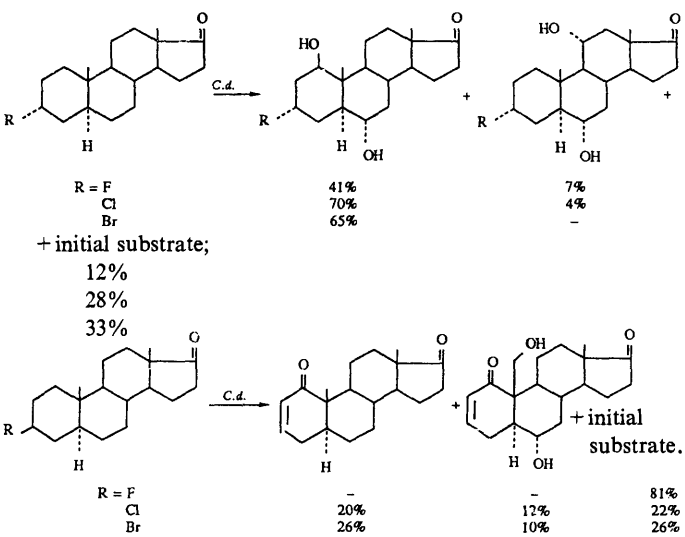




IV. Transformations of halo-5α-*H*-androstanes

In order to elucidate the influence of halo-substituents on the hydroxylation of 5α-*H*-androstanes (3-, 16-, and 17-oxo-derivatives), a number of monohalo-substituted (3-, 6-, and 17-) and *gem*-difluoro-substituted (6-, 7-, 12-, 16-, 17-) substrates were incubated under standard conditions with *C.d.*, *R.n.*, and *A.o.* micro-organisms[34,36] and the results were compared with those obtained for related unsubstituted 5α-*H*-androstanes. It was found that the catalytic properties of the biocatalysts are determined by the halogen atom: its nature, position, and configuration. This is illustrated by the results of the hydroxylation of 3α- and 3β-halo-5α-*H*-androstan-17-ones (Scheme 15).

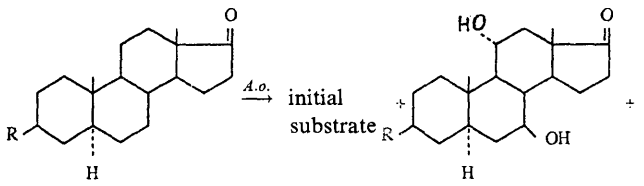
Scheme 15



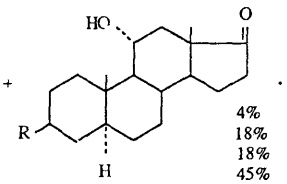
Another activity sequence in the halogenation of substrates has been observed for 17α-halogenated 5α-*H*-androstan-3-ones: in this case, the chloro-substituted derivatives are inactive in the presence of the *C.d.* microorganisms, while the fluoro-substituted derivatives undergo 12β,15α-dihydroxylation [like the unsubstituted 3-oxo-5α-*H*-androstanes (Table 3)]. A clear and very useful difference exists between the fluoro-ketones, on the one hand, and the chloro- and

bromo-ketones, on the other, in the hydroxylation of 3- and 17-oxoandrostanes catalysed by the *A.o.* microorganism. For example, 3α-chloro- and 3α-bromo-derivatives do not react, whereas the 3α-fluoroketone is effectively hydroxylated in the 11α-position by this culture. An extremely important conclusion, reached in a study of a wide range of fluorinated 5α-androstanes, is that the fluorine atom, which is remote from the site of attack specific to each 5α-androstanone (and microorganism), facilitates the hydroxylation process without altering its specificity. This can be clearly traced for the 11α-hydroxylating *A.o.* culture, which, in contrast to *C.d.* and *R.n.*, exhibits a low substrate specificity. The results presented in Scheme 16 demonstrate not only a clearly expressed induction of the hydroxylation process by the 3-fluoro-substituent but also the possibility of specific 11α-hydroxylation of 17-oxo-5α-androstanes by this culture (c.f. Table 3).

Scheme 16

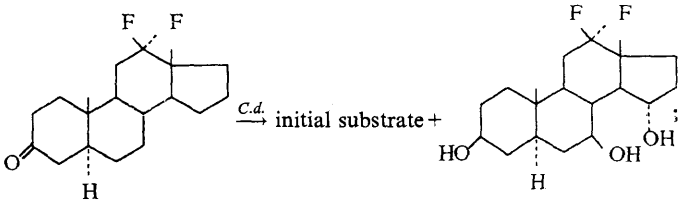


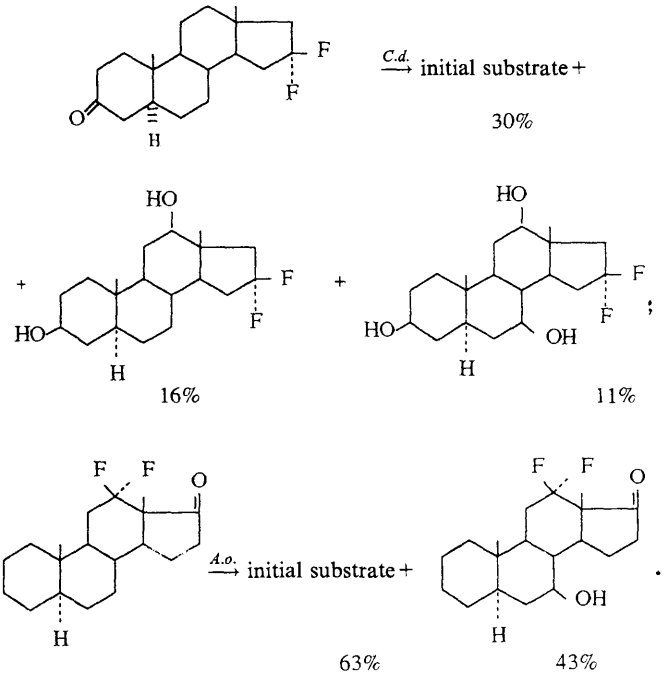
R = H	67%	34%
R = 3α-F	18%	41%
R = 3β-F	18%	40%
R = 3, 3-F_2	28%	–



On the other hand, a chlorine atom close to the standard points of attack as a rule blocks the hydroxylation process in these standard or neighbouring positions or directs it along the "reverse" pathway. For example, the 12β,15α-dihydroxylation by the *C.d.* culture, which is characteristic of 3-oxo-5α-*H*-androstanes, has not been observed in reactions with 12,12-difluoro- and 16,16-difluoro-3-ketones, where the main targets of attack are respectively the 7β,15α- and 7β,12β-atoms. A striking example of such displacement of the site attacked is provided by the result of the hydroxylation of 12,12-difluoro-17-oxoandrostanes to give the 7β-hydroxy-derivative. This result is particularly striking in the sense that the presence of the 11α-hydroxy-group is essential for the 6β- or 7α-hydroxylation by this enzyme, while monohydroxylation always takes place only in the 11α-position[76] (Scheme 17).

Scheme 17





V. Hydroxylation of 5α-*H*-*D*-homoandrostanes

In order to discover the additional factors determining the enzyme–substrate interaction, research groups in Venezuela and Great Britain[89–96] analysed the influence of the formation of *A*- and *D*-homo-derivatives in the series of 5α-*H*-androstanes on hydroxylation by three cultures—*A.o.*, *R.n.*,[80,81] and *C.el.* Comparison of the results with those for the transformation of similarly substituted 5α-*H*-androstanes permitted the conclusion that, firstly, the *A.o.* culture exhibits a narrow site-specificity also in relation to the *D*-homosteroids, hydroxylating the latter only in the 11α-position (Table 4). Secondly, compounds of this series do not induce the synthesis of a second hydroxylase, which is additionally confirmed by the absence of the hydroxylation of *D*-homo-5α-androstanes having two oxygen-containing substituents in the 3,11-positions. It is noteworthy that the same compounds are not hydroxylated by the *R.n.* culture either, which is evidence in support of the hypothesis put forward previously that two hydroxylases can also function in the *R.n.* cells but they are not quite so specific as in the *A.o.* culture. However, according to the authors,[80,81] in the main the results of the hydroxylation of *D*-homo-5α-androstanes by the *R.n.* culture fit satisfactorily within the framework of Jones's mechanism, from the standpoint of which virtually all the data obtained can be accounted for. In this series, the normal mode of hydroxylation is rarely observed and virtually all the substrates investigated are hydroxylated in the reverse manner, the reaction being accompanied to a large extent by the reduction of the keto-group. An exception is *D*-homo-5α-*H*-androstane-3,17-dione, which is hydroxylated to some extent in the normal way in the 11α-position. However, since only the 3-oxo-group is reduced to the 3β-hydroxy-group, favourably oriented for binding in the reverse manner, the process begins to proceed precisely in this direction with formation of 7β-hydroxy-derivatives. On the other hand, the 3,17*a*-*D*-homoketone (Table 4) is not hydroxylated even in the

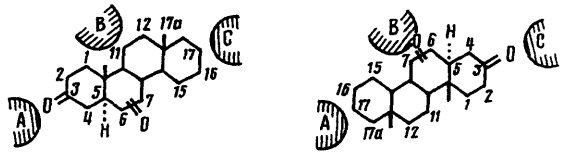
Table 4. Hydroxylation of *D*-homo-5α-*H*-androstanes by different cultures.

Substituents	Culture	Initial compound,%	Principal hydroxylation sites	Yield, %[a]	Secondary hydroxylation sites	Yield, %[a]	Refs.
2,17a-$(CO)_2$	*R.n.*	14	6α and 7α	20	2-CO → 2α-OH	14	[81]
3,6-$(CO)_2$	*R.n.*	47	17aα(3-CO → 3β-OH)	17	3-CO → 3α-OH	6	[81]
3,7-$(CO)_2$	*R.n.*	7	17aα	31	–	–	[81]
3,17-$(CO)_2$	*R.n.*	–	7β(3-CO → 3β-OH)	20	3-CO → 3α-OH	45	[81]
			11α(3-CO → 3α-OH)	29			
3,17a-$(CO)_2$	*R.n.*	35	–	–	3-CO → 3α-OH	19	[81]
11α-OH, 3-CO	*R.n.*	39	–	–	3-CO → 3β-OH	11	[81]
3β-OH, 17a-CO	*R.n.*	0	7β(17-CO → 17α-OH)	18	17-CO → 17α-OH	19	[81]
7β-OH, 17a-CO	*R.n.*	50	7β	47	17a-CO → 17α-OH	10	[81]
3α-OH, 17a-CO	*R.n.*	50	7 products				[81]
6-CO	*A.o.*	90			7β-OH → 7-CO	21	[80]
2,17a-$(CO)_2$	*A.o.*	61	11α	65	–		[80]
3,6-$(CO)_2$	*A.o.*	50	11α	29	–		[80]
3,7-$(CO)_2$	*A.o.*	24	11α	20	–		[80]
3,11-$(CO)_2$	*R.n., A.o.*	10	not isolated				[80]
3,17-$(CO)_2$	*A.o.*	24	11α	79	–		[80]
3,17a-$(CO)_2$	*A.o*	0	11α	73	–		[80]
11α-OH, 3-CO	*A.o*	85	not isolated				[80]
3β-OH, 17a-CO	*A.o*	38	11α	46	3β-OH → 3-CO	41	[80]
3β-OAc, 17a-CO	*A.o*	–	11α	–			[94, 95]
3α-OH, 17a-CO	*A.o.*	33	11α	48	–		[80]
3,17-$(CO)_2$	*C.el*	–	7α, 9α	35	7α	2	[94, 95]
			9α, 14α	20	3-CO → 3β-OH		
3,17a-$(CO)_2$	*C.el*	–	7α, 14α	33.5	7α	2	[94, 95]
					1β, 3β, 7-CO	1.5	
					1β, 7α	3.2	
					1β, 7β	1.2	
3β-OAc, 17-CO	*C.el.*	–	9α, 14α	36	–	–	[95]
3β-OAc, 17a-CO	*C.el.*	–	7β(3β-OAc → 3β-OH)	29	1β, 7-CO	4	
			7α(3β-OAc → 3β-OH)	9	1β, 6β	4	
					7-CO	0.6	
3β-OH, 17a-CO	*C.el.*	–	1β, 7-CO	4	–	–	[95]
			1β, 7β	4	–	–	
			1β, 7α	10	–	–	
17-CO	*C.d.*	–	6α, 17α	10	–	–	[19]
			7β, 12β, 15α	11	–	–	
			1β, 7β, 15α	6	–	–	
17aβ-OH, 17aα-Me-3,17-$(CO)_2$	*C.cl.*	–	11β	2	11β(3-CO → 3β-OH)	8	[117]
			6α	4	6α(3-CO → 3β-OH)	3	

reverse manner, because its 3α-hydroxy-derivative, having a hydroxy-group with an unfavourable orientation for binding to the site C, is formed initially. It is hydroxylated with the formation of a multicomponent mixture of unidentified products. The latter result probably justifies a general conclusion concerning the hydroxylation of steroids. If the structure of the substrate does not promote effective binding to the enzyme, then the latter is achieved with participation of molecules oriented in different ways, which leads to a non-uniform hydroxylation process or reduction of the keto-groups.

In contrast to 5α-androstanes, the 3,6- and 3,7-diketones of which are hydroxylated by *R.n.* in 16α- and 16β-positions, the corresponding homoanalogues form 17*a*α-hydroxy-products.[81] The authors suggest that the above *D*-homosteroids are hydroxylated by the reverse procedure at the site A, the formation of 16α-hydroxy-5α-androstane-3,6-dione is a consequence of the same hydroxylation pathway, while the 16β-epimer is formed in the normal way by transformation at the site C, provided, of course, that the "twisted" forms of the molecules do not participate in the process (Scheme 18).

Scheme 18

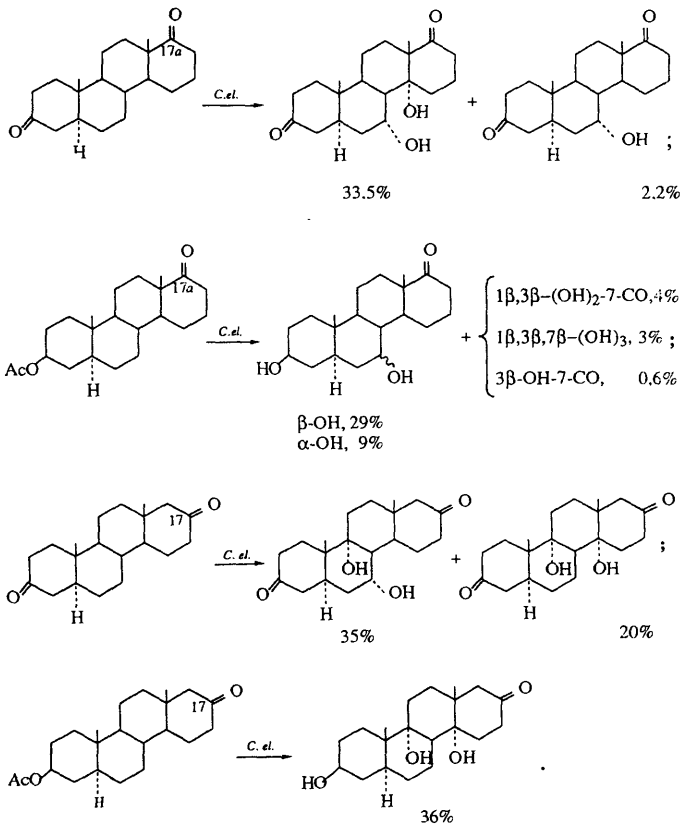


normal reverse

Unfortunately there have been no quite so systematic studies on the hydroxylation of *D*-homo-5α-*H*-androstanes by other cultures. However, one should note the different behaviour of the dihydroxylating *C.d.* culture in relation to 5α-*H*-androstan-17-one (Table 3) and its *D*-homoanalogue (Table 4): the 1β,6α-dihydroxylation in the former case and preferential trihydroxylation (7β,12β,15α- and 1β,7β,15α-) in the latter.

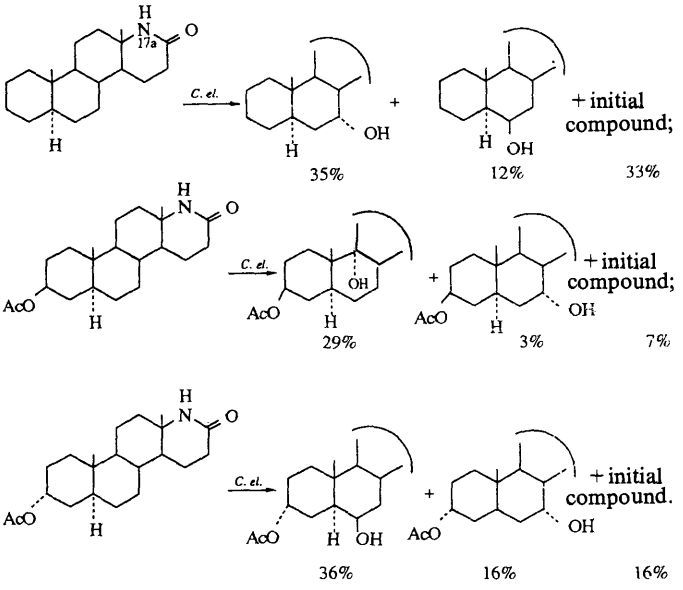
The existing, albeit few, results for the hydroxylation by the *C.el* culture of two pairs of *D*-homo-5α-*H*-androstanes 3,17-disubstituted by oxygen-containing groups (Table 4) and their comparison with data for the oxidation by the same culture of the corresponding 5α-*H*-androstane analogues (Table 2) can also be interpreted within the framework of the hydroxylation model mentioned above. The striking change, particularly notable in the series of 17*a*-*D*-homoanalogues, in the site at which *D*-homo-5α-*H*-androstan-17 (or 17*a*)-ones are hydroxylated on replacement of the 3-oxo-group by the 3β-acetate group, hydrolysing during the reaction, is noteworthy (Table 4, Scheme 19).

Scheme 19



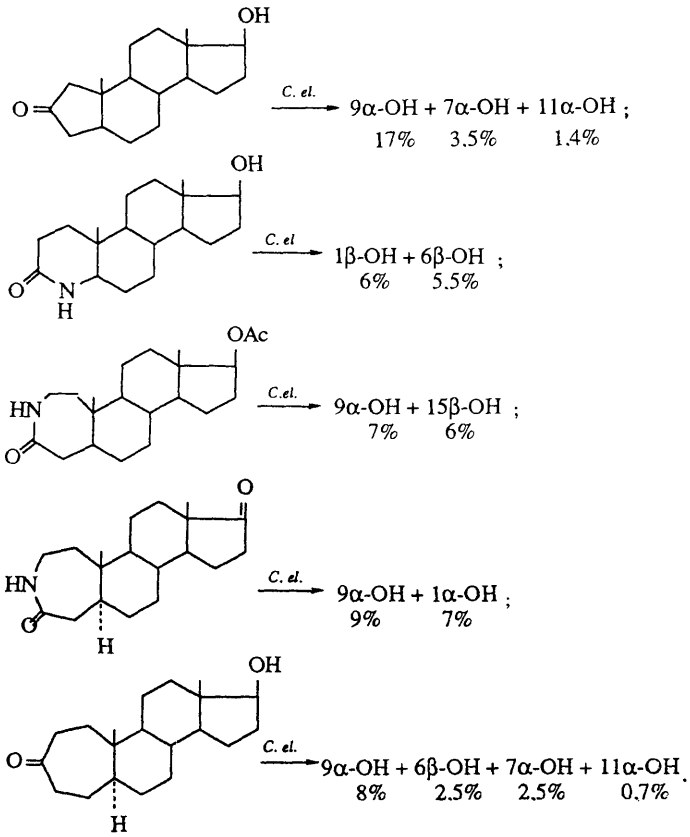
These data demonstrate convincingly also a significant dependence of the specificity of the hydroxylation on the position of the keto-group in the *D* ring. Thus, whereas the main product of the incubation of 3β-acetoxy-17*a*-*D*-homoketone is the 7β-hydroxy-derivative, the transformation of its 17-oxo-analogue affords preferentially the 9α,14α-dihydroxy-derivative. We may note that the introduction of a nitrogen atom in the 17*a*-position in *D*-homo-5α-*H*-androstan-17-one probably inhibits the 14α-hydroxylation process catalysed by this culture. Thus, only monohydroxylation, preferentially in the 9α-position, has been observed for 3β-acetoxy-17*a*-aza-*D*-homo-5α-*H*-androstan-17-one (Scheme 20), in contrast to its carbo-analogue (Scheme 19).[90,92]

Scheme 20



The influence of substitution at C(3) on the specificity of hydroxylation can be clearly traced in relation to the transformation of 17*a*-aza-5α-*H*-androstanes by the *C.el* culture. A change in the structure of the *A* ring of 5α-*H*-androstanes introduces no less significant changes into the specificity of the hydroxylation of the structure. In a series of studies by Crabb and co-workers,[86–96] the influence of the *A* and *D* rings on the hydroxylation by the *C.el.* culture was investigated. Analysis of these data did not lead to the discovery of definite correlations. One can only note that the *A*-nor-, *A*-homo-, and aza-*A*-homo-5α-*H*-androstanes, whilst exhibiting a tendency towards monohydroxylation (preferentially in the 9α-position), are nevertheless transformed with a low degree of conversion regardless of the substitution in the *D*-ring (CO or OH group) (Scheme 21). In contrast to *C.el.*, the *A.o.* culture hydroxylates *A*-homo-3,17-diketone at the site typical for this micro-organism, forming the 11α-hydroxy-product in 58% yield.[93]

Scheme 21



VI. Hydroxylation of 5α-*H*-pregnanes

The virtually specific use of 5α-*H*-pregnanes in the synthesis of corticosteroids probably determined the choice of the hydroxylating microorganism and substrates, the range of which is extremely limited compared with 5α-*H*-androstanes. In the series of 5α-*H*-pregnanes, studies have been made on cultures known to possess the ability to hydroxylate Δ^4-3-oxosteroids in the following positions: 11β-(*Curvularia, Cunninghamella, Tieghemella*), 11α-(*Rhizopus, Aspergillus*), and 12β-(*Calonectria decora*).[2,6,11] Among the 5α-*H*-pregnanes, the 9α-hydroxy-derivatives have also been obtained,[118–122] but this type of transformation should be considered separately, because it is effected by bacteria and, in contrast to hydroxylation by fungi, takes place as a stage in the microbiological cleavage of the steroid molecule after the introduction of the Δ^4-3-oxo-group.[2,6–9]

The introduction of a hydroxy-group in the C(9)-, C(11α)-, and C(12)-positions ensures their subsequent transformation into the 11β-hydroxy-derivatives by chemical methods. On the basis of the same practical considerations, 3β-hydroxy- and most frequently 3-oxo-5α-*H*-pregnanes have been mainly investigated as substrates. Studies on compounds of this series are not quite so fundamental as those on 5α-*H*-androstanes and the results summarised in Table 5, do not reveal a rigorous correlation in the enzyme–substrate interaction. However, a few systematic studies on the substrate specificity of a number of cultures are of undoubted interest.

Continuing the studies on the enzyme–substrate interaction, Jones et al.[35] turned their attention to compounds of the pregnane series assuming undoubtedly that, when the side chain is capable of rotation, certain corrections may be applied to the model constructed on the basis of data for the androstane series. They investigated the set of microorganisms most effective in the transformation of 5α-*H*-androstanes: *A.o.*, three Rhizopus species, *C.d.*, and *D.r.*[35] Unfortunately, not having at their disposal such a variable set of substrates as in the androstane series, the authors were forced to restrict their studies to 20-oxo-5α-*H*-pregnanes substituted in the 3-, 7-, and 11-positions by oxygen-containing groups (Table 5). Owing to the lack of quantitative data on the transformation of substituted 20-oxopregnanes by the *A.o.* culture, only a qualitative analysis of the results is possible. 5α-*H*-Pregnane is hardly transformed by *A.o.* or a complex mixture of unidentified products is formed. On incubation with 3,20-dioxopregnane, the transformation proceeds via the pathway usual for this microorganism with formation of the 11α-hydroxy-product. However, on incubation with its 3β-hydroxy-analogue, hydroxylation in the 1β-position, atypical for *A.o.*, is observed after the introduction of the 11α-hydroxy-group.

After prolonged incubation (6 days), 3β-hydroxy-5α-*H*-pregnan-20-one affords a mixture of the 1β,11α-dihydroxy- and 11α-monohydroxy-derivatives, the dihydroxy product being formed not synchronously but consecutively via the 11α-monohydroxy-product (Table 5). It has been noted[25] that 1β,11α-dihydroxylation is characteristic of 16β-methyl-Δ^{16}- and 16α-,17α-epoxy-analogues of 3β-hydroxy-5α-*H*-pregnan-20-one, but is not observed in the case of their 17α-hydroxy- and 16-methyl-Δ^{16}-derivatives. The behaviour of the 2,20- and 3,20-diketones[25] derived from 5α-*H*-pregnane contrasts sharply with that of the 3β-hydroxy-analogues, affording exclusively the products of 11α-monohydroxylation. Here it is noteworthy that the corresponding Δ^4-3-oxo-analogues are converted quantitatively into the 6β,11α-dihydroxy-derivatives.

A remarkable result has been achieved by hydroxylating the steroid alkaloids funtumidine (3α-NH_2) and funtumine (3α-NH_2, 20α-OH), which are hydroxylated by *A.o.* in the 12β- and 11α-positions.[98] It follows from the results that the nature and stereochemistry of the substitution at C(3) affect extremely significantly the hydroxylation of 5α-*H*-pregnanes by the *A.o.* microorganism.

The *C.d.* microorganism dihydroxylates 3-oxo- and 3β-hydroxy-20-oxo-5α-*H*-pregnane in the 12β,15α-positions. When the C(12) atom is blocked by the 11α-hydroxy-group, the attack is directed exclusively to C(15) and a similarity is thus manifested with the behaviour of this culture in the 5α-*H*-androstane series. The stability of this type of specificity of hydroxylation has been observed for various substrates of the pregnane series regardless of the presence or absence of the Δ^4- and Δ^5-double bonds and even the junction between the *A* and *B* rings.[100,102] The ability of the *C.d.* culture, indicated in Scheme 22, to effect, together with hydroxylation, the isomerisation of 3-hydroxy-Δ^5-analogues to the Δ^4-3-oxo-derivatives is striking.

Table 5. Hydroxylation of substituted 5α-*H*-pregnan-20-ones by mould fungi.

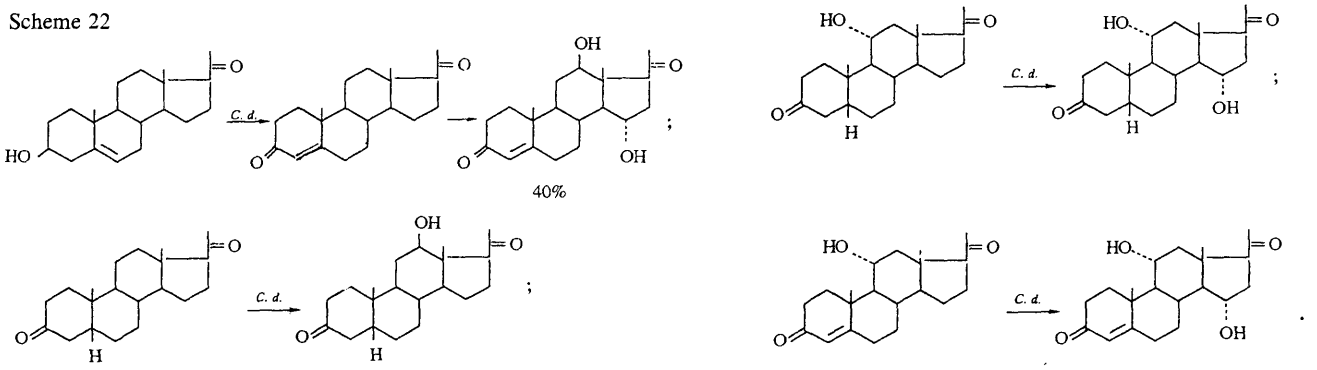
Substituent	Micro-organism	Initial compound, %	Principal hydroxylation site	Yield, %	Secondary hydroxylation site	Yield, %[a]	Refs.
–	*L.f.*	19	not isolated	–			[37]
–	*A.o.*	91	not transformed	–			[25]
2-CO	*A.o.*	0	11α	50	–	–	[25]
3-CO	*A.o.*	28	11α	38	11α, 17β	9	[25]
3-CO	*C.d.*	–	12β, 15α	40	–	–	[100, 102]
3-CO	*D.r.*	0	7α(3-CO → 3β-OH)	4	3-CO → 3β-OH	5	[35]
			7β(3-CO → 3β-OH)	5			
3-CO	*R.a.*	14	11α	12	7β, 11α(3-CO → 3β-OH)	7	[35]
3-CO	*R.c.*	7	11α	9	11α, 17-CO(3-CO → 3β-OH)	4	[35]
			11α, 17β	4	–	–	
			11α, 17-CO	7	11α(3-CO → 3β-OH)	3	
3-CO	*A.t.*	17	11β	10		5	[4]
3-CO	*S.c.*	–	11α	–			[63]
3-CO	*C.sp.*	–	9α	–			[67]
3-CO	*R.n.*	25	11α	22	7β, 11α(3-CO → 3-OH)	7	[35]
					11α(3-CO → 3β-OH)	5	
					3-CO → 3β-OH	3	
3-CO	*R.n.*	60	11α	40			[112]
7-CO	*C.d.*	45*	12β	18			[35]
7-CO	*C.d.*	10**	1α, 12β	33	1-CO, 12β	21	[35]
7-CO	*D.r.*	30	3β(7-CO → 7α-OH)	13	3β(7-CO) → 7β-OH)	3	[35]
7-CO	*R.n.*	21	3α, 11α	10			[35]
			3β, 11α	14			
			4α, 11α	12			
3-CO-11α-OH	*C.d.*	–	15α	–			[100]
11-CO	*D.r.*	10	3β	35			[35]
11-CO	*R.n.*	57	not isolated				[35]
11-CO	*C.d.*	58	not isolated				[35]
3β-OH	*R.n.*	12*	7β	15	7β, 12β	12	[35]
					11α	7	
3β-OH	*R.n.*	10**	7β, 12	22	7β, 11α	10	[35]
					7β	8	
					11α	5	
3β-OH	*R.a.*	14	11α, 7-CO	16	7β	11	[54]
3β-OH	*R.c.*	5	7β	11	11α	4	[35]
3β-OH	*A.o.*	3	1β, 11α	57	1β, 11α(3β-OH → 3-CO)	8	[17, 25]
3β-OH	*A.n.*	–	1β, 11α	–			[38]
3β-OH	*D.r.*	17	7α	9			[35]
7α-OH	*C.d.*	26	12β	17			[35]
7α-OH	*D.r.*	9	3β	27			[35]
7α-OH	*R.n.*	53	3β	24			[35]
11α-OH	*R.n.*	58	not isolated				[35]
11α-OH	*C.d.* *D.r.*	10	3β	35			[35]
11β-OH	*C.d.* *D.r.* *R.n.*	64—71	not isolated				[35]
3β-OH-Δ^{16}	*C.d.*	21	not isolated				[35]
3β-OH-Δ^{16}	*D.r.*	8	14α, 15β	21			[35]
3β-OH-Δ^{16}	*R.n.*	16	7α, 15α	12			[35]
			7α	13			
3β-OH-11-CO	*P.f.*	–	7-CO, 15β	12			[64]

Table 5 (cont'd).

Substituent	Micro-organism	Initial com-pound, %	Principal hydroxylation site	Yield, %	Secondary hydroxylation site	Yield, %*	Refs.
3β-11β-$(OH)_2$	*D.v.*	–	16α	–			[64]
3β, 21-$(OH)_2$	*R.a.*	–	7β	–			[69]
3β-OH-5, 6α-O	*C.l.*	–	11β	24—45			[105, 106]
3β, 21-$(OH)_2$-5, 6α-O	*C.l.*	–	11β	16			[105]
3β-OH-21-OAc-5, 6α-O	*C.l.*	–	11β	50			[105, 106]
3β, 17β-$(OH)_2$-5, 6α-O	*C.l.*	–	11β	20			[105]
3β, 17α, 21-$(OH)_3$-5, 6α-O	*C.l.*	–	11β	16			[105]
3β, 17α-$(OH)_2$-21-OAc-5, 6-O	*C.l.*	–	11β	28			[105]
3β, 17α, 20α-$(OH)_3$-5, 6α-O	*C.l.*	–	11β	33			[105]
3β, 20β-$(OH)_2$-5, 6α-O	*C.l.*	–	11β	52			[105]
3β-OH-16α-Me-5, 6α-O	*C.l.*	–	11β	45			[106]
3β, 20α-$(OH)_2$-5, 6α-O	*C.l.*	–	11β	8			[105]
3β, 20β, 21-$(OH)_3$-5, 6α-O	*C.l.*	–	11β	10			[105]
3β-OH-21-OAc-16α-Me-5, 6α-O	*C.l.*	–	11β	55			[105]
3β-OAc-21-OAc-16α-Me-5, 6α-O	*C.l.*	–	11β	36			[105]
3β,21-$(OH)_2$-5, 6α-O-17α, 20-O	*C.l.*	–	11β	28			[105]
3β-OH-5, 6α-O-16, 7α-O	*C.l.*	–	11β	45			[105, 106]
3β, 17β-$(OH)_2$-5, 6α-O	*C.l.*	–	11β	31—45			[105, 106]
3β-OH-16, 17α-O	*A.o.*	–	1β, 11α				[38]
3β, 21-$(OH)_2$-5α-Br-6β-F-16α-Me	*C.l.*	–	11β	45	3β-OH-5α-Br-6α-F-Δ^4-3-oxo-6α-F		[68]
3α-NH_2	*A.o.*	–	12β	6.7	11α	8.5	[98]
3-CO-11α-OH	*C.d.*	–	15α	60			[100, 102]
3-CO-16, 17α-O	*R.n.*	–	11α	60			[111]
3-CO-21-OH-16β-Alk	*Gi.c.*	–	11α	–			[58]
3-CO-21-OH-16α-тр.Bu	*Ph.*sp.	–	11β	–			[60]
			11α	–			
3-CO-17α, 21-$(OH)_2$	*C.l.*	–	11β, 14α	50—53			[107]
3-CO-17α, 21-$(OH)_2$	*C.bl.*	–	11α	70—75			[107]
3-CO-17α, 21-$(OH)_2$	*T.o.*	–	11α	40—45	11β	5	[107]
3-CO-16α, 17α-21-$(OH)_3$	*C.l.*	–	11β	38—42			[107]
»	*T.o.*	–	11α	30	11β	5	[107]
»	*C.bl.*	–	11α	60—65	11β	5	[107]
3-CO-21-OH-16, 17α-O_2CMe_2	*C.l.*	–	11β	10—12			[107]
»	*T.o.*	–	11β	40—45	11α-OH	5—8	[107]
»	*C.bl.*	–	11α	30—35			[107]
			11β	10—12	11-CO	5	

Notation. Incubation of the steroid dissolved in ethanol for 24 h (*), 6 days (**), 2 days (+), and 4 days (++).

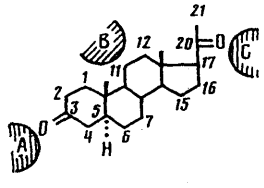
Scheme 22



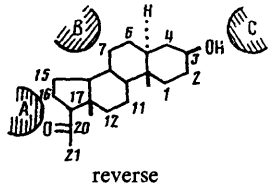
A surprising feature of *C.d.* is the 11α-hydroxylation of 3α,6α-dihydroxy-substituted derivatives, uncharacteristic of this microorganism, which is manifested only in the 5β-*H*-pregnane series.[101] Earlier data indicating 15β-hydroxylation by the *C.d.* culture[103] must be regarded as erroneous.

Three species of the Rhizopus bread fungi, namely *R.a.*, *R.c.*, and *R.n.*, have been investigated as regards the hydroxylation of 5α-*H*-pregnanes. The differences between these cultures are similar to those observed for 5α-*H*-androstanes[23,24] but are less appreciable. A tendency towards the degradation of the side chain is observed in the transformation effected by *R.n.* Analysis of the results presented in Table 5 indicates a distinct tendency of this microorganism to effect the preferential 11α-hydroxylation of 3-ketones derived from 5α-pregnane and the 7β-hydroxylation of 3β-hydroxy-5α-*H*-pregnanes: a deviation is observed only for the 3β-hydroxy-Δ^{16}-analogue, which is attacked by hydroxylase not only in the C(7) position (from the α-region) but also in the allylic 15-position. The hydroxylation in the 12β-position on incubation with 3β-hydroxy-pregnanolone is atypical for *R.n.*[35] Murray and Peterson[55] pointed out in an earlier patent that *R.n.* hydroxylates this compound, as well as its 3,20-dioxo-analogue, in the 11α-position. The general similarity in the differentiated behaviour of 3-oxo- and 3β-hydroxy-derivatives of 5α-*H*-pregnanes and 5α-*H*-androstan-17(or 16)-ones indicates probably the possibility of using the enzyme–substrate interaction model in the 5α-*H*-pregnane series, taking into account, naturally, the stereochemical possibilities of the side chain and the conditions in the binding of the 20-oxo-group (Scheme 23):

Scheme 23



normal



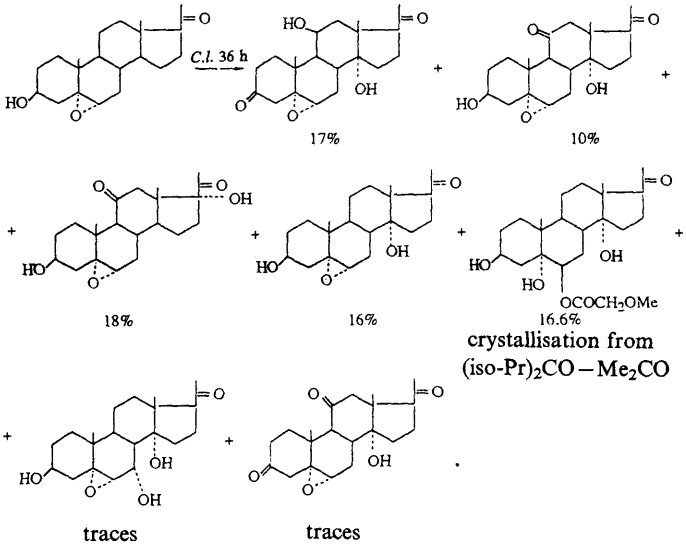
reverse

In constrast to 5α-androstanes, which are hydroxylated in the 9α-position by *C.el.*, *D.c.*, *A.r.*, *W.g.*, and *R.a.* cultures (Tables 2 and 4), only the *Circinella* sp. strain introduces the 9α-hydroxy-group into 5α-*H*-pregnanes.[67] This property is also manifested in relation to Δ^4-3-oxopregnane.[123] The series of data presented in Table 5 for transformations involving the 11α-position in 3β-hydroxy-5α,6α-disubstituted pregnanes, effected by the *C.l.* microorganism considered in the preceding context, shows that, when hydroxylation at C(7), (5,6-α-epoxy- or 6β-fluoro) is blocked, the reaction takes place exclusively at the C(11) atom. The same result casts doubt on the official view that the hydroxylation of 3β-hydroxy-derivatives of pregnanes unsaturated in the *A* ring is impossible.

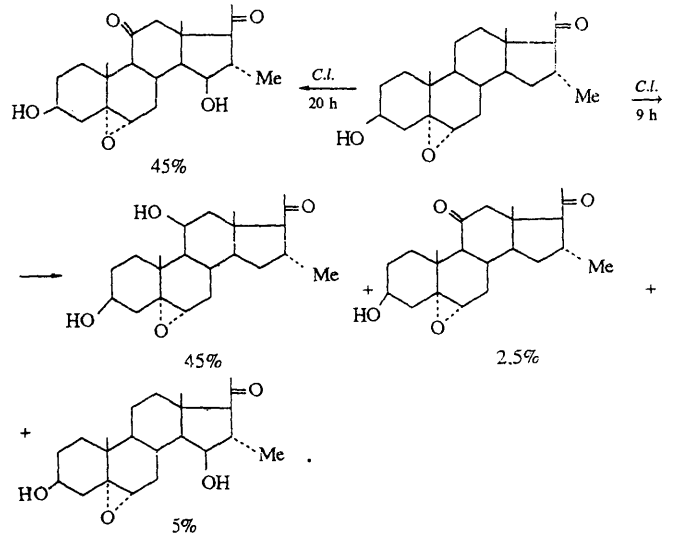
All the results presented in Table 5 concerning the transformation of 5,6-epoxides by *C.l.* are based on data obtained after brief incubation designed to achieve the maximum yield of the target product — 5,6α-epoxy-11β-hydroxy-5-pregnanones. Subsequent studies showed that this reaction proceeds with parallel formation of 14α-hydroxy-derivatives[104] and that prolonged incubation leads to a range of products[105] in which the hydroxylation site is now determined by the 11β- and 11α-hydroxy-groups and the 11-oxo-group (invariably formed by the subsequent oxidation of the 11β-hydroxy-group) already present in the molecule.[2,6]

For example, Scheme 24 presents the mixture of products obtained on transformation of 5,6α-epoxy-3β-hydroxy-5-pregnan-20-one by *C.l.* over a period of 36 h, in which the formation of 7α-hydroxy- and 17α-hydroxy-derivatives can be regarded, according to the authors, as a consequence of the directing effect of the 14α-hydroxy- and 11-oxo-groups introduced into the molecule beforehand,[105] while the formation of the 11,14α-disubstituted derivatives may be regarded as a consequence of the mutual influence of these groups. We shall show in relation to yet another example that the transformation time is an extremely important parameter in reactions of this type.[105] Here too the authors assume that the final oxidation product — the 15β-hydroxy-11-oxo-derivative — is formed as a result of the subsequent oxidation of both minor products (Scheme 25).

Scheme 24

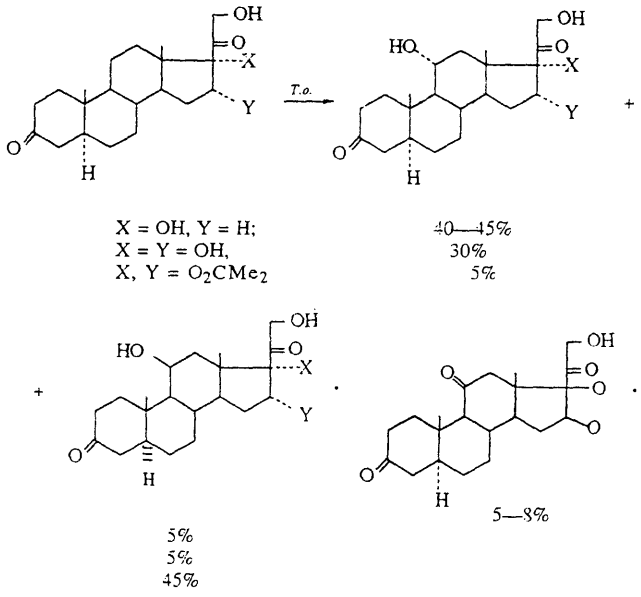


Scheme 25



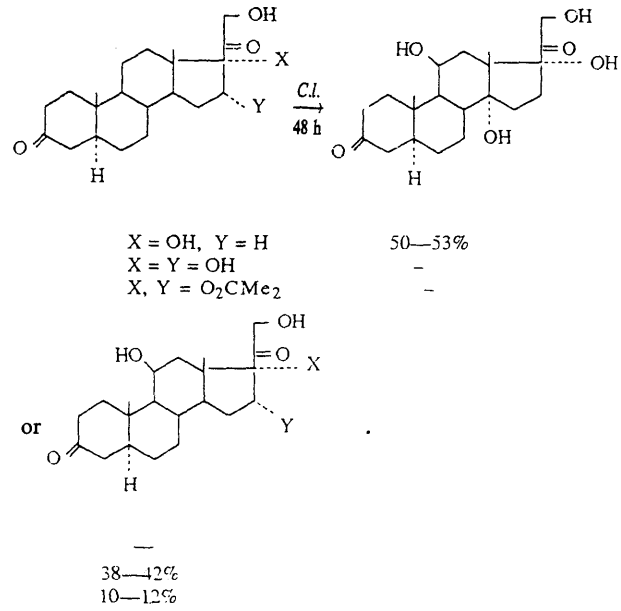
The *D* ring-substituted compounds are effectively transformed by *C.bl.* The 17α-hydroxy-, 16α,17α-dihydroxy-, and 16α,17α-dioxyisopropylidene-3,20-dioxo-5α-pregnanes are substituted preferentially in the 11α-position, the presence of an oxygen-containing 16α-substituent in the α-region of the steroid molecule stimulating the competitive 11β-hydroxylation (Table 5). The *T.o.* culture behaves similarly, but in this case the 16α,17α-acetonide group blocks 11α-hydroxylation almost completely, promoting 11β-hydroxylation (Scheme 26).

Scheme 26



All three types of substrate illustrated in Scheme 27 are hydroxylated by *C.l.* in the 11β-position, whereas in the case of the 16-unsubstituted compound (X = OH, Y = H) the subsequent 14α-hydroxylation is observed, being probably inhibited in the last two cases by the oxygen atom at C(16). Thin-layer chromatographic analysis of the reaction mixture after incubation of 17α,21-dihydroxy-5α-pregnane-3,20-dione for 24 h demonstrates the presence of 3–5% of the initial substrate, 15 and 20% respectively of the 14α- and 11β-monohydroxy-derivatives, and 30–35% of the 11β-,14α-dihydroxy-derivative, from which it follows that the 11β- and 14α-hydroxylation reactions take place consecutively. One must not fail to note that *C.l.* transforms cortexolone into a mixture of 11β- and 14α-monohydroxy-derivatives (67 and 15% respectively).[107] The authors conclude from this that 5α-*H*-steroids are sterically less hindered than their Δ^4-3-oxo-analogues. Because of this, the introduction of a hydroxy-group in one of the positions does not rule out the possibility of their reorientation relative to the enzyme, which leads to the formation of 11β,14α-dihydroxy-compounds. The authors therefore believe[107] that 16α,17α-dihydroxy-5α-pregnan-3-one is more susceptible to transformations by *C.bl.* and *T.o.*, affording 11α-hydroxy-groups in 65 and 30% yields respectively, while its Δ^4-3-oxo-analogue is not transformed by any of the cultures discussed.

Scheme 27



We do not find this view convincing; an explanation of the observed facts should probably be sought in the general model of the substrate–enzyme interaction involving pregnanes, in which the oxygen-containing functional group in the *D*-ring (its nature, position and stereochemistry) should not only participate but should also compete with the 20-oxo-group for geometrically or stereochemically favourable type of binding.

Analysing the data in Table 5 from the standpoint of Jones's model of the enzyme–substrate interaction, one may note that on the whole they agree with the postulate that three binding and simultaneously hydroxylating sites function on the surface of the enzyme. Indeed the pregnane monoketones, which can combine with the enzyme via only one centre, are hardly transformed, while in the presence of two terminal oxygen-containing groups in the steroid molecule hydroxylation at the site B takes place. In the presence of a second oxygen-containing substituent at the site B, hydroxylation can occur at the site A provided that it is not bound to a steroid molecule. When there are three oxygen-containing substituents, corresponding to the sites A, B, and C, in this case the transformation products can either not be isolated or, as happens when 11α-hydroxy-3,20-dioxopregnane is acted upon by *C.d.*, hydroxylation is apparently catalysed by one of the binding sites (Scheme 23).[102]

One should add to the foregoing that the transformation of 5α-*H*-pregnanes has also been achieved with the aid of streptomycetes of unidentified species and *S. roseochromogenes*, which introduce the 16-hydroxy-group into 3-oxo- and 3β-hydroxy-5α-*H*-pregnanes,[108,109] as in the case of compounds with the Δ^4-3-oxo-group. The mechanism of the hydroxylation of the *D* ring by these representatives of the Schizomycetes class as well as 9α-hydroxylation by *Rhodococcus*[118–122] probably differs from the mechanism proposed by Jones and co-workers for fungi.

Analysis of the data described makes it possible to trace the dependence of the specific capacity of microorganisms for hydroxylating 5α-*H*-steroids on the type of steroid and on the nature of the substituents in it (oxo-, hydroxy-, and acetoxy-groups), their

positions and stereochemistry, and their number. This makes it possible to achieve specific hydroxylation of steroids in a particular position within the molecule. Numerous examples, summarised in the tables, show that the saturation of the rings of the steroid molecule is not an obstacle to effective hydroxylation. This means that there is a possibility of altering the sequence in which 5α-*H*-steroids are converted into biologically active preparations, involving their initial hydroxylation and subsequent dehydrogenation of the *A* ring. The reverse and generally accepted sequence, involving the hydroxylation of the Δ^4-3-*H*-oxo-(or $\Delta^{1,4}$-3-oxo)-derivatives obtained initially from the 5α-*H*-steroids, is the subject of the next part of the review, in which emphasis is laid on the authors' own studies on the use of the *Rhodococcus* culture which catalyses both these processes.

References

1. A V Kamernitskii, R K Abubakirov, M B Gorovets, et al. *Khimiya Spirostanolov* (The Chemistry of Spirostanols), Nauka, Moscow, 1986
2. A A Akhrem, Yu A Titov *Steroidy i Mikroorganizmy* (Steroids and Microorganisms), Nauka, Moscow, 1970, pp 251, 323
3. A Noguchi, D K Fukushima *J. Org. Chem.*, 1965, **30**(1) 3552
4. D R Brannon, F W Parrish, B J Wiley, L Long *J. Org. Chem.*, 1967, **32**(5) 1521
5. H E Kenney, E A Weaver, M F Wall *J. Am. Chem. Soc.*, 1958, **80**(20) 5568
6. A A Akhrem, Yu A Titov *Mikrobiologicheskie Transformatsii Steroidov* (Microbiological Transformations of Steroids), Nauka, Moscow, 1965
7. W Charney, H L Herzog *Microbial Transformations of Steroids*, Acad. Press, New York, 1967
8. L L Smith *Terpenoids and Steroids*, 1974, Vol. 4, p. 394
9. K Kieslich *Microbial Enzymes and Bioconversions*, Acad. Press, London, 1980, p. 369
10. S B Mahato, S Banerjee *Phytochemistry*, 1985, **24**(2) 1403
11. S B Mahato, S Banerjee, S Podder *Phytochemistry*, 1989, **28**(1) 7
12. H L Holland *Chem. Soc. Rev.*, 1982, **11**(4) 371
13. J E Bridgeman, J W Browne, P C Cherry, et al. *Chem. Commun.*, 1969, 463
14. J M Evans, E R H Jones, A Kasai, et al. *Chem. Commun.*, 1969, 1491
15. J E Bridgeman, P C Cherry, A S Clegg, et al. *J. Chem. Soc., Perkins Trans. 1*, 1970, 250
16. J E Bridgeman, P C Cherry, E R H Jones, G D Meakins *Chem. Commun.*, 1997, 482
17. A S Clegg, E R H Jones, Q D Meakins, J T Pinhey *Chem. Commun.*, 1970, 1029
18. G D Meakins, J W Blunt, I M Clark, et al. *J. Chem. Soc., Perkin Trans. 1*, 1971, (6) 1136
19. A M Bell, P C Cherry, I M Clark, et al. *J. Chem. Soc., Perkin Trans. 1*, 1972, (16) 2081
20. A M Bell, W A Denny, E R H Jones, et al. *J. Chem. Soc., Perkins Trans. 1*, 1972, (21) 2759
21. A M Bell, J W Browne, W A Denny, E R H Jones, *J. Chem. Soc., Perkin Trans. 1*, 1972, (23) 2930
22. J W Browne, W A Denny, E R H Jones, et al. *J. Chem. Soc., Perkin Trans. 1*, 1973, (14) 1493
23. V E M Chambers, W A Denny, J M Evans, et al. *J. Chem. Soc., Perkin Trans. 1*, 1973, (14) 1500
24. A M Bell, I M Clark, W A Denny, et al. *J. Chem. Soc., Perkin Trans. 1*, 1973, (19) 2131
25. A S Clegg, W A Denny, E R H Jones, et al. *J. Chem. Soc., Perkin Trans. 1*, 1973, (19) 2137
26. A M Bell, V E M Chambers, E R H Jones, et al. *J. Chem. Soc., Perkin Trans. 1*, 1974, (2) 312
27. V E M Chambers, E R H Jones, G D Meakins, et al. *J. Chem. Soc., Perkin Trans. 1*, 1975, (1) 55
28. A M Bell, E R H Jones, G D Meakins, et al. *J. Chem. Soc., Perkin Trans. 1*, 1975, (4) 357
29. J M Evans, E R H Jones, G D Meakins, et al. *J. Chem. Soc., Perkin Trans. 1*, 1975, (14) 1356
30. V E M Chambers, W A Denny, E R H Jones, et al. *J. Chem. Soc., Perkin Trans. 1*, 1975, (14) 1359
31. A M Bell, A D Boul, E R H Jones, G D Meakins *J. Chem. Soc., Perkin Trans. 1*, 1975, (14) 1364
32. E R H Jones, G D Meakins, J O Miners, et al. *J. Chem. Soc., Perkin Trans. 1*, 1975, (16) 1552
33. A M Bell, E R H Jones, G D Meakins, et al. *J. Chem. Soc., Perkin Trans. 1*, 1975, (20) 2040
34. E R H Jones, G D Meakins, J D Miners, A L Wilkins *J. Chem. Soc., Perkin Trans. 1*, 1975, (22) 2308
35. E R H Jones, G D Meakins, J O Miners, et al. *J. Chem. Soc., Perkin Trans. 1*, 1976, (17) 1842
36. G C Bird, P M Fredericks, E R H Jones, G D Meakins *J. Chem. Soc., Perkin Trans. 1*, 1980, (3) 750
37. W A Denny, P M Fredericks, I Ghileran, E R H Jones, et al. *J. Chem. Res. (S)*, 1980, (1) 20
38. B. P. 1342583, *Chem Abs.*, 1972, **76** 125417
39. D H Peterson, H C Murray *J. Am. Chem. Soc.*, 1952, **74** 1871
40. R F Mininger, M E Wall, R G Dworshac, R W Jackson *Arch. Biochem. Biophys.*, 1956, **60** 427
41. Y Sato, S Hayakawa *J. Org. Chem.*, 1961, **26** 4181
42. S Hayakawa, Y Sato *J. Org. Chem.*, 1962, **27** 704
43. Y Sato, S Hayakawa *J. Org. Chem.*, 1963, **28** 2739
44. S Hayakawa, Y Sato *J. Org. Chem.*, 1963, **28** 2742
45. Y Sato, S Hayakawa *J. Org. Chem.*, 1964, **29** 198
46. Y Sato, J A Waters, H Kaneko *J. Org. Chem.*, 1964, **29** 3732
47. J A Jaffer, C Blunden, T A Crabb *Phytochemistry*, 1983, **22**(1) 304
48. E Kondo, T Mitsugi *J. Am. Chem. Soc.*, 1966, **88**(20) 4737
49. Japanese P. 71. 39067; *Ref. Zh. Khim.*, 1972, 20N403
50. Japanese P. 71. 39068; *Ref. Zh. Khim.*, 1972, 20N404
51. Japanese P. 71. 40754; *Chem. Abs.*, 1972, **76** 71013
52. Japanese P. 72. 13716; *Ref. Zh. Khim.*, 1972, 20N405
53. US P. 3575810
54. US P. 2602769; *Chem. Abs.*, 1952, **46** 8331
55. US P. 2877162; *Chem. Abs.*, 1960, **54** 1625
56. U Valcavi, P Martelli, U C Sironi, S Tedeschi *Il Farmaco*, 1975, **30**(6) 464
57. US P. 2889255; *Chem. Abs.*, 1959, **53** 22098
58. US P. 2985563; *Chem. Abs.*, 1961, **55** 23923
59. US P. 3009933; *Chem. Abs.*, 1962, **57** 3527
60. US P. 3054725; *Chem. Abs.*, 1963, **58** 912
61. US P. 3087938; *Chem. Abs.*, 1963, **59** 11625
62. US P. 3013945; *Chem. Abs.*, 1962, **56** 11586
63. BRD P. 1048579; *Chem. Abs.*, 1961, **55** 3656
64. BRD P. 1102733; *Chem. Abs.*, 1962, **56** 8803
65. BRD P. 1768203; *Chem. Abs.*, 1970, **73** 75656

66. US P. 2 876 170; *Chem. Abs.*, 1959, **53** 16 226
67. DDR P 20 643; *Chem. Abs.*, 1961, **55** 25 156
68. K Kieslich, G Schulz *Annalen*, 1969, **726** 152
69. F W Kahnt, C Meystre, R Neher, et al. *Experientia*, 1952, **8** 422
70. R M Dodson, A H Goldkamp, R D Muir *J. Am. Chem. Soc.*, 1960, **82** 4026
71. G Defaye, M J Luche, E M Chambar *J. Steroid Biochem.*, 1978, **9** 331
72. R C Meeks, P D Meister, S H Eppstein, et al. *Chem. Ind.*, 1958, (13) 392
73. BRD P. 1 021 845; *Chem. Abs.*, 1960, **54** 4686
74. US P. 2 981 659; *Chem. Abs.*, 1961, **55** 18 007
75. L Tan, P Falardeau *J Steroid Biochem.*, 1970, **1** 221
76. M Shibahara, J A Moody, L L Smith *Biochim. Biophys. Acta*, 1970, **202** 172
77. US P. 2 833 792; *Chem. Abs.*, 1958, **52** 20 272
78. E R H Jones *Pure Appl. Chem.*, 1973, **33** 39
79. R McCrindle, J K Turnbull, A B Anderson *J. Chem. Soc., Perkin Trans. 1*, 1975, (13) 1202
80. D Marcano, J F Giorgio, J M Evans, et al. *J. Org. Chem.*, 1978, **43**(20) 3960
81. D Marcano, J F Giorgio, J M Evans, et al. *Steroids*, 1983, **41** 1
82. R Jankov, M Stefanovic *Glas. Hem. Drus., Beograd*, 1975, **39**(9–10) 577
83. R Jankov, M Stefanovic *Glas. Hem. Drus., Beograd*, 1975, **39**(9–10) 591
84. M Stefanovic, R Jankov, G Urošević *Bull. Acad. Serbvesci et Arts*, 1977, **60**(16) 55
85. R Jankov, G Urošević, M Stefanovic *Glas. Hem. Drus., Beograd*, 1977, **42**(3) 237
86. R Jankov, G Urošević, M Stefanovic *Glas. Hem. Drus., Beograd*, 1980, **45**(11) 517
87. R Jankov, V Soskic, M Stefanovic *Glas. Hem. Drus., Beograd*, 1982, **47**(6) 241
88. R Jankov, V Soskic, M Stefanovic *Glas. Hem. Drus., Beograd*, 1983, **48**(4) 121
89. T A Crabb, P J Dawson, R O Williams *Tetrahedron Lett.*, 1975, (42) 3623
90. T A Crabb, J A Saul, R O Williams *J. Chem. Soc., Perkin Trans. 1*, 1977, (23) 2599
91. T A Crabb, P J Dawson, R O Williams *J. Chem. Soc., Perkin Trans. 1*, 1980, (11) 2535
92. T A Crabb, J A Saul, R O Williams *J. Chem. Soc., Perkin Trans. 1*, 1981, (4) 1041
93. T A Crabb, N M Ratcliffe *J. Chem. Res. (S)*, 1986, (2) 48
94. S A Campbell, T A Crabb, R O Williams *J. Chem. Res. (S)*, 1986, (6) 208
95. T A Crabb, M M Ratcliffe *J. Chem. Res. (S)*, 1986, (6) 1928
96. T A Crabb, M M Ratcliffe *J. Chem. Res. (S)*, 1988, (7) 207
97. I Belič, V Gaberc-Porekar, H Sočič, M Žakeg *Z. Allg. Microbiol.*, 1982, **22**(6) 359
98. G Creenspan, R Rees, L L Smith, H E Alburn *J. Org. Chem.*, 1965, **30**(12) 4215
99. DDR P. 19 658; *Chem Abs.*, 1961, **55** 26 361
100. BRD P. 1 067 020; *Chem. Abs.*, 1961, **55** 7758
101. A Schubert, K Heller, R Siebert *Tetrahedron*, 1962, **18** 993
102. A Schubert, R Siebert *Chem. Ber.*, 1958, **91**(9) 1856
103. A Schubert, G Langbein, R Siebert *Chem. Ber.*, 1957, **90**(11) 2576
104. E Caspi, P J Ramm, R E Gain *J. Am. Chem. Soc.*, 1969, **91**(14) 4012
105. K Kieslich, H Wieglepp *Chem. Ber.*, 1971, **104**(1) 205
106. G Cleve, G A Hoyer, K Kieslich, H Wieglepp *Chem. Ber.*, 1972, **105**(2) 658
107. M L Gerasimova, T I Gusarova, V M Ryzhkova *Khim.-Farm. Zh.*, 1986, (10) 1259
108. US P. 3 033 749; *Chem. Abs.*, 1953, **58** 4630
109. R Neher, P Desaulles, E Vischer *Helv. Chim. Acta*, 1958, **41** 1667
110. US P. 3 033 748; *Chem. Abs.*, 1962, **57** 16712
111. H E Kenney, S Serota, E A Weaver, M E Wall *J. Am. Chem. Soc.*, 1960, **82**(14) 3689
112. S H Eppstein, D H Peterson, H M Leigh, et al. *J. Am. Chem. Soc.*, 1953, **75**(2) 421
113. US P. 2 882 205; *Chem. Abs.*, 1959, **53** 16 226
114. US P. 2 875 134; *Chem. Abs.*, 1959, **53** 16 226
115. S C Pan, A I Laskin, B Junta, et al. *Abstr. 148th Meeting Am. Chem. Soc.*, Chicago, 1964, p. 140
116. US P. 2 721 828; *Chem. Abs.*, 1956, **50** 7891
117. M Stefanovic, S J Husinec, R M Jankov, M Bralovic *Glas. Hem. Drus., Beograd*, 1981, **46**(7) 319
118. A M Turuta, A B Kamernitzky, N E Voishvillo, et al. *Mendeleev Commun.*, 1991, (3) 113
119. N E Voishvillo, A M Turuta, A V Kamernitskii, et al. *Khim.-Farm. Zh.*, 1992, (2) 64
120. N V Dzhlantiashvili, A M Turuta, A V Kamernitskii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1992, (5) 1182
121. N E Voishvillo, A M Turuta, A V Kamernitskii, et al. *Prikl. Biokhim. Mikrobiol.*, 1992 (in the press)
122. A M Turuta, N E Voishvillo, A M Kamernitskii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1992, (8) (in the press)
123. A Schubert, D Onken, R Siebert, K Heller *Chem. Ber.*, 1958, **91** 2549
124. US P. 3 117 144; *Chem. Abs.*, 1964, **60** 11 344g

Received 6th May 1992

Translated from *Uspekhi Khimii* 61 1932–1966 (1992) U.D.C. 632.95:504.06

Pesticides in the environment

N N Mel'nikov
Institute of Chemical Plant Protecting Agents

ABSTRACT. The most important studies on the behaviour of six classes of pesticides in objects within the environment are described systematically and discussed. General schemes for the metabolism of certain pesticides in animal organisms, plants, and the soil are presented. The principal requirements which must be met by modern pesticides and the conditions for their safe use are characterised.

The bibliography includes 250 references.

Contents

I. Introduction 1058
II. Chlorohydrocarbons 1059
III. Organophosphorus pesticides 1060
IV. Synthetic pyrethroids 1065
V. Carbamic acid derivatives 1066
VI. Urea derivatives 1068
VII. Conclusion 1071

I. Introduction

Nature began to be acted upon by human society in the period when human activity changed from food gathering to farming and cattle rearing. As a consequence of the vigorous development of industry in the XXth century, the pollution of the environment proceeded most vigorously. In a simplified way, the term environment is understood to imply the upper part of the lithosphere (in the main soil) together with the biosphere and cosmic space surrounding the terrestrial globe and acting upon vital processes. The biosphere comprises all living organisms, including animals, plants, microorganisms, as well as the residues from these organisms at different stages of their decomposition and conversion into the simplest organic and inorganic compounds. The atmosphere, the hydrosphere, and the soil are included here. An enormous number of organisms live in these spheres. For example, according to the data of different investigators, one hectare of soil contains 1000–7000 kg of bacteria, 100–1000 kg of microfungi, 10–300 kg of algae, 5–10 kg of protozoa, 1000 kg of arthropods, and 300–1000 kg of earthworms.[1]

In connection with the considerable pollution due to man's economic activity, the problem of the protection of the environment has become urgent in our time.[2–5]

The scale and nature of the pollution of the environment by various products of anthropogenic activity can be inferred even from the following examples: as a result of the combustion of coal and brown coal, about 3000 tonnes of mercury enter the atmosphere annually and, when account is taken of the waste from different branches of industry and medical services about 10000 tonnes of mercury enter the environment.[6–10] Since mercury is able to accumulate in living organisms and can be converted into the ethylmercury ion, which is highly toxic and carcinogenic, it constitutes a serious danger to man.[10–12]

Many marine and river organisms already contain considerable amounts of mercury and its concentration increases every year. In view of this, the use of mercury compounds as pesticides in economically developed countries has virtually ceased despite their considerable value.

A second important pollutant of the environment is lead, which is known to exhibit a psychotropic activity. Lead compounds enter the environment in large amounts with the exhaust gases of automobiles employing petrol containing lead compounds as anti-knock additives.[13] In addition, polyhalodibenzofurans and polyhalodibenzo-*p*-dioxins, which exhibit teratogenic and blastomogenic activities, affect the skin, and are acutely toxic,[14] as well as carcinogens such as benzopyrene and benzanthracenes[18] enter the environment with exhaust gases. According to the results of some investigators,[15] the amount of the above compounds formed per kilometre of highways is 1.5 μg. We may note that the use of lead anti-knock agents has continued in many countries to this day, as a result of which lead salts and many organochlorine compounds accumulate in the environment.

One should also note that the accumulation of heavy metals such as cadmium[8,15] and chromium[17] in the environment has likewise increased.

Nitrogen and sulphur oxides, which are the products of the combustion of various types of fuel containing sulphur, are fairly serious pollutants.[19] Polycyclic hydrocarbons with blastomogenic activity are known to be formed on combustion of wood, coal, and brown coal. We may note that tobacco smoke is also a pollutant, since it contains about 800 different substances, including extremely toxic aromatic and heterocyclic compounds.

The pollution of the environment by arsenic compounds is significant.[10,20,20a] Some of them were used until the end of the 1940's as agents combating agricultural pests and also for the protection of wood against rotting. Organic arsenic compounds also continue to be used as herbicides at the present time.[21] Arsenic compounds can penetrate into plants and can migrate via their vascular systems, which frequently leads to the pollution of the products of the cultivation of plants. The soil of many countries as well as the world ocean contain nowadays very large amounts of arsenic compounds.[20,22] Up to 8 million tonnes of petroleum and petroleum products enter the world ocean annually.[22]

Polychlorobiphenyls, used in the electrical industry, as plasticisers, and in other branches of industry, polychlorodibenzofurans and polychlorodibenzo-*p*-dioxins, formed mainly on chlorination of various products and on combustion of refuse and industrial waste are also pollutants.[23] The latter compounds are so stable that they withstand heating above 600 °C.[14] Certain polychlorodibenzo-*p*-dioxins are extremely toxic and exhibit teratogenic and carcinogenic

activities and affect the skin. Thus LD_{50} for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in relation to monkeys is only 70 μg kg^{-1}.[14] The high solubility of the above compounds in lipids leads to their accumulation in human and animal fatty tissue and also in human milk.[23,24] Polychloro-derivatives have been detected in human milk in many countries. All these compounds are extremely stable in objects within the environment and can persist for more than 10 years even under tropical conditions.

We may point out that about 55000 chemical compounds have now been detected in objects within the environment. According to our calculations, about 500 million tonnes of different products of anthropogenic activity are discharged into the environment annually.

Pesticides are physiologically active substances and therefore special requirements ensuring adequate safety in their practical application must be imposed on them. Altogether a little more than 1 million tonnes of pesticides are used annually. As the relevant data accumulate, the requirements which must be met by pesticides become more stringent. The fraction of pesticides in all the pollutants introduced by man into the environment is ~0.2%, which is less almost by a factor of 5 than the fraction of detergents.

Standards which must be satisfied by modern pesticides have been established in terms of the following parameters: persistence characterised by the half-life (or the total decomposition into simplest chemical compounds safe to man and to useful organisms); minimum chronic toxicity for man and animals; the absence of mutagenic, carcinogenic, and teratogenic activities;[25,26] the absence of negative effects when small doses of the preparations are consumed with food products by man and animals; the absence of cumulative activity; selectivity of action in relation to useful organisms; low toxicity for useful hydrobionts and many others.[27]

Together with acute and chromic toxicity and the existence of other remote effects resulting from the action of the preparation on man, animals, birds, and other useful organisms, the persistence of pesticides, which depends on their chemical stability and the rate of their metabolism in objects within the environment, is very important. The type of metabolism is also significant, since it determines the safety of the preparation.[28] The following formula has been proposed to compare the ecological stresses exerted by different preparations:[29]

$$ES = (C/LD_{50})H,$$

where ES is the ecological stress per hectare, C the norm set for the consumption of the preparation (g ha^{-1}), H the half-life (persistence) of the preparation in weeks, and LD_{50} the acute toxicity for the given organism. Naturally the above formula does not yield an absolute value, but it makes it possible to obtain comparative characteristics of individual preparations.

Despite the vigorous propaganda by the "greens" against the use of pesticides, the scale of their practical employment has continuously expanded, which is indicated by the data in Table 1. However, by virtue of the systematic improvement of the range of preparations, their tonnage has significantly decreased. This is associated with the fact that the new preparations, developed in recent years, have extremely low consumption norms which are tens of times and in certain cases hundreds of times lower than the consumption norms of the pesticides used previously. There has been not only a growth of the requirement for pesticides but also a decrease in the employment of obsolete preparations and preparations with large consumption norms and a high persistence. Thus there has been a sharp decrease in the requirement for all organochlorine insecticides and in the economically developed countries their use has ceased altogether. For example, DDT is used only in China, India, and in certain countries of Asia and Africa. The use of herbicides such as sodium trichloroacetate and dalapon has been reduced.

Table 1. The amounts of pesticides sold in 1972 and 1989 and the forecast for 1995 in millions of US dollars.[30]

Group of pesticides	1972	1989	1995 (forecast)
Herbicides	4160	9500	10940
Insecticides	4090	6200	7110
Fungicides	2525	4490	5055
Plant growth regulators	375	800	1080
Nematocides and fumigants	410	510	575
Total	11560	21500	24760

New insecticides with consumption norms up to 20 g ha^{-1},[31,32] herbicides with consumption norms of 10–50 g ha^{-1},[33–35] and fungicides with consumption norms up to 150 g ha^{-1} [36–38] have appeared and the use of insect pheromones has also accelerated,[39] which makes it possible to reduce significantly the consumption of insecticides.

Data on individual most important classes of compounds are presented below.

II. Chlorohydrocarbons

Among organochlorine insecticides, preparations such as DDT, hexachlorocyclohexane, aldrin, dieldrin, heptachlor, endrin, chlordan, mirex, kepone, endosulfan, and certain others have found practical applications in agriculture, industry, and the health service. DDT has been used on the largest scale. During 50 years (since the discovery of its insecticidal properties), approximately 5 million tonnes have been used. Hexachlorocyclohexane is employed on a somewhat smaller scale and preparations obtained by diene synthesis are used in still smaller amounts. Their accumulation in the environment is therefore significantly smaller than that of DDT.

Despite the negative attitude of many specialists to DDT, one cannot fail to note its positive role in health protection and in agriculture. In agriculture, DDT replaced extremely toxic arsenic compounds and in health protection measures it saved more than 15 million people from malaria and prevented epidemics of typhus, encephalitis, sleeping sickness, elephantiasis, the plague, tularemia, and others. However, one cannot close one's eyes also to the negative properties of this preparation, which include primarily a high persistence in a wide variety of objects in the environment and in living organisms. DDT can accumulate in the tissues of man, animals, birds, and fish.[50] In particular, DDT has been detected in human blood and fatty tissues,[40–45] in human[46,47] and cows'[48] milk, and in food products.[49]

The behaviour of organochlorine insecticides in aqueous ecosystems[51-54] and in the eggs and flesh of wild and domestic birds[54-56] has been studied. Table 2 presents data on the contents of DDT and its first metabolite—dichlorodiphenylethylene (DDE)—in the fatty tissues of inhabitants of different countries.[40]

Table 2 shows that the greatest amounts of DDT and DDE are present in the fatty tissues of the inhabitants of those countries where DDT is widely used. We may note that the content of DDT has diminished in the tissues of the inhabitants of those countries where its use has been stopped.

Table 2. The contents of DDT and DDE in the fatty tissues of the inhabitants of different countries (mg/kg of fat).

Country	Year	DDT	DDE
Belgium	1975	8.29	6.50
Great Britain	1976–77	2.6	2.1
Holland	1969	4.0	1.26
Denmark	1972–73	4.8	—
Zaire	1983	62.45	—
India	1982	5.43	5.48
Iran	1974–76	8.13	5.26
Italy	1981–82	0.8	7.35
Canada	1979–81	3.69	2.56
Mexico	1975	8.31–21.47	18.36
New Zealand	1973	6.36	5.34
Pakistan	1971	25.0	13.6
Poland	—	4.08	7.28
Romania	1983	3.33	—
USA	1972	6.88	9.58
USA	1970	7.88	5.03
Turkey	1984–85	7.12	5.83
Finland	1983	0.33	1.58
France	—	3.27	—
Federal Republic of Germany	—	1.1	4.4
Czechoslovakia	1980–81	12.33	8.74
Japan	1984	1.99	1.85

The bioconcentration of DDT in various objects in the environment has also been investigated in both natural and model experiments.[57,58] The bioconcentration of DDT in biological objects is to a large extent associated with the type of its metabolism,[59] in which hydrophobic metabolites, accumulating in lipids, are formed in the first place.

Hexachlorocyclohexane accumulates in much smaller amounts in the fatty tissues of man and in milk, which is associated not only with the smaller scale of its use but also with its significantly smaller persistence.[40] Among all the isomers of hexachlorocyclohexane, the β-isomer accumulates in greatest amounts. It is distinguished not only by a lower volatility but also by a greater chemical stability.

Endosulfan,[60] toxaphene,[61] and other organochlorine insecticides[40] accumulate in objects in the environment in much smaller amounts. In view of the sharp decrease in the use of organochlorine insecticides, their content in the environment is being gradually reduced.

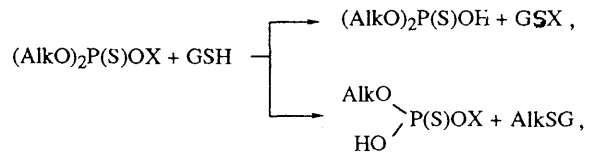
The effect of organochlorine pesticides on the soil microflora has been studied.[62-64] It has been established that, when aldrin and certain other insecticides are systematically applied, microorganisms are suppressed and the pesticide is gradually degraded.[64]

Despite the appreciable contamination of food products by organochlorine insecticides, in most cases their content in milk and other food products is within the limits of the norms established by the World Health Organisation.[65,66]

It is of interest that methoxychlor (I), whose metabolism leads to the formation of hydrophilic products, does not accumulate in the organisms of mammals and hardly contaminates milk.[67] Furthermore, methoxychlor is less toxic by an order of magnitude than DDT (for many arthropods, it is less toxic by only a factor of 1.5 than DDT).

$$CH_3OC_6H_4CHC_6H_4OCH_3$$
$$\quad\quad\quad

formation of diesters from triesters, interaction with glutathione transferase, for example[68]



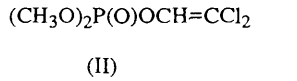
degradation of the ester part of the molecule containing the carboxy-group, and the formation of conjugates with carbohydrates in plants, with glucuronic and humic acids in the soil, and with sulphates in mammalian organisms.

Some of the reactions listed above are illustrated below by individual examples. We may note that the reactions of organophosphorus compounds depend not only on the structure of the phosphorus-containing part of the molecule but also on the structure of the organic groups linked to the phosphorus atom.[68]

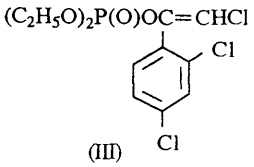
The methyl esters of phosphorus acids are comparatively effective alkylating agents, which also leads to their degradation and conversion into compounds with an extremely low toxicity.

About 100 organophosphorus pesticides are used nowadays on different scales.[69] In the present review, it is impossible to characterise the behaviour in the environment of all the organophosphorus compounds employed, so that only substances used on a fairly wide scale will be described.

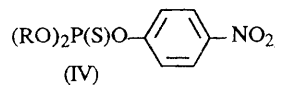
Among phosphoric acid esters these are dichlorophos (II) and chlorfenvinphos (III); among phosphorothioic acid esters these are metaphos (methylparathion) and thiophos (parathion) (IV), chlorpyrifos (V), diazinon (VI), fenitrothion (VII), fenthion (VIII); among phosphorodithioic acid derivatives these are phorate and terbufos (IX), phosalone (X), azinphos (XI), dimethoate (XII), thiometon (XIII), carbofos (malathion) (XIV), ninosan (XV), and also kitazin P (XVI), and acephate (XVII); phosphonates include chlorophos (XVIII) and glyphosate (XIX).



(II)

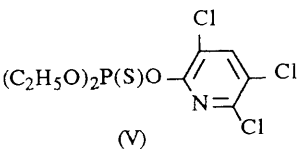


(III)

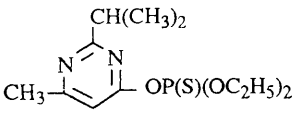


(IV)

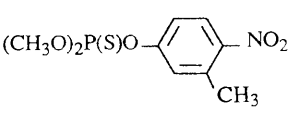
R = CH_3, C_2H_5



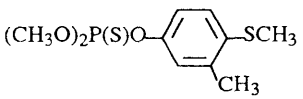
(V)



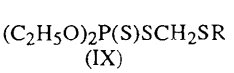
(VI)



(VII)

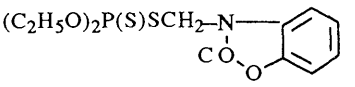


(VIII)

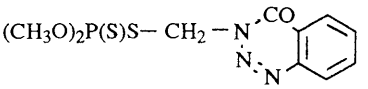


(IX)

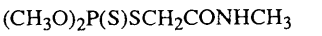
R = C_2H_5, $C(CH_3)_3$.



(X)

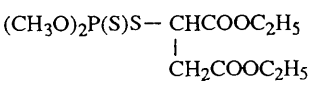


(XI)

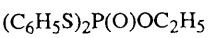


(XII)

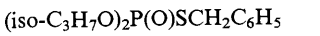
(XIII)



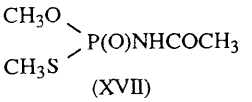
(XIV)



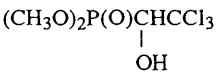
(XV)



(XVI)



(XVII)



(XVIII)

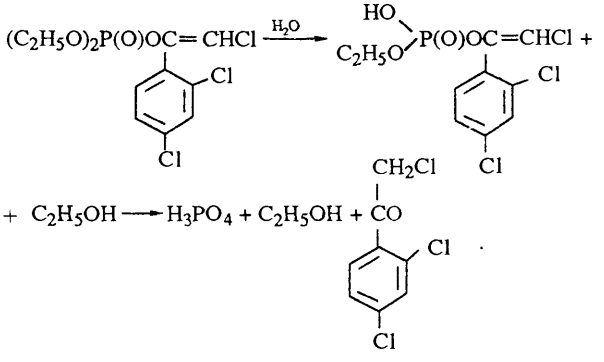
(XIX)

As stated above, the behaviour of pesticides in objects in the environment is influenced by numerous factors, including chemical and biological ones; the most important are the hydrolytic and oxidation reactions as well as the metabolism in various species of living organisms.

The first representative of the organophosphorus compounds listed above, namely dichlorophos, is a fairly labile substance and is readily hydrolysed by water even at comparatively low temperatures.[68,69] Thus in the tissues of the Atlantic salmon dichlorophos is not detected at all one day after entry at a water temperature of 12 °C, whilst at 4 °C only traces are found.[70] A similar picture has been observed also in milk: the preparation introduced into milk at 4–6 °C is not detected after 24 h.

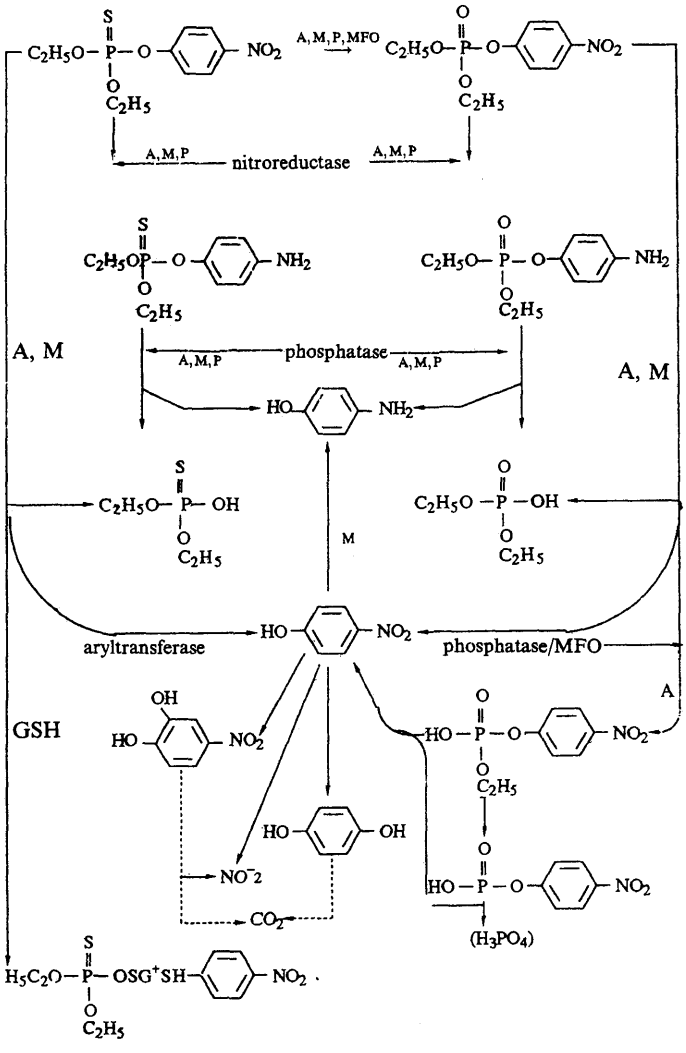
Dichlorophos decomposes to phosphoric acid and dichloroacetaldehyde and the latter is converted as a result of hydrolysis and oxidation into hydrochloric and oxalic acids.

Chlorfenvinphos decomposes in a more complex manner, forming on hydrolysis phosphoric acid and the lipophilic trichloro-acetophenone, which can accumulate in living organisms like other organochlorine compounds. For this reason, the application of this preparation is limited.



Parathion and methylparathion, whose behaviour in the environment has been studied in detail,[68,69,71–77] have found the greatest application in agriculture. The metabolism of parathion is different in different organisms, which can be clearly seen from Scheme 1.[68] We may note that the decomposition of methylparathion in the soil and other objects is significantly faster than that of parathion. Furthermore, it is less toxic and for this reason it has been successfully replacing parathion in recent years. The rate of decomposition of parathion and methylparathion depends not only on the nature of the soil, its moisture content, its content of organic substances, and the concentration of the insecticide, but also on the microflora, since different species of microorganisms will react with the preparations at different rates.[71,78]

Scheme 1

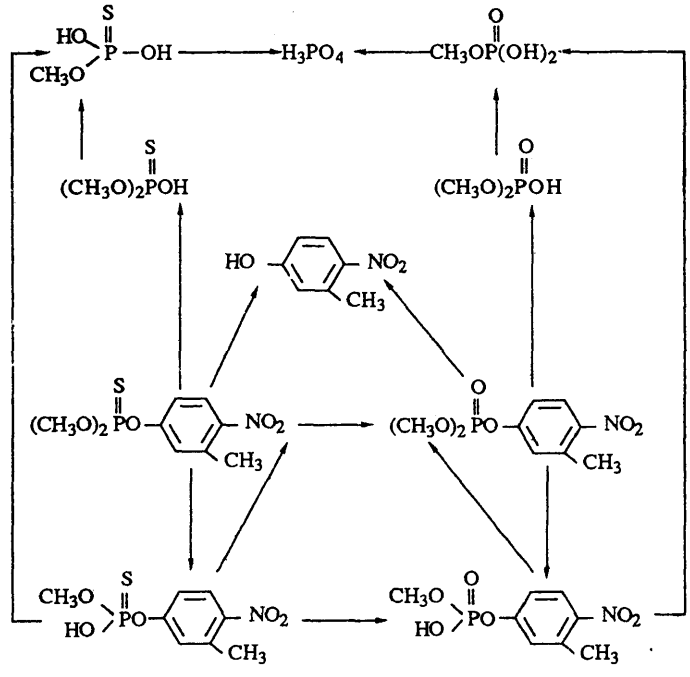


Scheme 1. Metabolism of parathion.
A = animals, M = microorganisms, P = plants, MFO = mixed function oxidases.

It is of interest to note that, in combination with toxaphene, polychlorcamphene, and oils, the duration of action of methylparathion on the cotton plant increases significantly,[77,79,80] which is apparently associated with the decrease in the rate of its hydrolysis in solutions in hydrophobic solvents such as the substances listed above. There are grounds for the assumption that a similar phenomenon may occur also in the soil. However, methylparathion decomposes in the soil in the course of 15–20 days, whilst parathion decomposes in 30–45 days, being fully converted into simple compounds (CO_2 and H_3PO_4 [71]).

We may point out that the accumulation of parathion and methylparathion in the organisms of mammals or hydrobionts has not been observed.[10,71] Special experiments on cows have shown that parathion administered in sublethal doses is almost completely eliminated from the organism in the course of 48 h.[10] The preparation does not remain in milk either.

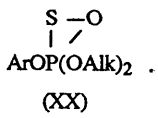
The closest homologue of methylparathion is fenitrothion, which exhibits a significantly smaller toxicity for animals compared with methylparathion.[81–83] The persistence of fenitrothion in ponds and bottom deposits,[84,85] in running water,[85] on leaves of the apple tree,[87] the poplar, and the birch,[86] and also its toxicity for fish[88] have been investigated. It has been shown that the persistence of fenitrothion is greater than that of methylparathion. The photolysis of fenitrothion[89,90] as well as its metabolism in vertebrates (mammals),[91] in the blue crab,[92] in the house fly which is resistant to the preparation,[93] and in the wheat plant,[94] as well as its oxidative dealkylation when acted upon by cytochrome P450 [95] have been studied. The general scheme illustrating the metabolism of phenitrothion in mammals is presented below (Scheme 2).



Scheme 2. Metabolism of fenitrothion in mammals.

In contrast to metabolism in mammals (rats), in which demethylation and dearylation take place, in the organisms of insects (the resistant house flies), the methyl group bound to the benzene ring is oxidised.[93] It may be that cytochrome P450 participates in this process. Many enzymes, including mixed function monoxidases, are involved in the degradation of insecticides of this type.

It has been suggested that the oxidation to oxones proceeds via a stage involving the formation of an unstable intermediate:



(XX)

We may note that soil microorganisms utilise in most cases the products of the metabolism of organophosphorus compounds as a source of carbon and phosphorus and that ultimately the majority of organophosphorus compounds decompose to CO_2 and H_3PO_4. The thione sulphur is converted into sulphuric acid, but the amount of the latter is so small that it has no practical importance as regards the acidification of the soil; in most cases the amount is only several tens of grammes per hectare.

The metabolism of fenthion is similar to that of fenitrothion,[68] but, in view of the presence of the sulphide group in the fenthion molecule, it is oxidised to a sulphoxide and a sulphone by the successive decomposition of the molecule by soil microorganisms. Fenthion is safe to a number of microorganisms and small invertebrates,[96] is moderately toxic for fish,[97] is moderately persistent in aqueous ecosystems,[98] and its toxicity is comparatively low for fungi and nitrogen-fixing bacteria and also for the little brown bat (*Myotis lucifugus*).[99]

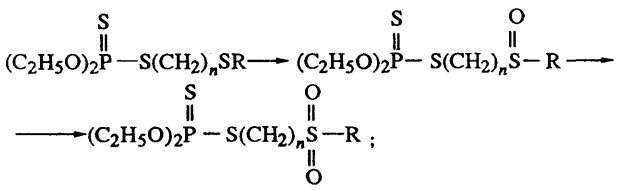
The persistence of diazinon is somewhat greater than that of the preparations described above.[100–106] Thus diazinon can be retained in organic soils for more than a year.[100] As a result of being washed out of the surface of the soil, it contaminates water bearing strata. It has been noted that diazinon is capable of being bioconcentrated by the aqueous fauna[101] but it is relatively rapidly eliminated from the organisms of fish. After 8 days, it cannot be found in the fish tissues. The metabolism of diazinon is even faster in warm blooded animals. It takes place in accordance with the general mechanism of the metabolism of phosphorothioates.[68,102,105] The principal reactions are oxidation and hydrolysis. Together with the formation of diazinonoxone derivatives, the side chains of the pyrimidine residue are oxidised at both the methyl and the isopropyl groups.[10,68,105] The main products of its metabolism in the soil are CO_2, H_3PO_4, and nitrogen. In plants diazinon also undergoes degradation. Thus, after cranberries have been treated with diazinon, the latter cannot be dectected in them after 42 days.[106]

Chlorpyrifos has similar properties.[107–118] In terms of its stability in the soil and in water, it approaches diazinon and in certain cases is superior to the latter.[107,108] The metabolism of chlorpyrifos involves, together with the hydrolysis of the ester linkages, the replacement of one or two chlorine atoms in the pyridine ring by the methylthio- and hydroxy-groups.[68,112] The hydrolysis of chlorpyrifos is fastest in an alkaline medium.[110]

It is of interest to note that phosphorothiolates (kitazin and hinosan) are hydroxylated in the aromatic ring in the course of their metabolism in plants (rice).[68]

In most cases the first product of the metabolism of organophosphorus insecticides forms conjugates with plant substances, which are sometimes fairly stable.[68] Such conjugates are obtained with carbohydrates and aminoacids. Acid sulphates are formed in animal organisms, being eliminated from them with products of their vital activity.

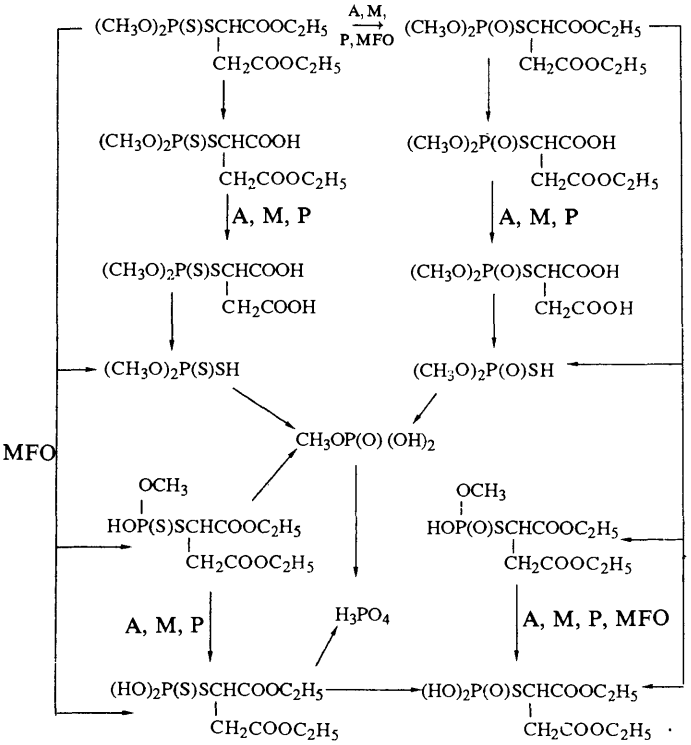
The behaviour of phosphorodithioic acid derivatives in objects in the environment depends to a large extent on the structure of the ester groups in the phosphorodithioate.[68] In this respect, the preparations phorate, terbufos, and disulfoton behave similarly.[119–125] Hydrolysis and oxidation of sulphide sulphur to the corresponding sulphoxides and sulphones are characteristic of these substances.



$R = C_2H_5$, $C(CH_3)_3$, $n = 1.2$.

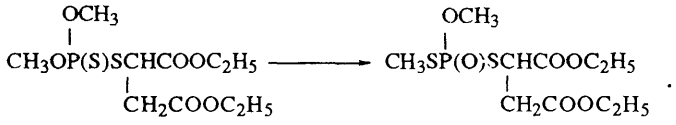
Together with the reactions described, oxidation of the thione sulphur and hydrolysis to phosphoric acid take place.[68,119] These preparations are used as soil insecticides.[121–123] Their complete degradation in the soil takes place in the course of 65–120 days, which depends to a large extent on the temperature and the nature of the soil. We may note that the preparations have a weak effect on the soil microflora.

Among phosphorodithioic acid derivatives, malathion (carbofos) has found the most extensive application as a contact insecticide.[71,126–135] A positive property of malathion is its low toxicity for mammals and its comparatively rapid decomposition in objects in the environment.[71] The metabolism of malathion is illustrated in Scheme 3.



Scheme 3. Metabolism of malathion.

Under the influence of certain inorganic substances and after prolonged heating, malathion may be converted into isomalathion, which is extremely toxic for mammals. It is sufficient to state that an admixture of 4% of isomalathion in malathion increases the toxicity of the preparation by an order of magnitude. The toxicity of malathion is also increased by an order of magnitude by an admixture of a side product of its manufacture—trimethyl phosphorodithioate.[126,131,132] The isomerisation of malathion to its toxic isomer led to the poisoning of humans in the course of its widespread application in the fight against the malaria mosquito in Pakistan.[71] The purity of the preparation used is therefore very important.

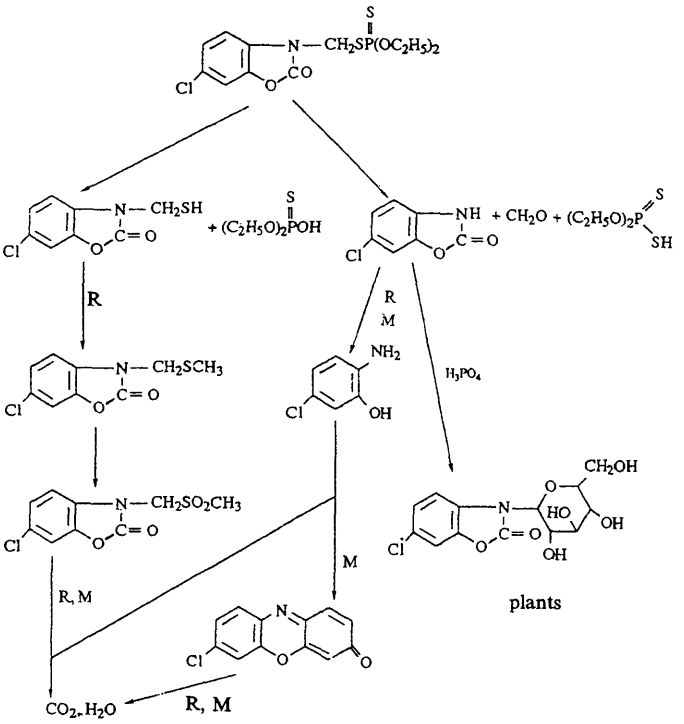


The rate of decomposition of malathion in objects in the environment is high and it vanishes rapidly from plants and animal organisms.[71,135] In the soil, malathion is also unstable and decomposes fairly rapidly. For example, in cherries, in red and black currants, and in other plants, malathion is hardly detected only 6–8 days after treatment with the preparation.[71]

Table 3. Toxicity of pyrethroid metabolites (LC_{50}) for hydrobionts (mg litre^{-1}).

Metabolite	LC_{50} (daphnia)	LC_{50} (fish)
3-(2,2-Dichlorovinyl)-2,2-dimethylcyclopropane-carboxylic acid	130	3
3-(2,2-Dibromovinyl)-2,2-dimethylcyclopropane-carboxylic acid	> 0.05	—
3-(2-Chloro-3,3,3-trifluoroprophenyl)-2,2-dimethyl-cyclopropanecarboxylic acid	100	16
3-Phenoxybenzyl alcohol	200	3–7
3-Phenoxybenzoic acid	85	13–36
2-(4-Chlorophenyl)-3-methylbutyric acid	—	10
3-Phenoxybenzaldehyde	> 0.025	—

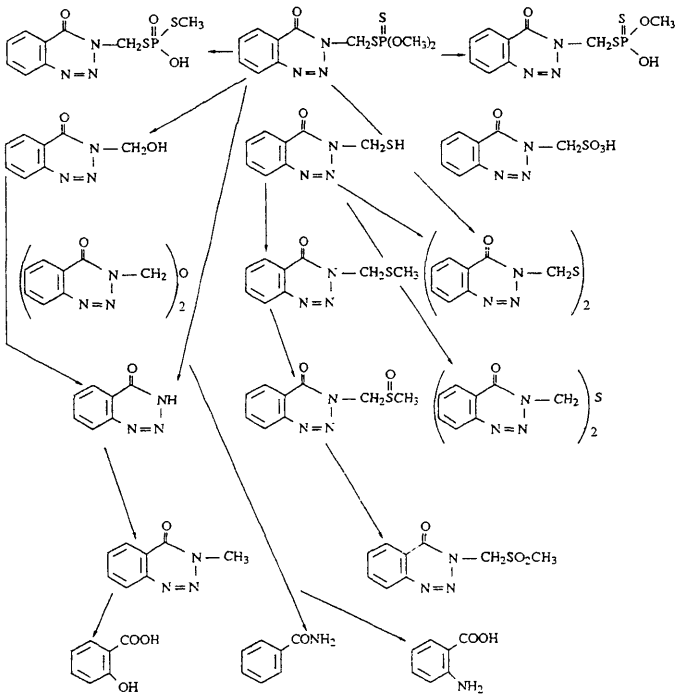
Phosalone persists in the environment for a longer time.[10] Thus it disappears from oak leaves on the twentieth day after spraying. During this period, it also decomposes in turf. Naturally, the phosalone decomposition time depends on the temperature and humidity. The higher the temperature, the faster the decomposition of the preparation. Phosalone decomposes in the soil over approximately the same period. The rate of its decomposition depends greatly on the composition and nature of the soil. However, in most cases part of the pesticide is bound firmly to the soil colloids and is included in the metabolism of organic substances.[136,137] The general direction of the metabolism of phosalone is illustrated in Scheme 4.[10,27,138]



Scheme 4. Metabolism of phosalone.
R = rats; M = microorganisms.

The final products of its metabolism in the soil under the influence of microorganisms are CO_2, H_3PO_4, N_2, etc.

Azinphos-methyl and especially azinphos-ethyl are more stable in objects in the environment. They have found fairly extensive applications in the fight against many plant pests. As can be seen from Scheme 5, even a relatively stable insecticide, such as azinphos-methyl, is almost completely decomposed by soil microorganisms.[139]



Scheme 5. Metabolism of azinphos-methyl.[139–143]

Other organophosphorus insecticides are less stable and are rapidly degraded to simple compounds.[10,27,71,68]

Among phosphonates, glyphosate, which is used nowadays in the fight against weeds, has found the most extensive application in agriculture. Numerous communications have been published on the properties of glyphosate and its behaviour in objects in the environment.[144,145]

Like all organophosphorus compounds, glyphosate decomposes almost completely in objects in the enviornment in the course of one vegetation period.[144] The decomposition products are phosphoric acid, CO_2, and other simple compounds.

It is seen from the data presented that among organophosphorus pesticides there are substances with different persistences, and from the necessary range of preparations available, it is possible to select the best substances for use under specific conditions.

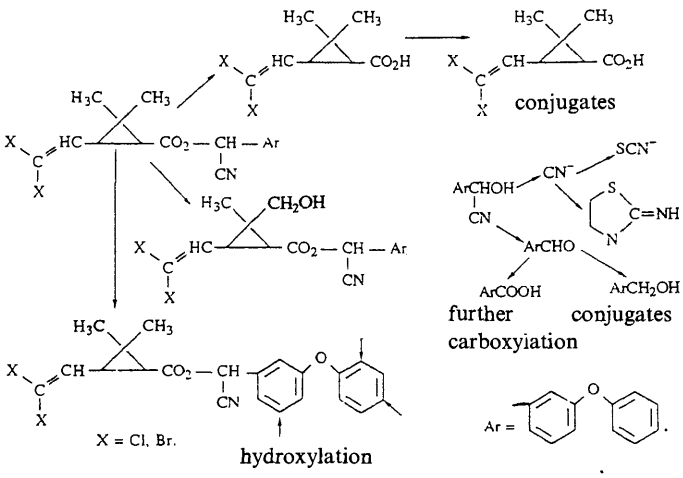
IV. Synthetic pyrethroids

The manufacture and use in agriculture of synthetic pyrethroids began only in the 1970's but at the present time they occupy a firm position in the range of modern insecticides. More than 15 preparations have found practical applications, the most important of which are permethrin, cypermethrin, and decis.

A positive property of this group of compounds is their relatively moderate toxicity for mammals and birds and also their low consumption norms, not exceeding 10–20 g ha^{-1} for a number of preparations.[146,147] Their comparatively high toxicity for hydrobionts, and in the first place for fish, must be included among the disadvantages of this group of substances.[148] Since synthetic pyrethroids are esters, they are relatively readily hydrolysed. The hydrolysis is faster in an alkaline medium. Synthetic pyrethroids decompose even more rapidly under the influence of soil microorganisms and also in animal organisms.[149,150] The rates of decomposition (%) of certain synthetic pyrethroids over a period of 8 weeks in mineral and organic soils are given below.[150]

	Permethrin	Cypermethrin	Fenvalerate	Decis
Mineral soil	94	96	88	48
Organic soil	84	84	42	26

Naturally not only the soil composition but also temperature and humidity are important for the decomposition of pyrethroids. The higher the temperature, the faster the decomposition of the preparations. The metabolism of cypermethrin and decis is indicated in Scheme 6.



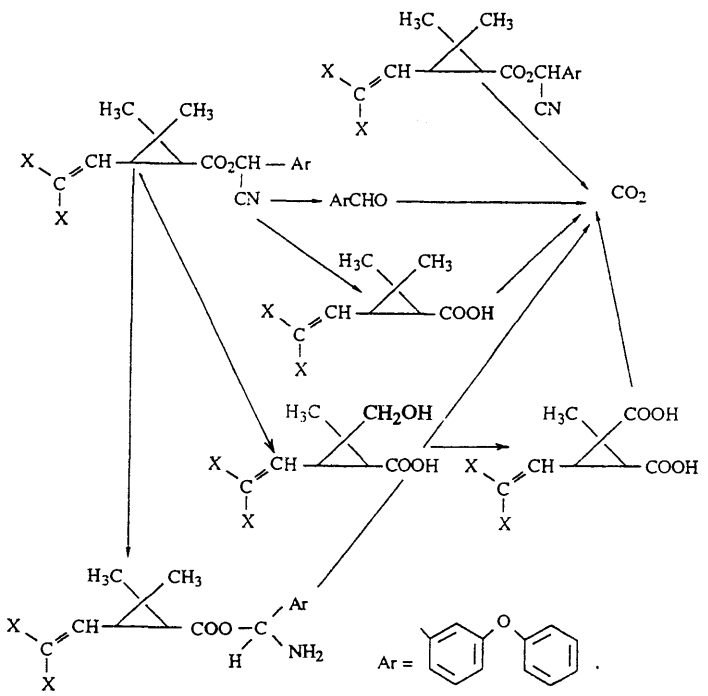
Scheme 6. Metabolism of cypermethrin and decis in animal organisms.

Since the products of the metabolism of pyrethroids are readily soluble in water, they do not accumulate in animal organisms, are rapidly eliminated with the products of their vital activity, and synthetic pyrethroids do not accumulate in milk.[148] The products of the metabolism of synthetic pyrethroids are much less toxic than the initial compounds for the majority of organisms, including hydrobionts.[151,152] Table 3 indicates the toxicity of certain metabolites of synthetic pyrethroids for hydrobionts.

For comparison we may point out that in the case of fish LC_{50} after exposure for 96 h is 0.0004–0.0007 mg $litre^{-1}$ for permethrin, 0.0004–0.002 mg $litre^{-1}$ for cypermethrin, 0.002 mg $litre^{-1}$ for fenvalerate, and 0.001 mg $litre^{-1}$ for decis.[151]

The metabolism of synthetic pyrethroids in plants also yields conjugates with glucose and other carbohydrates whose toxicity for mammals is low. However, these conjugates are incorporated in the general plant metabolism and their amount gradually diminishes.

In the soil, pyrethroids are fully decomposed to simple compounds, as shown in Scheme 7.[151]



Scheme 7. Metabolism of cypermethrin and decis in the soil.

It must also be pointed out that pyrethroids undergo photochemical transformations in the atmosphere and in an aqueous medium with almost complete degradation of the molecule.[149]

Analogues of cypermethrin and other pyrethroids which do not contain the phenoxybenzoyl fragment have now been synthesised. The study of the metabolism of the new groups of pyrethroids is being continued.[153]

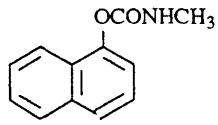
It is seen from the foregoing that synthetic pyrethroids are of great practical interest, particularly bearing in mind their extremely low consumption norms.

V. Carbamic acid derivatives

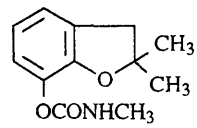
More than 40 carbamic acid derivatives have now found applications as pesticides in agriculture. They include mainly derivatives of *N*-methylcarbamic acid as insecticides[69] and arylcarbamic acid esters as herbicides.

Carbamic acid derivatives include compounds with different acute toxicities and different persistence. Despite their high toxicity, many such preparations have found fairly extensive applications in agriculture. Not being able to consider in detail all the preparations which have found practical applications, we shall examine certain typical examples.

The behaviour of carbamic acid derivatives in objects in the environment depends not only on the specific compound but also on the object in which the preparation is present. The metabolism of carbamic derivatives is most complete when the latter are acted upon by soil microorganisms.[154–165] Soil microorganisms also decompose stable preparations such as carbaryl (XXI) [154–156] and carbofuran (XXII).[157–165]

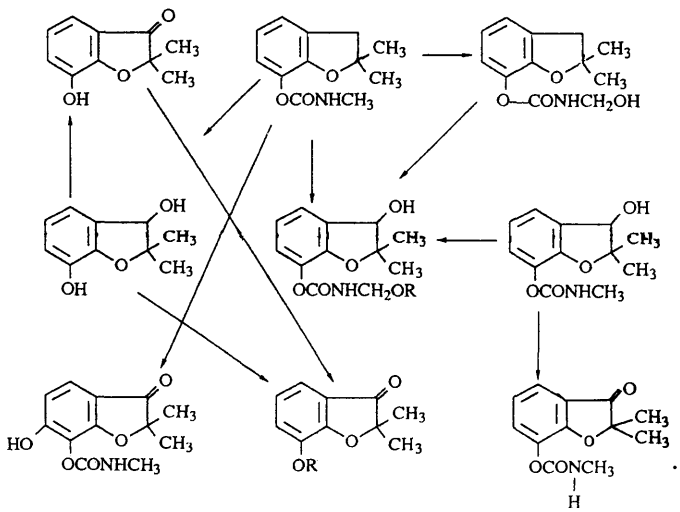


(XXI)



(XXII)

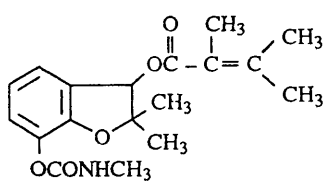
The main metabolic reactions of the carbamate insecticides are hydrolysis and oxidation.[155] The hydrolysis of the aryl esters of methylcarbamic acid leads to the formation of the corresponding phenol or other hydroxy-compound and methylcarbamic acid, which decomposes to an amine and CO_2.[155] This is accompanied by simultaneous oxidation processes which involve the methyl group and the aromatic or heterocyclic ring. Hydroxy-compounds form conjugates with organic substances (for example, humates) in the soil, with glucose in plants, and with sulphates and glucuronic acid in animal tissues. Scheme 8 presents the metabolism of carbofuran as an example.



R = glucose, glucuronic acid, or sulphate.

Scheme 8. Metabolism of carbofuran.

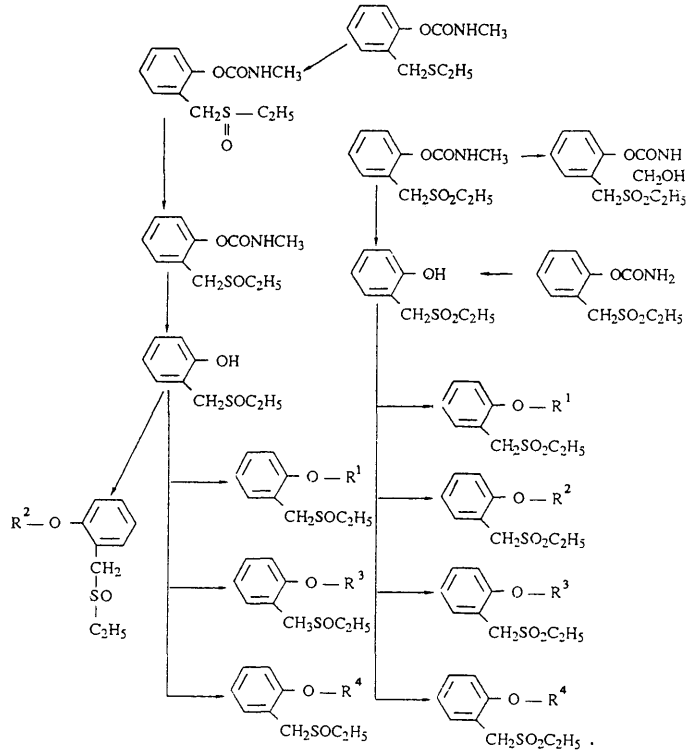
We may note that after the first stages of the metabolism shown in Scheme 8 the aromatic ring is hydroxylated and this is followed by further conversion into simple compounds. Conjugation with glucose in the 3-position takes place in plants. The carbofuran metabolites have been found in peppermint,[166] carrots,[167] ground nuts, and the cotton plant.[168] The 3-ester between carbofuran and angelic acid (XXIII) has been detected in the carrot.[167]



(XXIII)

It is of interest that the carbofuran 3-glucoside, obtained from carbofuran in plants, gives rise to glucuronides and the sulphates of the hydroxylated carbofuran metabolites in the rat organism.[169]

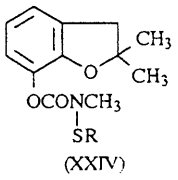
The metabolism of croneton may serve as a second example.[155] Like other preparations, croneton is fully decomposed in the soil, while in other objects it affords the products illustrated in Scheme 9.



R^1 = glucuronate, R^2 = glucoside, R^3 = condensation product, R^4 = sulphate.

Scheme 9. Metabolism of croneton.

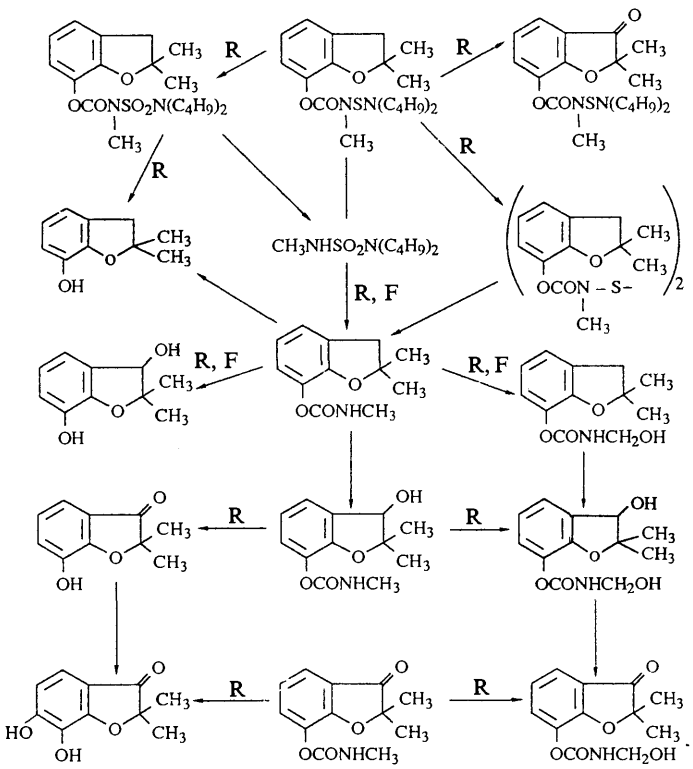
In view of the valuable properties of carbofuran as a pesticide, a new group of preparations with the general formula (XXIV) has been devised. These exhibit moderate insecticidal properties but are converted into carbofuran in the soil or in the insect organism.[170] This group of preparations has been called propesticides. Carbosulfan, promecarb, benfuracarb, and a number of others have found nowadays practical applications as insecticides. The study of the metabolism of this group of compounds showed that their metabolism in insect organisms differs somewhat from that in warm blooded animals.[170–177]



(XXIV)

R = $N(C_4H_9)_2$ (carbosulfan), $N{-}COOC_2H_5$ (promecarb), $N{-}CH(CH_3)_2$, $CH_2CH_2COOC_2H_5$ (benfunacarb).

Thus the metabolism of carbosulfan is different in the rat and fly organisms (Scheme 10). A greater amount of toxic substances is formed in flies, which results in an increase in the selectivity of the action of the preparation. A similar picture is observed also for other compounds of this type. The creation of propesticides is an example of the way in which an approach may be made to the creation of selective preparations on the basis of the study of metabolism in different species of living organisms.



Scheme 10. Metabolism of carbosulfan in the organisms of rats (R) and flies (F).[171]

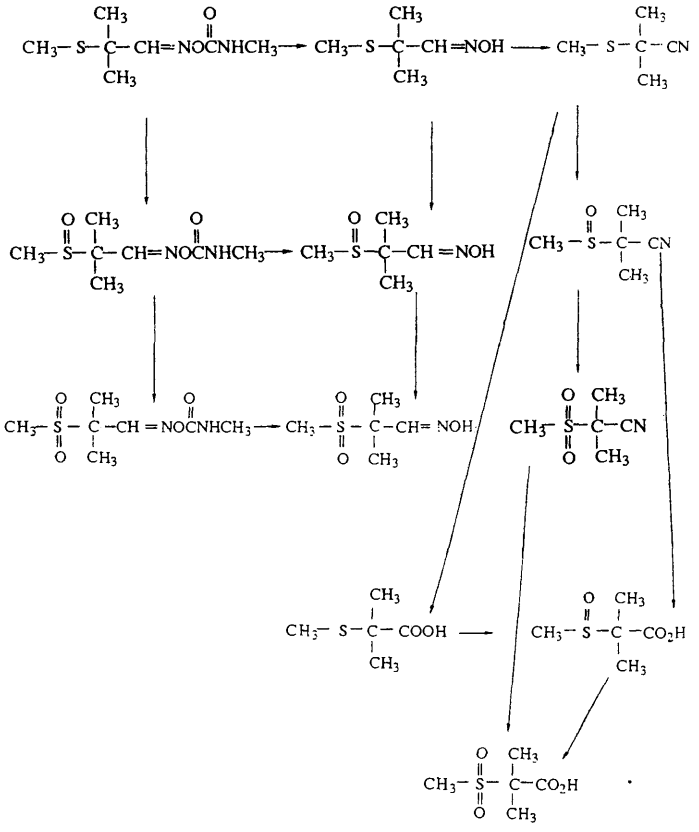
Carbosulfan is one of numerous examples. Such selective action has been observed not only in insecticides but also in herbicides and fungicides.

An important group of carbamate insecticides, which has found fairly extensive application in agriculture, is that of carbamate oximes, the commonest representative of which are aldicarb, aldoxicarb, oxamyl, and methomyl. However, the substances in this group are extremely toxic[178] and fairly stable in objects in the environment.[179–185]

One of the most toxic and stable preparations is aldicarb. In addition, its metabolites—the sulphoxide and the sulphone—are likewise highly toxic. The latter, called aldoxycarb, has found practical application as a soil insecticide. Aldicarb and its sulphoxide and sulphone are fairly stable and, when used systematically, can accumulate in the soil and can enter ground waters.[179,181–184] Even in dilute solutions, their hydrolysis is fairly slow.[186] It is of interest to note that the hydrolysis in chlorine water is faster (by 80% in 20 h).[185] The accumulation of aldicarb and of its toxic metabolites in the radish,[187] in the leaves and roots of sugar beet,[188–190], the potato, the pumpkin,[191,192] and a number of other

cultivated plants has been noted. It has been established that aldicarb and its metabolites persist in soil for up to 400 days after the introduction of the preparation in an amount of 15 kg ha^{-1},[181] but after only 10 days it is converted into the sulphoxide and the sulphone.[181] On the other hand, the sulphoxide is 99% converted into the sulphone after 120 days, the amount of sulphone by that time constituting more than 20% of the aldicarb introduced initially.[181] It has been shown with the aid of the ^{14}C-labelled preparation that ultimately aldicarb decomposes in the soil to CO_2 and other simple compounds.

The general aspects of the metabolism of aldicarb in various objects are presented in Scheme 11.[178,181,182,189] The use of aldicarb and similar preparations requires much caution and the maintenance of techniques and conditions ensuring the safety and protection of the environment. Bearing in mind the possibility of the accumulation of aldicarb and its toxic metabolites in ground waters, the use of this preparation in a number of states of the USA has been restricted. Under aerobic conditions, aldoxycarb was found to decompose in the soil in Florida after 42 days.[193]



Scheme 11. Metabolism of aldicarb.

Aldicarb can decompose photochemically with formation of methylamine, dimethyl disulphide, tetramethylsuccinodinitrile, dimethylurea, 2-methylthioisobutyronitrile, methacrylonitrile, and certain other products.[194] The aldicarb molecule undergoes almost total degradation under the influence of light. Such decomposition is possible, in particular, in an aqueous medium. Carbamate oximes such as methomyl and oxamyl are less stable and decompose faster in the environment.[155,195–201]

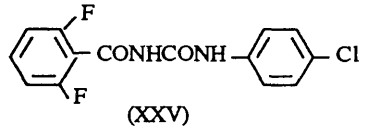
Despite the lower stability of the carbamate oximes enumerated above, work involving them requires much care and caution. This group of compounds is apparently one of the most dangerous among pesticides. However, their complete decomposition in the soil over one year does not give grounds for fear of contamination over any kind of long period.

VI. Urea derivatives

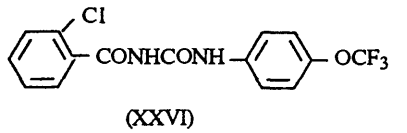
Among urea derivatives, four groups of substances have found practical application as pesticides: aryldimethylureas, arylmethoxymethylureas, benzoylureas, and sulphonylureas.[27,32,35,69]

Since the behaviour of the first groups of urea derivatives in objects within the environment has been fairly adequately described in our literature,[10,202,203] they will not be considered in this review.

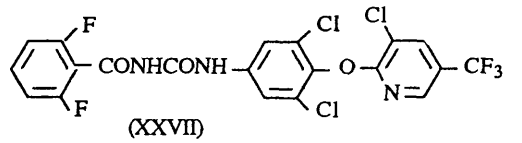
Insecticidal benzoylureas and herbicidal sulphonylureas have been vigorously investigated in recent years.[34,35,204] Among the insecticidal benzoylureas, diflubenzuron (XXV), triflumuron (XXVI), chlorfluazuron (XXVII), triflubenzuron (XXVIII), and certain others[204] have found practical applications.



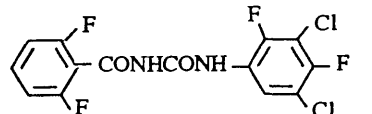
(XXV)



(XXVI)



(XXVII)



(XXVIII)

The insecticidal activity of compounds of this group is based on the inhibition of the formation of chitin during the development of insects and hence their destruction. The decomposition of these substances begins with hydrolysis accompanied by the elimination of the benzoyl group.[204–209] This may be accompanied by the simultaneous hydroxylation of the aniline ring. Next, arylurea decomposes with formation of aniline, which subsequently fully decomposes in the soil.[211]

Experiments with a carbon-labelled preparation showed that the decomposition, for example in the cotton plant, takes place over a period of two weeks.[208] The decomposition is most complete in the soil under the influence of microorganisms. In animal organisms, most of the preparation is eliminated with excrement[205] and virtually none enters milk.

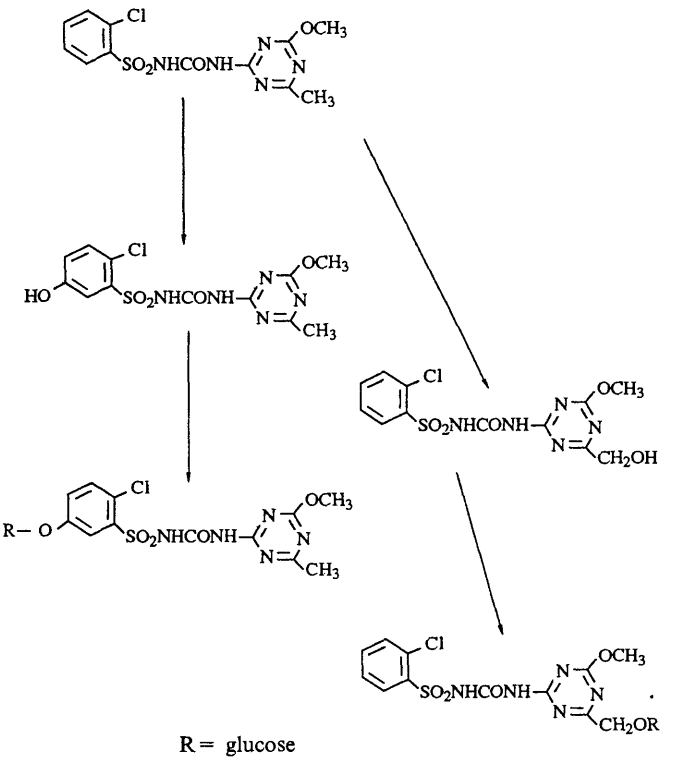
This group of compounds is of great practical interest, since they do not accumulate in objects within the environment and hydrolyse fairly rapidly in water and in the soil. A positive property of these substances is also the high selectivity of their action and low consumption norms (20 – 50 g ha^{-1}).

The herbicidal properties of sulphonylurea were discovered about 15 years ago and more than 15 preparations have now found practical applications. They are distinguished by a high selectivity of their action and low consumption norms when used to combat weeds, which is associated with their different metabolism in different plant cultures.[210] In plants resistant to sulphonylureas, their metabolism is fairly rapid and terminates after several hours,[210,212–215] whereas in plants sensitive to these compounds the metabolism is extremely slow.

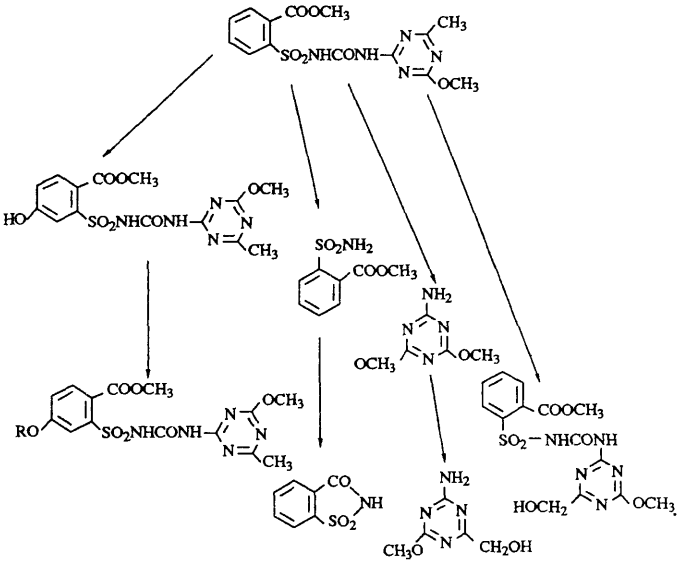
Table 4 presents certain sulphonylureas which are used as herbicides and which have found industrial or experimental industrial applications.

In the series of herbicidal sulphonylureas there are compounds with different persistence. These preparations range from those decomposing in the soil in several hours to those whose decomposition can occur over several months and even more than a year. An example is provided by chlorsulfuron. A plant culture sensitive to this compound may be damaged even a year after the preparation has been used (for a consumption norm up to 20 g ha^{-1}). A plant culture of this kind is, in particular, sugar beet.

The behaviour of a large number of derivatives of sulphonylurea in soil,[225–234] in various plant species,[210,219,235–239] and in animal,[219] bird, and fish organisms has now been studied in detail. It has been shown that the duration of their storage in the soil and their migration along the soil profile depend on the temperature and moisture content of the soil, on the pH of the medium, and on the composition of the soil. Certain sulphonylureas decompose in the soil in several hours. However, such decomposition takes place only as far as the hydrolytic stage and leads to the loss of herbicidal activity of the compound, while the complete decomposition of the majority of preparations in the soil takes place over a period of 15 – 30 days.[233,234] The complete decomposition of sulphonylureas in the soil by microorganisms takes place with total degradation of the molecule, while in plants a series of products non-toxic to the given plant are formed, as can be seen from Schemes 12 and 13 for the metabolism of chlorsulfuron in wheat and metsulfuron methyl in wheat and barley.[210,219]



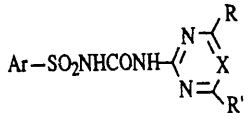
Scheme 12. Metabolism of chlorsulfuron in wheat.



Scheme 13. Metabolism of metsulfuron methyl in the wheat and barley plants.

Scheme 14 presents the metabolism of thifensulfuron in the rat organisms[219] and Scheme 15 illustrates the metabolism of bensulfuron in the rat and goat organisms.[219] We may note that significant amounts of the preparations were not detected in the milk of the animals.

Table 4. Certain herbicidal sulphonylureas



which have found practical applications.

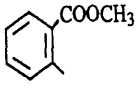
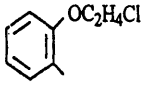
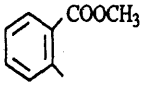
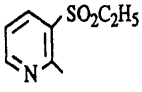
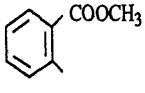
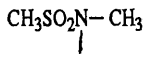
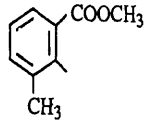
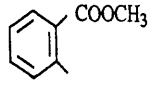
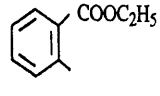
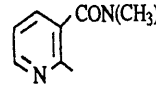
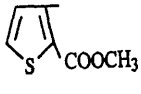
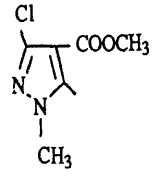
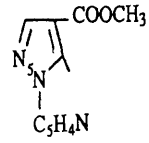
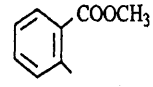
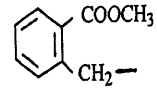
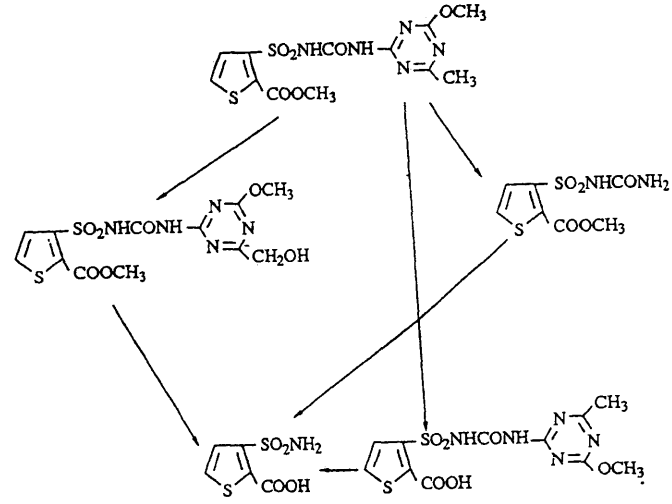
Ar	R	R′	X	Name	LD_{50} for rats, mg kg^{-1}	Consumption norm, g ha^{-1}	Refs.
	CH_3	OCH_3	N	Chlorsulfuron	5000	4–20	[216]
	CH_3	OCH_3	N	Metsulfuron methyl	5000	5–20	[217]
	CH_3	OCH_3	N	Triasulfuron	5000	10–20	[218]
	CH_3	OCH_3	CH	DPX-H6564	5000	20–50	
	OCH_3	OCH_3	CH	DPX E-9636	5000	20–40	[219]
	CH_3	CH_3	CH	Sulometuron methyl	5000	10–20	
	OCH_3	OCH_3	CH	Amidosulfuron	5000	40–60	—
	OCH_2CF_3	$N(CH_3)_2$	N	DPX-66037	5000	10–20	[221]
	$OCHF_2$	$OCHF_2$	CH	Primisulfuron	5000	10–30	—
	OCH_3	Cl	CH	Chlorimuron	4100	10–30	[214]
	OCH_3	OCH_3	CH	Nicosulfuron	5000	15–30	—
	CH_3	OCH_3	N	Thifensulfuron	5000	15–20	[222]

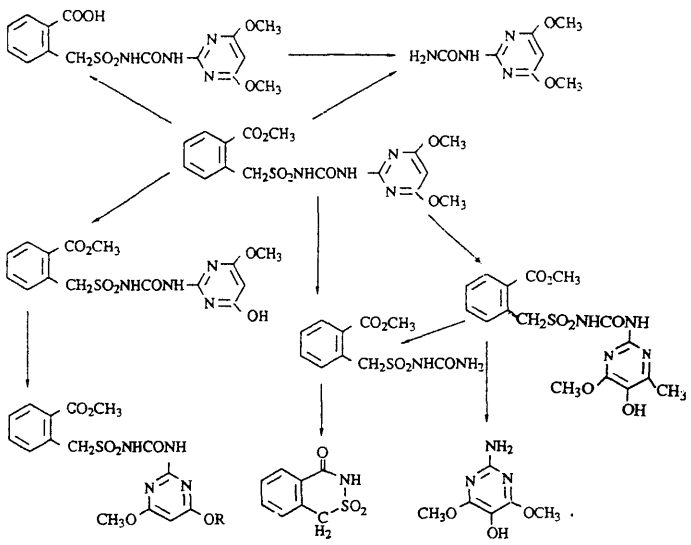
Table 4 (contd.).

Ar	R	R′	X	Name	LD_{50} for rats, mg kg^{-1}	Consumption norm, g ha^{-1}	Refs.
	OCH_3	OCH_3	CH	NC-319	8800	20–30	[223]
	CH_3	CH_3	CH	NC-330	5000	20–30	[224]
	$NHCH_3$	OC_2H_5	N	Cabbadi *	5000	20–40	—
	OCH_3	OCH_3	CH	Bensulfuron-methyl	5000	20–75	—

*Tentative spelling (Ed. of Translation).



Scheme 14. Metabolism of thifensulfuron in the rat organism.



R = glucuronide

Scheme 15. Metabolism of bensulfuron in the rat and goat organisms.

We may note that, together with individual sulphonylureas, their mixtures with other herbicides, including 2,4-D salts, benzoic acid derivatives, and a number of other substances, have found extensive applications. The use of such mixtures makes it possible to reduce significantly the consumption of the preparations and to diminish the amount of herbicide applied per unit treated area, accelerating thereby its total decomposition in the soil. In addition, the use of mixtures makes it possible to reduce the amount of preparations which may enter ground waters. We may note that much attention is being devoted to this problem at the present time because certain preparations do enter ground waters when applied systematically on the same areas (like aldicarb).

The products of the metabolism of sulphonylureas are eliminated from animal organisms in most cases with excrement in the form of glucuronates and sulphates.

The photochemical decomposition of a series of sulphonylureas,[219] including sulphometuron, has been investigated in an aqueous medium.[236,237] It has been established that the main products of the photochemical conversion of sulphometuron are hydrolysis products and two other substances of unknown structure.[237] It is noteworthy that the pyrimidine and triazine rings forming part of the molecule of the majority of sulphonylureas are apparently fairly stable and decompose only slowly. Table 4 shows that virtually all sulphonylureas contain either triazine or pyrimidine rings, whose decomposition has been thoroughly investigated in relation to triazine herbicides.[240–247]

It is seen from the foregoing that sulphonylurea derivatives are of significant interest for use in agriculture and, by virtue of their low toxicity for animals, fish, and birds, they constitute no danger to the environment, particularly since the consumption norms for the majority of these substances are extremely low, as shown by the data in Table 4.

Table 5. The maximum permissible contents of pesticides in drinking water (μg litre^{-1}).

Preparation	CIS (1984)	Australia (1987)	England (1986)	Canada (1987)	USA (1983)
Acephate	—	20	—	—	—
Acifluorfen	—	—	—	—	9
Alachlor	0.3	3	—	—	0.15–1
Aldicarb	—	—	—	9	10
Atrazine	2	—	30	60	3
Benomyl	—	200	—	—	—
Bentazon	25	400	—	—	17.5
Bioresmethrin	—	60	—	—	—
Butilate	—	—	—	—	50
Carbaryl	—	60	—	90	700
BMC	—	200	3	—	—
Carbofuran	—	30	—	90	36
Carboxin	—	—	—	—	700
Cyanazine	—	—	—	10	9
2,4-D	100	100	—	100	70
DDT	1	3	—	30	—
Diazinon	—	10	—	20	—
Dimethoate	—	100	7	20	—
Diuron	—	40	—	150	14
Endosulfan	—	40	—	—	—
Fenitrothion	—	20	—	—	—
Fenvalerate	—	40	—	—	—
Fluometuron	—	100	—	—	90
Glyphosate	—	200	70	280	700
Lindane	3	100	—	4	0.0265
Linuron	—	—	2	—	—
Malathion	—	100	—	190	—
Mancozeb	—	—	1	—	—
Maneb	—	—	1	—	—
Methromyl	—	60	—	—	175
Metalachlor	5	800	—	50	10
Molinat	7	1	—	—	—
Metaphos	—	6	—	7	2
Permethrin	—	300	—	—	—
Propanide	175	1000	—	—	—
Simazine	17	—	30	10	35
TMTD	—	30	—	—	—
Triadimefon	—	—	30	—	—
Trifloralin	170	500	—	—	2
Zineb	—	30	—	—	—

VII. Conclusion

The behaviour of pesticides in the environment has been considered in relation to several classes of chemical compounds. Analysis shows that, having at one's disposal fairly extensive knowledge, it is possible to ensure, by setting standards for the consumption of pesticides in agriculture and other fields, for example in the fight against agents transferring infectious diseases in man and animals, the use of pesticides which are completely safe both to man and a wide variety of objects in the environment can be ensured.

In order to characterise the possible contamination of food products and drinking water by pesticides, the maximum permissible levels of certain pesticides in drinking water and in food products, calculated per kilogram of human body weight per day, are

presented in Tables 5 and 6, which show that pesticides can enter the human organism in insignificant amounts. For example, if one considers diazinon, then it is found that only 0.07 mg of this substance enters the organism of a human being weighing 70 kg in 24 h, which is several times less than the amount of caffeine consumed with one cup of coffee and yet the toxicity of caffeine is approximately twice as high as that of diazinon.

Table 6. The maximum permissible levels of residual amounts of pesticides in food products (mg/kg of weight of a person per day).

Preparation	WHO	USA	CIS
Acephate	0.03	0.004	—
Acifluorfen	—	0.013	—
Alachlor	—	0.01	0.002
Aldicarb	0.005	0.0013	—
Atrazine	—	0.005	0.004
Benomyl	0.02	0.05	0.02
Bentazon	—	0.0025	0.002
Butilate	—	0.05	0.02
Carbaryl	0.01	—	0.01
BMC	0.01	—	0.01
Carbofuran	0.01	0.005	0.01
Carboxin	—	0.1	—
Cartap	0.1	—	—
Chlorthalonil	0.003	0.015	0.03
Cyanazine	—	0.002	—
Cyhalothrin	0.02	0.005	—
Cypermethrin	0.05	—	0.003
2,4-D	0.3	0.01	0
DDT	0.02	0.0005	0.0005
Deltamethrin	0.01	—	0.0003
Diazinon	0.002	—	0.001
Dienzoquat	—	0.08	—
Dimethoate	0.01	0.0002	0.01
Diuron	—	0.002	—
Endosulfan	0.008	0.00005	—
	—	0.00001	—
Fenitrothion	0.005	0.025	0.003
Fenvalerate	0.02	—	0.034
Ferbam	0.02	—	—
Fluometuron	—	0.013	0.03
Folpet	0.01	0.1	0
Fonophos	—	0.002	—
Glyphosate	0.3	0.1	0.01
Lindane	0.01	0.0003	0.01
Linuron	—	0.002	0.01
Malathion	0.02	0.02	0.02
Mancozeb	0.05	—	0.005
Maneb	0.05	0.005	—
Methomyl	0.01	0.025	—
Metalachlor	—	0.15	0.02
Metribuzin	—	0.025	0.004
Molinat	—	0.022	0.01
Metaphos	0.02	—	0.001
Permethrin	0.05	0.05	0.035
Phenmedipham	—	0.04	0.08
Phosalone	0.006	—	0.006
Prochloraz	0.01	0.0075	—
Propanide	—	0.005	0.04
Propiconazole	0.03	0.013	0.04
TMTD	—	0.005	0.005
Triadimefon	0.03	0.025	0.03
Zineb	0.05	0.05	0.02

A similar situation is also observed for the majority of other preparations. Despite the vigorous studies designed to create alternative methods for the protection of plants against pests, diseases, and weeds, the chemical method will undoubtedly occupy a dominant position in the foreseeable future in the integrated system for the protection of plants.[249]

When the modern assortment of pesticides is used intelligently, the latter present no danger either to man or to the environment in view of their moderate persistence and extremely low consumption limits. For example, monitoring of the content of pesticides in California (USA) in 1989 failed to detect pesticides in 80% of the samples, in 19.3% of the samples pesticides were found within permissible limits, and in only 0.7% of the samples was the content of pesticide in excess of the permissible limits.[250]

References

1. P Agius *Keys to Ecology* (Translated into Russian), Gidrometeoizdat, Leningrad, 1982, 97 pp
2. *Programma Biosfernykh i Ekologicheskikh Issledovanii Akad. Nauk SSSR* (Program of Biospheric and Ecological Studies by the USSR Academy of Sciences), Vestn. Akad. Nauk SSSR, 1988, No. 11, p. 3
3. *Ekologicheskaya Situatsiya kak Ob'ekt Nauchnykh Issledovanii. Materialy Obshchego Sobraniya Akademii Nauk SSSR* (The Ecological Situation as an Object of Scientific Research. Proceedings of the General Meeting of the USSR Academy of Sciences), Vestn. Akad. Nauk SSSR, 1989, No. 5, p. 3
4. V E Sokolov, E A Shilov *Ekologicheskaya Situatsiya kak Ob'ekt Nauchnykh Issledovanii. Materialy Obshchego Sobraniya Akademii Nauk SSSR* (The Ecological Situation as an Object of Scientific Research. Proceedings of the General Meeting of the USSR Academy of Sciences), Vestn. Akad. Nauk SSSR, 1989, No. 7, p. 91
5. *Ekologiya i Zemledelie* (Ecology and Farming), Nauka, Moscow, 1980, 295 pp
6. I M Trakhtenberg, M N Korshun *Rtut' i Ee Soedineniya v Okruzhayushchei Srede* (Mercury and Its Compounds in the Environment), Vyshcha Shkola, Kiev, 1990, 232 pp
7. M G Mineev, T A Trishina *Agrokhimiya,* 1983, (1) 122
8. M Lademius *Environmental Mobilization of Mercury and Cadmium,* Univ. Pres, Helsinki, 1990, p. 31
9. W Lokeretz *Air and Soil Poll.,* 1974, **3** 179
10. N N Mel'nikov, A I Volkov, O A Korotkova *Pestitsidy i Okruzhayushchaya Sreda* (Pesticides and the Environment), Khimiya, Moscow, 1977, 240 pp
11. A Kambananoli-Dinoua, S Kilkidis, S Kananonos *Bull. Environ. Contam. Toxicol.,* 1989, **42** 728
12. K Nakamura *Bull. Environ. Contam. Toxicol.,* 1989, **42** 785
13. V G Mineev, T A Trishina *Agrokhimiya,* 1982, (9) 112
14. N N Mel'nikov, S R Belan *Khim. Prom.,* 1989, (5) 328
15. A G Bingham, C J Edmunds, J J Gibson, et al. *The 8th International Symposium on Chlorinated Compounds, Sweden, Umea,* 1988, Abstr. 243 pp
16. K Honda, R Tasukawa, P Van *Bull. Environ. Contam. Toxicol.,* 1989, **43** 350
17. H M Hassan, H T Mustafa, T T Rhen *Bull. Environ. Contam. Toxicol.,* 1989, **43** 529

18. M S Newman, B Tierney, S Meeranghavan *The Chemistry and Biology of Benz(a)antracenes,* Camb. Univ., Cambridge, 1988, 228 pp
19. G Howells *Acid Rain and Acid Waters* Ellis Horwood, Chichester, 1990, 215 pp
20. P M Ouridge, B N Moller *Rev. Environ. Contam. Toxicol.,* 1991, **121** 1
20a. S Tamaki, W T Frankenberger *Rev. Environ. Contam. Toxicol.,* 1992, **124** 79
21. G Matolcsy, M Nadasy, V Andriska *Pesticide Chemistry,* Akadem. Kiado, Budapest, 1988, 808 pp
22. S A Levin, M A Harwell, J R Kelly, K D Kinball *Ecotoxicology: Problems and Approaches,* Springer, New York, 1989, 547 pp
23. D B Peakall *Rev. Environ. Contam. Toxicol.,* 1972, **44** 1
24. I Hara *Environ. Health Persp.,* 1985, **59** 85
25. Yu S Kagan *Rev. Environ. Contam. Toxicol.,* 1991, **117** 96
26. Yu S Kagan *Zh. Vses. Khim. Ova im D I Mendeleeva,* 1988, **33** 624
27. N N Mel'nikov *Pestitsidy, Khimiya Tekhnologiya i Primenenie* (Pesticides. Chemistry, Technology, and Applications), Khimiya, Moscow, 1987, 710 pp
28. S R Belan, N N Mel'nikov *Zh. Vses. Khim. Ova im D I Mendeleeva,* 1988, **33** 708
29. N N Mel'nikov *Agrokhimiya,* 1986, (3) 119
30. M Phillips, J McDougal *J. Agrochemical Service,* Woodmac., April, 1990, 90 pp
31. A Kh Khusid, O M Nefedov *Zh. Vses. Khim. Ova im D I Mendeleeva,* 1988, **33** 653
32. A F Grapov, L V Razvodovskaya *Agrokhimiya,* 1990, (7) 126
33. Yu A Baskakov *Zh. Vses. Khim. Ova im D I Mendeleeva,* 1988, **33** 631
34. V K Promonenkov, V I Sorokin, L M Nesterova, et al. *Sul'fonilmocheviny* (Sulphonylureas), Izd. NIITEKhIM, Moscow, 1985, 35 pp
35. N N Mel'nikov, N I Aronova *Khim. Prom.,* 1990, 643
36. I M Mil'shtein *Zh. Vses. Khim. Ova im D I Mendeleeva,* 1988, **33** 687
37. N N Mel'nikov, I M Mil'shtein *Agrokhimiya,* 1991, (7) 139
38. N N Mel'nikov, I M Mil'shtein *Agrokhimiya,* 1986, (6) 115
39. K V Lebedeva *Zh. Vses. Khim. Ova im D I Mendeleeva,* 1988, **33** 678
40. F M Kutz, P H Wood, D P Bottimore *Rev. Environ. Contam. Toxicol.,* 1991, **120** 1
41. R Guitart, J L Ru, A Puicdemont, et al. *Bull. Environ. Contam. Toxicol.,* 1990, **44** 555
42. C F Nahchi, O Kasilo *Bull. Environ. Contam. Toxicol.,* 1990, **45** 189
43. J H Driver, J J Konz, G K Witmire *Bull. Environ. Contam. Toxicol.,* 1988, **43** 814
44. S M Waliszewek, G A Scymczynski *Bull. Environ. Contam. Toxicol.,* 1991, **46** 863
45. K Sasaki, T Ishizaka, T Suzuki, et al. *Bull. Environ. Contam. Toxicol.,* 1991, **46** 662
46. B Krautchaker *Bull. Environ. Contam. Toxicol.,* 1991, **46** 787
47. R Galetin, S Pavlov, N Roncevic *Bull. Environ. Contam. Toxicol.,* 1990, **45** 811
48. H M Ip *Arch. Environ. Contam. Toxicol.,* 1990, **19** 291
49. C de la Riva, A Anadon *Bull. Environ. Contam. Toxicol.,* 1991, **46** 291
50. A J Nimi *Rev. Environ. Contam. Toxicol.,* 1987, **99** 1
51. D J H Phillips *Environ. Contam. Toxicol.,* 1991, **120** 105
52. W M Ford, E P Hill *Bull. Environ. Contam. Toxicol.,* 1990, **45** 870
53. M Saiki, C J Schimitt *Arch. Environ. Contam. Toxicol.,* 1986, **15** 357
54. W M Ford, E P Hill *Bull. Environ. Contam. Toxicol.,* 1990, **45** 870
55. J K Bennett, S E Donningucz, W L Griffiths *Arch. Environ. Contam. Toxicol.,* 1990, **19** 907
56. L N Vangilder, T J Peterle *Bull. Environ. Contam. Toxicol.,* 1980, **25** 23
57. R Frank, H E Braun, B D Ripley, B S Clegg *Bull. Environ. Contam. Toxicol.,* 1990, **44** 401
58. J D MacNeil, J R Patterson, A C Feesser, S V Tessaro *Bull. Environ. Contam. Toxicol.,* 1991, **46** 300
59. S C Faweett, L J King *Xenobiotica,* 1987, **17** 525
60. H Goebel, S Gorbach, W Knauf, et al. *Residue Rev.,* 1982, **83** 1
61. M A Saleh *Rev. Environ. Contam. Toxicol.,* 1991, **118** 1
62. S H Nash *Residue Rev.,* 1983, **85** 199
63. K H Domsch, G Jagnow, T Anderson *Residue Rev.,* 1983, **86** 65
64. L A Golov'eva, Z I Fil'kel'shtein, O V Mal'tseva *Agrokhimiya,* 1991, (7) 118
65. A A Jensen *Residue Rev.,* 1983, **89** 1
66. M Sprinder *Residue Rev.,* 1984, **90** 1
67. J R Coats *Pesticide Transformation Products,* ACS, Washington, 1991, p. 10
68. C Fest, K-J Schmidt *The Chemistry of Organophosphorus Pesticides,* Springer, Berlin, 1983, 366 pp
69. N N Mel'nikov, K V Novozhilov, S R Belan, T N Pylova *Spravochnik po Pestitsidam* (Handbook of Pesticides), Khimiya, Moscow, 1985, 351 pp
70. T E Horsberg, T Hoy *J. Agric. Food Chem.,* 1990, **38** 1403
71. M S Mulla, L S Mian, A Kawecki *Residue Rev.,* 1981, **81** 1
72. Ou Li-Tse, A Sharma *J. Agric. Food Chem.,* 1989, **37** 1514
73. F M Kishk, T El-Essawi, S Abdel-Ghafar, et al. *J. Agric. Food Chem.,* 1976, **24** 305
74. G Saroja, S Bose *Bull. Environ. Contam. Toxicol.,* 1984, **32** 102
75. A R Tipton, R J Kendall, J F Coyle *Bull. Environ. Contam. Toxicol.,* 1980, **25** 586
76. M Sharmila, K Ramanand, N Sethunsthan *Bull. Environ. Contam. Toxicol.,* 1989, **43** 45
77. L L Radulovic, A P Kulkarni *Xenobiotica,* 1987, **17** 105
78. W S Bigley, F W Plapp, R L Hanna, et al. *Bull. Environ. Contam. Toxicol.,* 1981, **27** 90
79. G W Ware, B J Estesen, N A Buck *Bull. Environ. Contam. Toxicol.,* 1979, **21** 657
80. G W Ware, T F Watson, N A Estesen *J. Econ. Entom.,* 1980, **73** 15
81. H D Durham, A M Comeau, P H Cameron, et al. *Toxicol. Appl. Pharm.,* 1982, **62** 455
82. G Chevaler, I Bastie, M G Cote *Toxicol. Appl. Pharm.,* 1982, **63** 9
83. D J Ecobichon, A M Comeau, P H Cameron *Toxicol. Appl. Pharm.,* 1980, **56** 409
84. R J Maguire, E J Hale *J. Agric. Food Chem.,* 1980, **28** 372
85. F Anjum, S S Qadri *Bull. Environ. Contam. Toxicol.,* 1986, **36** 140
86. L E LaPiere *Bull. Environ. Contam. Toxicol.,* 1985, **35** 471
87. L Chang, G Nickles, A Pickard *J. Agric. Food Chem.,* 1983, **31** 1137

88. M Yasumo, S Hatakeyama, M Miyachita *Bull. Environ. Contam. Toxicol.*, 1980, **25** 29
89. T Katagi *J. Agric. Food Chem.*, 1989, **37** 1124
90. J B Addison *Bull. Environ. Contam. Toxicol.*, 1981, **27** 250
91. P J Tscaplinski, D R Gardner *Pestic. Biochem. Physiol.*, 1981, **17** 47
92. J J Johnston, M D Corbett *Pestic. Biochem. Physiol.*, 1986, **26** 193
93. M Ugaki, T Shono, J Fukami *Pestic. Biochem. Physiol.*, 1985, **23** 33
94. D J Hallett, R Greenhalgh, P Weimberger, et al. *J. Environ. Sci. Health*, 1977, **B12** 53
95. P E Levi, R M Hollingworth, E Hodgson *Pestic. Biochem. Physiol.*, 1988, **32** 224
96. S Y Newell, K E Coocsey, J W Fell, et al. *Arch. Environ. Contam. Toxicol.*, 1981, **10** 427
97. C Q Thompson, J W Tucker *Bull. Environ. Contam. Toxicol.*, 1989, **43** 789
98. T Wang, R Lenahan, T Kablac *Bull. Environ. Contam. Toxicol.*, 1989, **42** 389
99. S Hurley, N B Fenton *Bull. Environ. Contam. Toxicol.*, 1980, **25** 503
100. J B Robertson, C Mazzella *Bull. Environ. Contam. Toxicol.*, 1989, **42** 320
101. J Kanazawa *Bull. Environ. Contam. Toxicol.*, 1978, **20** 613
102. K Seguchi, S Asaka *Bull. Environ. Contam. Toxicol.*, 1981, **27** 244
103. R Frank, P Mineau, E Barker, et al. *Bull. Environ. Contam. Toxicol.*, 1991, **46** 852
104. R J Kuhr, H Tashiro *Bull. Environ. Contam. Toxicol.*, 1978, **20** 652
105. Y Fujii, S Asaka *Bull. Environ. Contam. Toxicol.*, 1982, **29** 455
106. S Szeto, M Wan, P Price, et al. *J. Agric. Food Chem.*, 1990, **38** 281
107. I C MacRae *Rev. Environ. Contam. Toxicol.*, 1989, **109** 1
108. K D Racke, D A Laskowski, M R Schultz *J. Agric. Food Chem.*, 1990, **38** 1430
109. K S Goh, S Edmiston, K T Maddy, et al. *Bull. Environ. Contam. Toxicol.*, 1986, **37** 33
110. D L Macalsdy, N L Wolfe *J. Agric. Food Chem.*, 1985, **33** 167
111. K S Goh, K T Maddy, S Edmiston *Bull. Environ. Contam. Toxicol.*, 1976, **37** 27
112. T Cheng, R M Bodden, R J Puhl *J. Agric. Food Chem.*, 1989, **37** 1108
113. P F Blanchet, A St-George *Pestic. Sci.*, 1982, **13** 85
114. N H Kurihara, R W Meikle, D H de Vries *Arch. Environ. Contam. Toxicol.*, 1983, **12** 189
115. D L Macalady, N L Wolfe *J. Agric. Food. Chem.*, 1983, **31** 1139
116. R D Inman, U Kügemagi, M L Deinzer *J. Agric. Food Chem.*, 1981, **29** 321
117. K P Thomas *Pestic. Sci.*, 1990, **29** 135
118. K L Beatty, M L Sohn *Bull. Environ. Contam. Toxicol.*, 1986, **35** 533
119. C J Milles *Pesticide Transformation Products*, ACS, Washington, 1991, p. 61
120. B N Anderegg, E P Lichtenstein *J. Agric. Food Chem.*, 1984, **32** 610
121. R A Chapmann, C R Harris *J. Econ. Entom.*, 1980, **73** 536
122. S Y Szeto, P M Price, J R Mackenzie, et al. *J. Agric. Food Chem.*, 1990, **38** 501
123. G Walter-Echlos, E P Lichtenstein *J. Agric. Food Chem.*, 1978, **26** 599
124. S Y Szeti, M J Brown, J R Mackenzie, et al. *J. Agric. Food Chem.*, 1986, **34** 876
125. S Y Szeti, R S Vernon, M J Brown *J. Agric. Food Chem.*, 1983, **31** 217
126. C J Miles, S Takashima *Arch. Environ. Contam. Toxicol.*, 1991, **20**, 325
127. W L Lockhart, D A Metner, F J Ward, et al. *Pestic. Biochem. Physiol.*, 1985, **24** 12
128. B Muan, N E Soli, J U Skare *J. Agric. Food Chem.*, 1989 **37** 1085
129. A K Singh, P K Seth *Bull. Environ. Contam. Toxicol.*, 1989, **43** 28
130. W A Matheus *Pestic. Biochem. Physiol.*, 1980, **13** 303
131. R F Toia, R B March, N Unetzu, et al., *J. Agric. Food Chem.*, 1980, **28**, 599
132. S Rengasamy, B S Parmar *J. Agric. Food Chem.*, 1989, **37** 430
133. K R Pawar, H V Ghate, M Katdare *Bull. Environ. Contam. Toxicol.*, 1983, **31** 170
134. G E Carman, Y Iwata, M E Düsch, et al. *Bull. Environ. Contam. Toxicol.*, 1981, **27** 864
135. B N Anderegg, L J Madisen *J. Agric. Food Chem.*, 1983, **31** 700
136. A Calderbank *Rev. Environ. Contam. Toxicol.*, 1989, **108** 71
137. S U Khan *Pesticide Transformation Products*, ACS, Washington, 1991, p. 108
138. L A Golovleva, B P Baskunov, Z I Finkel'shtein, M Yu Nefedova *Izv. Akad. Nauk SSSR, Ser. Biol.*, 1983, (1) 60
139. G Engelhardt, L Oehlmann, K Wagner, et al. *J. Agric. Food Chem.*, 1984, **32** 102
140. V Drevenkar, Z Radic, Z Vasilic, et al. *Arch. Environ. Contam. Toxicol.*, 1991, **20** 417
141. J J Jankins, M J Zabik, R Kon, et al. *Arch. Environ. Contam. Toxicol.*, 1983, **12** 99
142. J Wieneke, W Steffens *J. Agric. Food Chem.*, 1976, **24** 416
143. R J Bushway, W Litten, K Porter, et al. *Bull. Environ. Contam. Toxicol.*, 1982, **28** 141
144. E Grossbard, D Atkinson (Editors) *The Herbicide Glyphosac*, Butterworths, London, 1985, 490 pp
145. P C Kemney, D D Kaufman (Editors) *Herbicides. Chemistry and Mode of Action*, Marcel Dekker, New York, 1988, 189 pp
146. M Elliott *Pesticides and Alternatives*, Elsevier, Amsterdam, 1990, p. 345
147. M Hirano *Pestic. Sci.*, 1989, **27** 353
148. S P Bradbury, J R Coats *Rev. Environ. Contam. Toxicol.*, 1989, **108** 133
149. L P Demoute *Pestic. Sci.*, 1989, **27** 375
150. N N Mel'nikov, N I Aronova *Agrokhimiya*, 1987, (9) 109
151. J R Hill *Pestic. Sci.*, 1989, **27** 429
152. K E Day *Pesticide Transformation Products* ACS, Washington, 1991, p. 217
153. J R Finney *Pesticide Chemistry*, VCH, Weinheim, 1991, 555 pp
154. N B Murthy, K Raghu *Bull. Environ. Contam. Toxicol.*, 1991, **46** 374
155. M Cooland, K Jankowski *Environmental Fate of Pesticides*, Wiley, New York, 1985, Vol. 5, p. 87
156. B S Rjagopal, S Panda, N Sethunathan *Bull. Environ. Contam. Toxicol.*, 1986, **36** 827
157. K M Scow, R R Merica, M Alexander *J. Agric. Food Chem.*, 1990, **38** 908
158. W B Wheeler *J. Agric. Food Chem.*, 1991, **39** 588

159. K Ramanan, M Aharmila, N Sigh, et al. *Bull. Environ. Contam. Toxicol.*, 1991, **46** 380
160. A Sahoo, S Sahu, M Sharnila, et al. *Bull. Environ. Contam. Toxicol.*, 1990, **44** 948
161. K Venkateswarlu, N Sethunathan *Bull. Environ. Contam. Toxicol.*, 1984, **33** 556
162. A R Isensee, N Tayaputch *Bull. Environ. Contam. Toxicol.*, 1986, **36** 763
163. S P Kale, N B Murthy, K Raghu *Bull. Environ. Contam. Toxicol.*, 1989, **42** 769
164. P Kalberer, E Vogel *Pestic. Sci.*, 1978, **9** 146
165. J S Karns, W W Mulbry, J O Nelson, et al. *Pestic. Biochem. Physiol.*, 1986, **25** 211
166. R D Inman, U Kügemagi, D A Griffin, et al. *J. Agric. Food Chem.*, 1983, **31** 722, 918
167. H Sonobe, R Kamps, P Mazzola *J. Agric. Food Chem.*, 1981, **29** 1125
168. K Arunachalam, M Lakshmanan *Bull. Environ. Contam. Toxicol.*, 1982, **28** 230
169. T C Marshall, H W Dorough *J. Agric. Food Chem.*, 1984, **32** 882
170. J Drabek, R Neumann *Environmental Fate of Pesticides*, Wiley, New York, 1985, p. 48
171. P J Marsden, E Luwano, T R Fukuto *Pestic. Biochem. Physiol.*, 1982, **18** 38
172. V E Clay, M A H Fahmy, J P Martin, et al. *J. Agric. Food Chem.*, 1980, **28** 1122
173. N Umetsu, T R Fukuto *J. Agric. Food Chem.*, 1982, **30** 555
174. V E Clay, T R Fujuto *Arch. Environ. Contam. Toxicol.*, 1984, **13** 53
175. N Umetsu, T Nishioka, T R Fukuto *J. Agric. Food Chem.*, 1984, **32** 765
176. A K Tanaka, N Umetsu, T R Fukuto *J. Agric. Food Chem.*, 1985, **33** 1049
177. V E Clay, J P Martin, T R Fukuto *J. Agric. Food Chem.*, 1980, **28** 1129
178. J F Risher, F L Mink, J F Stara *Environ. Health Perspec.*, 1987, **72** 267
179. L H Wright, M D Jackson, R G Lewis *Bull. Environ. Contam. Toxicol.*, 1982, **28** 740
180. J A Foran, P J Germuska, J J Delfino *Bull. Environ. Contam. Toxicol.*, 1985, **35** 546
181. R H Bromlow, R J Baker, A H Freenman, et al. *Pestic. Sci.*, 1980, **11** 371
182. C J Miles, J J Delfino *J. Agric. Food Chem.*, 1985, **33** 455
183. P H Nichols, R H Bromilow, T M Atdiscott *Pestic. Sci.*, 1983, **13** 475
184. R H Bromilow, M Leistra *Pestic. Sci.*, 1980, **11** 389
185. C J Miles, M L Trehy, R A Yost *Bull. Environ. Contam. Toxicol.*, 1988, **41** 838
186. A T Lemley, W Z Zhong *J. Agric. Food Chem.*, 1984, **32** 714
187. J C Maitlen, D M Powell *J. Agric. Food Chem.*, 1982, **30** 589
188. J Rouchand, C Moons, J Meyer *Pestic. Sci.*, 1982, **13** 17
189. J Rouchand, C Moons, J Meyer *Pestic. Sci.*, 1980, **11** 483
190. J Rouchand, C Moons, J Meyer *Pestic. Sci.*, 1981, **12** 548
191. T Carins, E G Siegmund, T S Savage *Bull. Environ. Contam. Toxicol.*, 1984, **32** 274
192. B W Wilson, J N Seiber, M Stelies, et al. *Bull. Environ. Contam. Toxicol.*, 1989, **42** 915
193. Ou Li-Tse, K S Edvardson, J E Thomas, et al. *J. Agric. Food Chem.*, 1985, **33** 545
194. P K Freeman, K D McCarthy *J. Agric. Food Chem.*, 1984, **32** 873
195. J Harvey, J Han, R Reiser *J. Agric. Food Chem.*, 1978, **26** 529
196. U Kügemagi, C Heatherbell, M Deinzer *J. Agric. Food Chem.*, 1984, **32** 628
197. J Harvey, J Han *J. Agric. Food Chem.*, 1978, **26** 536
198. Z Gersti *Pestic. Sci.*, 1984, **15** 9
199. J Stenersen, N Oien *Pestic. Sci.*, 1980, **11** 396
200. M Leistra, R H Bromlow, T I Boesten *Pestic. Sci.*, 1980, **11** 379
201. I J Belasco, J Harvey *J. Agric. Food Chem.*, 1980, **28** 689
202. *Decomposition of Herbicides* (Translated into Russian), Mir, Moscow, 1971, 358 pp
203. G Meyer-Bode *Herbicides and Their Residues* (Translated into Russian), Mir, Moscow, 1972, 560 pp
204. T Mitsui *Jpn. Pestic. Inform.*, 1985, **47** 3
205. G W Ivie *J. Agric. Food Chem.*, 1978, **26** 81
206. C H Schceter, E E Dupras *J. Agric. Food Chem.*, 1979, **27** 1031
207. C W Ivie, D L Bull, J A Vrece *J. Agric. Food Chem.*, 1980, **28** 330
208. W B Nimmo, P C De Wilde, A Verlop *Pestic. Sci.*, 1984, **15** 574
209. F Darvas, R Eker *Pesticide Chemistry*, VCH, Weinheim, 1991, 297 pp
210. H M Brown, T P Fuester, T B Ray, S D Strachan *Pesticide Chemistry*, VCH, Weinheim, 1991, p. 257
211. F K Higson *Rev. Environ. Contam. Toxicol.*, 1991, **122** 111
212. H Rouchaud, F Himmelsbach, R Bulere, et al. *J. Agric. Food Chem.*, 1991, **39** 968
213. M A Koeppe, C F Mucha *J. Agric. Food Chem.*, 1991, **39** 2304
214. A M Blair, T D Martin *Pestic. Sci.*, 1988, **22** 195
215. J J Anderson, J J Dulka *J. Agric. Food Chem.*, 1985, **33** 596
216. H L Palm, J D Riggleman, D A Allison *Proc. Br. Crop Prot. Conf. Weeds*, 1980, Vol. 1, p. 1
217. A P Selley, P J Haney, J R Austin *Proc. Br. Crop Prot. Conf. Weeds*, 1985, Vol. 3, p. 931
218. J Anrein, H R Gerber *Proc. Br. Crop Prot. Conf. Weeds*, 1980, Vol. 1, p. 55
219. E Bayer, M Duffy, D Hay, et al. *Herbicides*, Marcel Dekker, New York, 1988, p. 117
220. H L Palm, P H Liang, T-P Fuesler *Proc. Br. Crop Prot. Conf. Weeds*, 1989, Vol. 1, p. 23
221. K A Peeples, V Mon, et al. *Proc. Br. Crop Prot. Conf. Weeds*, 1991, Vol. 1, p. 25
222. S Stons, H Drabny, P Lefebvre *J. Agric. Food Chem.*, 1990, **38** 159
223. K Suzuki, T Nowamuki, S Watanabe *Proc. Br. Crop Prot. Conf. Weeds*, 1991, Vol. 1, p. 31
224. T Nawamaki, K Suzuki, S Watanabe *Proc. Br. Crop Prot. Conf. Weeds*, 1991, Vol. 1 p. 45
225. L T Makeeva-Gur'yanova, Yu Ya Spiridonov, V G Shestakov *Agrokhimiya*, 1987, (2) 115
226. I S Khalikov, Yu I Savin *Agrokhimiya*, 1989, (7) 112
227. I S Khalikov, A A Bulgakov, Yu I Savin *Agrokhimiya*, 1989, (10) 109
228. Yu Ya Spiridonov, V G Shestakov, V S Gorbatov, et al. *Agrokhimiya*, 1988, (12) 101
229. L T Makeeva-Gur'yanova, Yu Ya Spiridonov, V G Shestakov *Agrokhimiya*, 1987, (1) 127
230. Yu I Savin, I S Khalikov, V D Pomeshchikova *Agrokhimiya*, 1989, (9) 102

231. A D Fokin, V F Ladonin, V K Kukushkin, et al. *Agrokhimiya,* 1990, (4) 111
232. J J Anderson, J J Dulka *J. Agric. Food Chem.,* 1985, **33** 596
233. R L Anderson *Environ. Quality,* 1985, **14** 517
234. E M Bayer, H M Brown *Proc. Br. Crop Prot. Conf. Weeds,* 1987. Vol. 2, p. 5
235. P B Sweetser, G S Schow, J M Hutchison *Pestic. Biochem. Physiol.,* 1982, **17** 18
236. J J Anderson, T M Priester, L M Shalaby *J. Agric. Food Chem.,* 1989, **37** 1429
237. S Neighbors, L S Privalle *Pestic. Biochem. Physiol.,* 1990, **37** 145
238. H M Brown, S M Neighbors *Pestic. Biochem. Physiol.,* 1987, **29** 112
239. J M Hutchison, R Shapiro, P B Sweetser *Pestic. Biochem. Physiol.,* 1984, **22** 243
240. R M Behki, S U Khan *J. Agric. Food Chem.,* 1986, **34** 749
241. A M Cook, R Hutter *J. Agric. Food. Chem.,* 1981, **29** 1135
242. A M Cook, R Hutter *Appl. Environ. Microbiol.,* 1982, **43** 781
243. G Engelhardt. W Ziegler, P R Wallhofer, et al. *J. Agr. Food Chem.,* 1982, **30** 278
244. M C Giardina, M T Giardi, G Filacchioni *Agric. Biol. Chem.,* 1982, **46** 1439
245. H Grossenbacher, C Horn, A M Cook, et al. *Appl. Environ. Mircobiol.,* 1984, **48** 451
246. J A Jessee, R E Benoit, A C Hendricks, et al. *Appl. Environ. Microbiol.,* 1983, **45** 97
247. I C MacRae *Rev. Environ. Contam. Toxicol.* 1989, **109** 1
248. G Eksrom, M Akerblom *Rev. Environ. Contam. Toxicol.,* 1990, **114** 23
249. J E Casida (Editor) *Pesticides and Alternatives: Innovative Chemical and Biological Approaches to Pest Control,* Elsevier, Amsterdam, 1990, 586 pp
250. C K Winter *Rev. Environ. Contam. Toxicol.,* 1992, **127** 23

Received 2nd April 1992

Translated from *Uspekhi Khimii* **61** 1969–1982 (1992) U.D.C. 541.124+541.127+547.51

Investigation of molecular carbonium ion rearrangements by the molecular mechanics method

Yu V Gatilov, V A Barkhash
Novosibirsk Institute of Organic Chemistry, Siberian Division of the Russian Academy of Sciences

ABSTRACT. The review considers problems of the application of the molecular mechanics method in the prediction of the conversion reactions of hydrocarbon carbonium ions with a localised charge. The methods for the estimation of the heights of the activation barriers to the 1,2-shift of the migrating species, the possibilities of the method for the prediction of the transannular cyclisation of carbonium ions, and certain examples of the influence of the acidity of the medium are discussed.

Contents

I. Introduction 1077
II. Calculation of the stabilities and geometries of carbonium ions 1077
III. Estimation of the heights of the activation barriers to 1,2-shifts 1078
IV. Transannular cyclisation of carbonium ions 1080
V. The influence of the medium on the rearrangements 1082

I. Introduction

The foundations of the method of molecular mechanics (MM) [1] or the method of atom–atom potentials[2,3] were laid in Hill's study in 1946.[4] At the present time, this method has been widely used in a wide variety of chemical fields. This review deals with only a narrow range of applications of the method, namely the possibilities of the MM method in the study of complex multistage carbonium ion rearrangements involving carbocyclic cations (excluding π-delocalised ions, ions with a heteroatom in the α-position relative to the carbonium ion centre, and ions with the charge on a heteroatom).

The MM method deals with an isolated molecule (unless otherwise stipulated) and its results can be compared directly only with certain gas-phase data. On the other hand, carbonium ion reactions are investigated in media of different acidity, frequently under the so called long life conditions.[5] In general, the influence of the medium, for example, on the heat of formation, is enormous. Thus the heats of formation of the t-butyl cation in the gas phase and in the SO_2FCl system differ by 239 kcal mol^{-1}.[6] Direct allowance for the interaction of carbonium ions with the medium is very difficult. However, it has been shown by Arnett and Pienta,[6] who compared the enthalpies of formation in the gas phase and in SO_2FCl, that there is a satisfactory correlation (with a slope of 0.973 and $r = 0.986$) between the values of $\Delta H_f^\circ(R^+, \text{gas})$ and $\Delta H_f^\circ(R^+, SO_2FCl)$. Thus the absence of specific solvation of the cations by the medium was demonstrated in this instance, so that we can use directly the results of calculations by the MM and quantum-chemical methods.

II. Calculation of the stabilities and geometries of carbonium ions

In the early studies,[7] the MM method was used to predict the preferred carbonium ion reaction pathways, but, in order to estimate the stabilities of different cations, the values of ΔH_f° were calculated in these investigations for neutral hydrocarbons on the basis of the idea of the parallel nature of the stability series of carbonium ions and the corresponding neutral hydrocarbons. The MM method was first used directly for calculations involving carbonium ions in the study of Gleicher and Schleyer.[8] They found the parameters of the force field by the MM method and successfully compared the solvolysis rate constants and the differences between the steric energies of the carbonium ions and the corresponding hydrocarbons.

The next important step in the establishment of the MM method in the chemistry of carbonium ions was the introduction of an additive scheme for the calculation of gas-phase heats of formation,[9] which made it possible to compare quantitatively the stabilities of secondary and tertiary ions. As a result, it became possible to carry out calculations for the energetics of carbonium ion reactions, i.e. to establish whether the given process proceeds "uphill" or leads to more stable final ions.

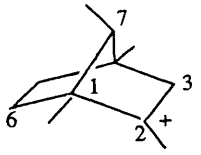
A study[10] in which the conformational analysis was carried out for tertiary (C_6, C_7, and C_8) cycloalkyl carbonium ions by the NMR method is noteworthy. The authors observed the unexpected preference (to the extent of 0.5 kcal mol^{-1}) for the twist conformation of the methylcyclohexyl cation compared with the chair conformation. This investigation was followed by a study[11] on the conformational analysis of the above tertiary carbonium ions by the MM method. According to the authors' calculations, the twist conformation of the methylcyclohexyl cation is less stable than the chair conformation by only 0.14 kcal mol^{-1} and, if account is taken of the known fact[12] that the MM method overestimates the stability of the chair form by ~0.3 kcal mol^{-1}, then the result obtained agrees well with experimental data.

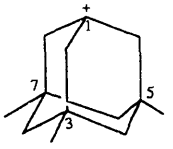
The study of Olah, et al.[13] on 1,4-bicyclo[2.2.2]octyl dication—a new pseudoaromatic system—is of interest. The causes of the surprising stability of this cation were discovered with the aid of the MM and MINDO/3 methods.

After the publication of calculations in which the force field and Allinger's MM2 method[14] were resorted to, it was natural to expect the extension of this version of the MM method also to carbonium ions, which was in fact achieved by Muller and co-workers,[15–18]

who found the necessary parameters of the MM method from kinetic data for the solvolysis of secondary[15] and tertiary[16,17] alcohols and obtained the enthalpy parameters from the experimental gas-phase heats of formation.[18] It is noteworthy that the parametrisation of the MM method for carbonium ions in the MMX program is different from that proposed by Muller.

Whilst recognising the advantages of the MM method (compared with quantum-chemical and semi-empirical methods) such as speed and reliability of the results for carbonium ions which fall within the sphere of the existing parametrisation, its disadvantages should also be noted. Firstly, at the present time the MM method cannot take into account explicitly the stabilisation of certain carbonium ions owing to the σ-delocalisation of the positive charge. The underestimation of the stability of ions with σ-delocalisation is therefore to be expected. For example, in the case of 2-norbornyl cations the underestimate is by 5 kcal mol^{-1},[9] 6 kcal mol^{-1},[19] or 7.6 kcal mol^{-1}.[20] However, it is difficult to say *a priori* for which cations such a correction should be applied, except for the thoroughly investigated 2-norbornyl cations. (We may note that there is no reliable parametrisation of the MM method for π-delocalised carbonium ions.) Secondly, X-ray diffraction studies on the salts of the 1,2,4,7-*anti*-tetramethyl-2-norbornyl[21] and 3,5,7-trimethyl-1-adamantyl[22] cations revealed an appreciable deviation of the bond lengths from the values used as a basis for the parametrisation of the MM method for carbonium ions. Thus the C(1)–C(2), C(2)–C(3), C(2)–CH_3, and C(1)–C(6) bond lengths in the norbornyl ion are 1.48, 1.48, 1.48, and 1.54 Å respectively according to the calculation by the MM2 method using Muller's parameters, while the experimental bond lengths are 1.44(2), 1.50(1), 1.47(2), and 1.74(2) Å.





In the adamantyl ion, the calculated C^+–C and (C^+)C–C bond lengths are 1.48 and 1.54 Å respectively, while the experimental values are 1.42–1.47 and 1.61–1.62 Å, i.e. the real interaction of the unoccupied orbital of the carbonium ion centre with the nearest valence bonds has not so far been incorporated with adequate accuracy in the MM method. However, it is only fair to note that the MM method reproduces the enthalpies of formation fairly reliably.[18]

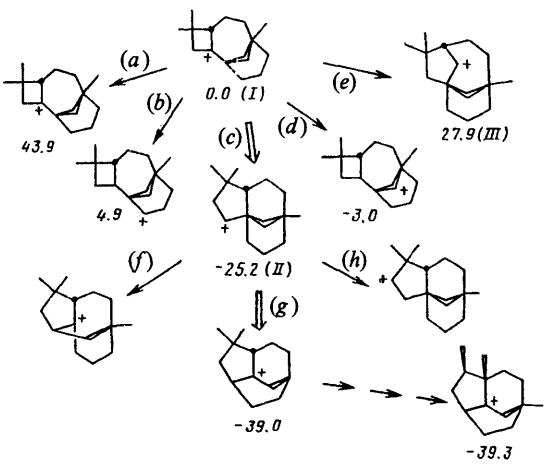
III. Estimation of the heights of the activation barriers to 1,2-shifts

One of the important problems of the chemistry of carbonium ions is that of the prediction of the heights of the activation barriers to intramolecular rearrangements. The direct procedure for the solution of this problem involves non-empirical quantum-chemical calculations (the semi-empirical method yields heats of formation for the transition states in 1,2-shifts which differ very greatly and the best results for hydrocarbon carbonium ions can be obtained with the aid of the MINDO/3 method[23]). In view of the laborious nature of these methods, the search for other approaches has been stimulated. The principal factors determining the activation barriers to the rearrangement of carbonium ions are the size of the positive charge on the carbon atom to which the migrating species moves and the difference between the thermodynamic stabilities of the rearranging and final ions.[5] If carbonium ions with π-delocalisation are disregarded, then the thermodynamic factor becomes one of the decisive ones. For example, the most probable pathway leading to the conversion of 2,3-tetramethylenebicyclo[2.2.1]heptane into adamantane has been refined[9] on the basis of the heats of formation of the carbonium ions calculated by the MM method.

However, the height of the activation barrier to the 1,2-shift of the migrating species may be influenced by specific structural factors responsible for the increased strain in the transition state. In particular, this may be the unfavourable orientation of the unoccupied orbital of the carbonium ion centre relative to the orbital of the carbon–migrating species bond (the orbital factor characterised by the torsional angle Φ between the specified orbitals). Indeed, it has been shown in relation to the solvolysis of *exo*-twistbrendan-2-ol[24] that both factors—the thermodynamic and orbital factors—are important for the prediction of the direction of the 1,2-shift. The attempt to incorporate both factors simultaneously at a qualitative level was undertaken[25] in the analysis of the mechanism of the acid-catalysed reactions of 2- and 4-homoprotoadamantanes. In this case, the pathways leading to the most stable ions and having at the same time the most favourable interorbital angles for the corresponding 1,2-shifts were recognised as the most probable.

In a later study of the rearrangement of 1-substituted caryolanes in superacids,[26] the authors encountered the situation where the pathway to the most stable ion (II) is associated with an extremely unfavourable[7] interorbital angle (Φ = 69°, Scheme 1). The heats of formation ($\Delta\Delta H_f^\circ$, kcal mol^{-1}) of the corresponding ions relative to the initial carbonium ion are indicated in Schemes 1–3 under the structural formulae.

Scheme 1



Pathway	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
Φ, deg	54	59	69	55	2	50	4	30
$\Delta G^{\neq}$, kcal mol^{-1}	44	24	8	17	28	20	4	12

On the other hand, the pathway which is very favourable as regards the orbital factor (Φ = 2°) leads to the highly strained cation (III). Since both these factors are important for the prediction of the rearrangements, the authors put forward the empirical hypothesis that the internal barrier (Λ) to the 1,2-shift in a degenerate

rearrangement depends on the interorbital angle in the following manner:

$$\Lambda = \Lambda_0 / \cos\Phi \,. \qquad (1)$$

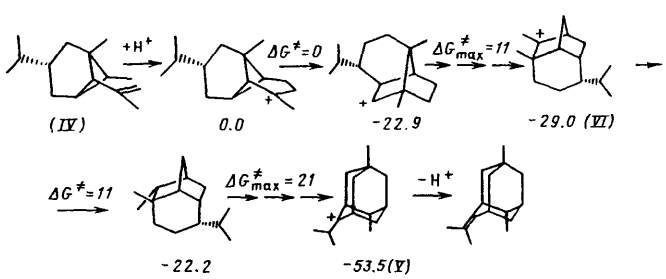
The thermodynamic factor for non-degenerate processes was taken into account with the aid of the Marcus equation, which assumes the following form for isentropic reactions:

$$\Delta G^{\neq} = \Lambda(1 + \Delta\Delta H_f/4\Lambda)^2 , \qquad (2)$$

where $\Delta\Delta H_f$ is the difference between the values of ΔH_f° for the product ion and the rearranging ion. The free energies of activation ($\Delta G^{\neq}$, kcal mol^{-1}), estimated with the aid of Eqns. (1) and (2), are presented in Schemes 1–3. They permit an unambiguous choice between the modes of rearrangement of the initial ion (I). Thus the possibility of predicting the reaction pathway, leading to the conversion of the ion (I) into the final cation with a relative heat of formation of −39.3 kcal mol^{-1} and a length equivalent to seven different 1,2-shifts, was demonstrated in the above study.

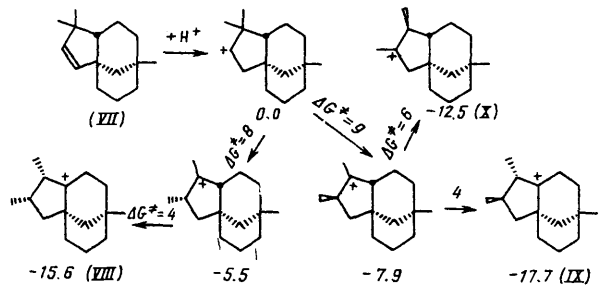
The method for the estimation of the activation barriers to 1,2-shifts examined above has been used[27] to predict the most probable reaction pathways of the sesquiterpene α-copaene (IV). The authors[27] obtained for the first time tricyclic compounds of the adamantane type from α-copaene in superacid media. About 100 structures of different carbonium ions were examined for the purpose of this prediction. Scheme 2 illustrates the fragments of the most probable pathway, consisting of 19 consecutive 1,2-shifts, leading to the rearrangement of the α-copayl ion to the adamantyl ion (V) via the intermediate isosativyl cation (VI).

Scheme 2



The above examples of the reactions of ions generated from 1-substituted caryolanes and α-copaene have in common the feature that the initial carbonium ion is converted into a much more stable ion. A different situation was observed[28] when a "map" of the possible pathways leading to the rearrangement of the cation generated from clovene (VII) was drawn on the basis of Eqns. (1) and (2). According to the prediction, the acid solution should contain in this case a mixture of the two most stable ions (VIII) and (IX) (Scheme 3). In conformity with these data, signals due to two tertiary ions were noted in the ^{13}C NMR spectrum of the reaction mixture, while olefins corresponding to the cations (VIII)–(X) were found among the products of the neutralisation of the mixture.

Scheme 3



Naturally, the simplified method for the estimation of activation barriers by Eqn. (1) has disadvantages (apart from the empirical form of the dependence on the angle Φ). Thus it has been noted in a recent study[29] that, according to the data of Bushmelev et al.,[30] the interorbital angle is not an unambiguous characteristic of the strain in the transition state due to the need for the sp^3-hybrid node of the $C(R_m)-C^+$ fragment to readjust rotationally relative to the unoccupied orbital of the carbonium ion centre, which should depend on the rigidity of the molecule. Little "tricks" such as the search for conformers with a more favourable interorbital angle Φ and the employment of the principle of microscopic reversibility cannot eliminate this disadvantage. Furthermore, the internal barriers Λ_0 to the 1,2-shifts were estimated[26] from Sorensen's kinetic data[31,32] (which include approximate and estimated quantities) for the rearrangements of δ-delocalised 2-norbornyl ions, which are specific models. The neglect of specificity leads to unduly high calculated data in the case of monocyclic and open-chain ions. It is necessary to note the very limited amount of experimental kinetic data for the rearrangements of non-arenium ions. For example, the Wagner–Meerwein rearrangement of the ions under consideration has been scarcely investigated quantitatively. This situation hinders the search for approaches to the description of the rates of the 1,2-shifts.

An attempt has been made[29] to model the strain in the transition and ground states of the 1,2-shift of the migrating species by the strains in the neutral hydrocarbons of the cyclopropane and alkane types.[29] However, it was shown that the difference between the steric energies of the components of the cyclopropane–alkane pair reflects with insufficient adequacy the changes in the quantity $\Delta G^{\neq}$ for the 1,2-shift as the molecular skeleton of the ion is altered. Other workers,[33] who investigated the reactions of 6-tricyclo[3.3.0.0^{2,7}]octyl ion, arrived at a similar conclusion. Nevertheless this approach constitutes the next step compared with the approach described by Eqns. (1) and (2) where the strain in the transition state is estimated solely from data for the ground state of the rearranging cation (i.e. an attempt is made to estimate the height of a mountain whilst standing at its base).

Further development of quantitative estimations of the activation barriers to the 1,2-shift of the migrating species in carbonium ions with a localised charge was stimulated by the successfully developing field of the chemistry of arenium ions. Thus the most general approach to the quantitative description of the rates of the 1,2-shifts of the hydrogen atom and the methyl group has been proposed[34] in relation to the degenerate rearrangement of a large series of benzenoid and non-benzenoid arenium ions. The following dependence of the energy barrier to degenerate 1,2-shifts of the

migrating species on the Hückel charge $q_{\pi x}$ on the atom to which the migrating species shifts and on the basicity constant K_i of this centre in the aromatic hydrocarbon formed after the abstraction of the migrating species was then discovered:

$$\Delta G_{\mathrm{H}}^{\neq} = 14.1 - 7.5\ q_{\pi_x} + 0.37\ \lg K_i\ (\text{kcal mol}^{-1}); \quad (3)$$

$$\Delta G_{\mathrm{CH_3}}^{\neq} = 26.5 - 23.4\ q_{\pi_x} + 0.32\ \lg K_i\ (\text{kcal mol}^{-1}). \quad (4)$$

The basicity constants can be calculated by the MM method with the aid of the relations

$$\lg K_i = -108.9 + 0.528\ PA_i\ (\text{kcal mol}^{-1}),\ \text{(Ref.34.)} \quad (5)$$

$$PA = 367.2 + \Delta H_f^0(\text{olefin}) = \Delta H_f^0(\mathrm{R}^+)\ (\text{kcal mol}^{-1}),\ \text{(Ref.35)} \quad (6)$$

where PA is the proton affinity.

Adopting $q_{\pi x} = 1$ for aliphatic and alicyclic carbonium ions, the authors[29] obtained with the aid of Eqns. (3) and (4) the free energies $\Delta G^{\neq}$, which on the whole agree quite well with experimental data. In the case of σ-delocalised carbonium ions, it was suggested that the chemical shifts (δC) of the corresponding carbon atom in the ^{13}C NMR spectrum be used to estimate the charge q^+: $q^+ = (\delta C - 115)/205$ for secondary ions and $q^+ = (\delta C - 123)/212$ for tertiary ions.

Having supplemented the basic set of the ions [for the correlations (3) and (4)] by aliphatic ions, the authors[29] obtained the following better founded relations for degenerate 1,2-shifts:

$$\Delta G_{\mathrm{H}}^{\neq} = 15.33 - 10.79\ q_{\pi_x} + 0.232\ \lg K_i\ (\text{kcal mol}^{-1}), \quad (7)$$

$r = 0.986,\ s = 0.90,\ n = 8;$

$$\Delta G_{\mathrm{CH_3}}^{\neq} = 25.74 - 21.48\ q_{\pi_x} + 0.303\ \lg K_i\ (\text{kcal mol}^{-1}), \quad (8)$$

$r = 0.995,\ s = 0.79,\ n = 7.$

Comparison of the available experimental activation energies $\Delta G^{\neq}$ and the values calculated by Eqns. (7) and (8) demonstrated that the relations are quite effective:

$$\Delta G_{\mathrm{H}}^{\neq}(\text{exp}) = 1.03\ \Delta G_{\mathrm{H}}^{\neq}(\text{calc.}) + 0.4,$$

$r = 0.943,\ s = 1.6,\ n = 23;$

$$\Delta G_{\mathrm{CH_3}}^{\neq}(\text{exp}) = 1.11\ \Delta G_{\mathrm{CH_3}}^{\neq}(\text{calc.}) - 1.2,$$

$r = 0.971,\ s = 1.7,\ n = 14.$

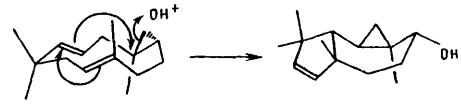
We emphasise the following advantages of this approach: (1) the use of proton affinity, which led to the indirect allowance for the orientation factor; (2) allowance for the "olefin" strain[33] arising from the Dewar representation of the transition state of the 1,2-shift in the form of the π-complex, which proved to be important for the estimation of the stability of the transition state. The "olefin" strain is also involved in the proton affinity.

It is necessary to say a few words about the disadvantages characteristic of the method under discussion. The method is unsuitable for the calculation of the free energies $\Delta G^{\neq}$ for the Wagner–Meerwein rearrangement, because in such cases it is impossible to abstract the migrating species from the skeleton in order to calculate the basicity of the corresponding olefin. Furthermore, in sterically hindered carbonium ions no account is taken of the repulsion of the migrating species (particularly the methyl group) from any other group which arises solely in the transition state of the 1,2-shift of the migrating species. Finally, this approach does not distinguish between the *exo*- and *endo*-shifts of the migrating species in 2-norbornyl cations, the difference between the $\Delta G_{\mathrm{CH_3}}^{\neq}$ for which reaches 10.6 kcal mol^{-1}.[36] We may note that semi-empirical quantum-chemical methods distinguish only imperfectly between the 2,3-*exo*- and 2,3-*endo*-shifts in the 2-norbornyl ion.[37]

IV. Transannular cyclisation of carbonium ions

The transannular cyclisation in the carbonium ion reactions of bifunctional and polyfunctional compounds, particularly of the terpene series, is fairly common. It is responsible for the possibility of the mutual approach in space of the carbonium ion centre and the double bond to a distance sufficient for effective interaction. Modelling of this process by the MM method is so far impossible owing to the lack of the corresponding parametrisation. Nevertheless, the MM method can already provide significant assistance in this case also.

The necessary mutual approach of the potential carbonium ion centre and the double bond is possible even in the ground state (or in the less stable conformer) of the neutral precursor. In this case, the appearance of the cationic centre may be accompanied by cyclisation. Such a phenomenon has been observed for the humulene 6,7-epoxide.[38] When the humulene epoxide is treated with HSO_3F, the concerted opening of the epoxide ring and transannular cyclisation are observed.

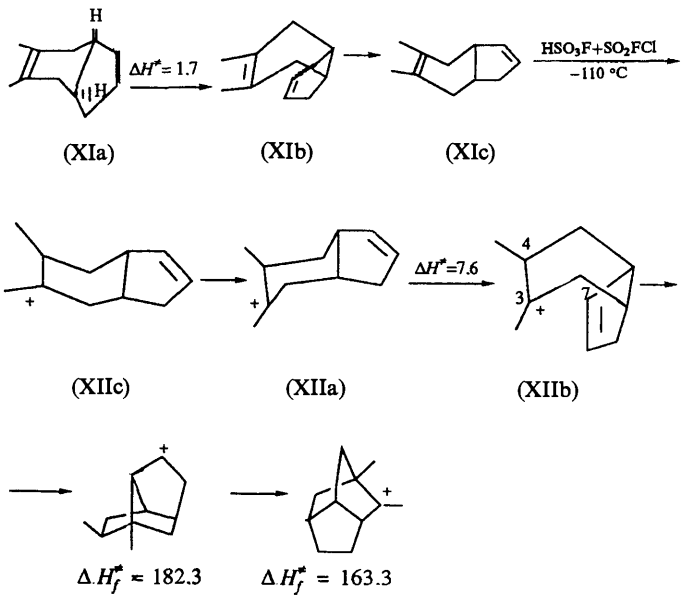


The initial protonation or opening of the epoxide ring provides an additional degree of freedom in the cation formed and hence may promote the mutual approach to the centres required for transannular cyclisation. The following method for the application of the MM method arises from these considerations: conformational analysis of the neutral precursor and of the cation formed initially and allowance for the heat of the possible cyclisation reaction.

We shall consider several examples. In a study[39] of the mechanism of the superacid transannular cyclisation of the bicyclic 1,5-diene (XI), an explanation was found for the experimental finding that the diene (XI) cyclises (Scheme 4), while the allyl ion (XIV) is formed in α-myrolene (XIII) (Scheme 5) under identical

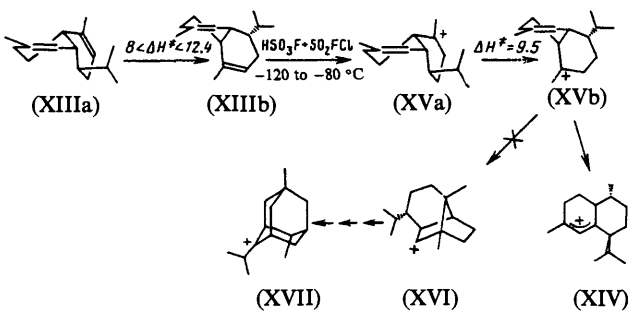
conditions. The fractions of the principal conformers (N, %) at 25 °C are indicated in Schemes 4 and 5.

Scheme 4



Conformer	(XIa)	(XIb)	(XIc)	(XIIa)	(XIIb)	(XIIc)
ΔH^0_f, kcal mol^{-1}	9.2	10.8	9.5	171.8	172.0	172.3
N, %	58.4	4.5	35.2	47.0	32.2	20.3

Scheme 5



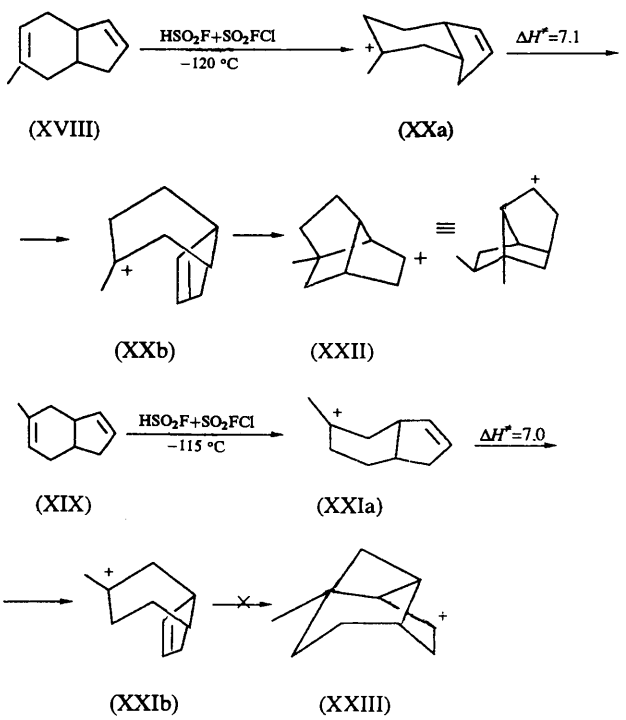
Conformer	(XIIIa)	(XIIIb)	(XVa)	(XVb)	(XVI)	(XVII)
ΔH^0_f, kcal mol^{-1}	−22.2	−20.0	145.7	150.1	150.7 (Ref.27)	102.5 (Ref.27)
N, %	82.4	18.6	99.9	0.06	–	–

Conformational analysis showed that the main conformer (XIa) of the diene (XI) can be very readily converted into the conformer (XIb), which has a geometry favourable for cyclisation. For the diene (XIII), the analogous transition requires an appreciable consumption of energy. Furthermore, one of the main conformers (XIIb), formed initially from the diene (XI), has a disposition of the interacting centres convenient for cyclisation, in contrast to the main conformer (XVa) of the initial cation formed from α-muurolene (XIII). Finally, the competing pathway operates for the ion (XV), involving conversion via the intermediate tertiary cations into the allyl ion (XIV), which constitutes a "potential well".[40]

It follows from the examination of the thermodynamics of the cyclisation of the ion (XIIb) that the quantity ΔH for this process should exceed 10.3 kcal mol^{-1}. At the same time, the cyclisation reaction in the ion (XVb) has a virtually zero heat and apparently not an unduly high activation barrier. This permits the hope that, on raising the reaction temperature, which increases the fraction of the conformer (XIIIb) or (XVb), there is a possibility of the appearance in the reaction mixture of the products of the transannular cyclisation α-muurolene. Indeed, knowing that temperature influences the composition of the ions formed on protonation of α-muurolene, Polovinka et al.[27] increased the temperature of the system (XII) + HSO_3F + SO_2FCl to −30 to −20 ° C and recorded the appearance of the tricyclic adamantyl cation (XVII).

In order to confirm the mechanism of the transannular cyclisation of the diene (XI) proposed by Tatarova et al.,[39] the behaviour of the 3- and 4- monomethyl derivatives of *cis*-bicyclo[4.3.0]nona-3,7-diene (XVIII) and (XIX) was investigated.[41] The conformational compositions of the dienes (XVIII) and (XIX) are almost indistinguishable, while there are differences (Scheme 6), albeit not very pronounced, between the ions (XX) and (XXI) formed from them initially.

Scheme 6



Conformer	(XXa)	(XXb)	(XXIa)	(XXIb)	(XXII)	(XXIII)
ΔH^0_f, kcal mol^{-1}	180.5	180.6	180.5	181.4	187.8	199.2
N, %	41.0	34.6	61.6	12.0	–	–

It is noteworthy that the distances between the interaction centres in the cyclisation reaction ($r_{3,7}$ and $r_{4,7}$) are not apparently the main factors determining the course of the reaction. In this case, the

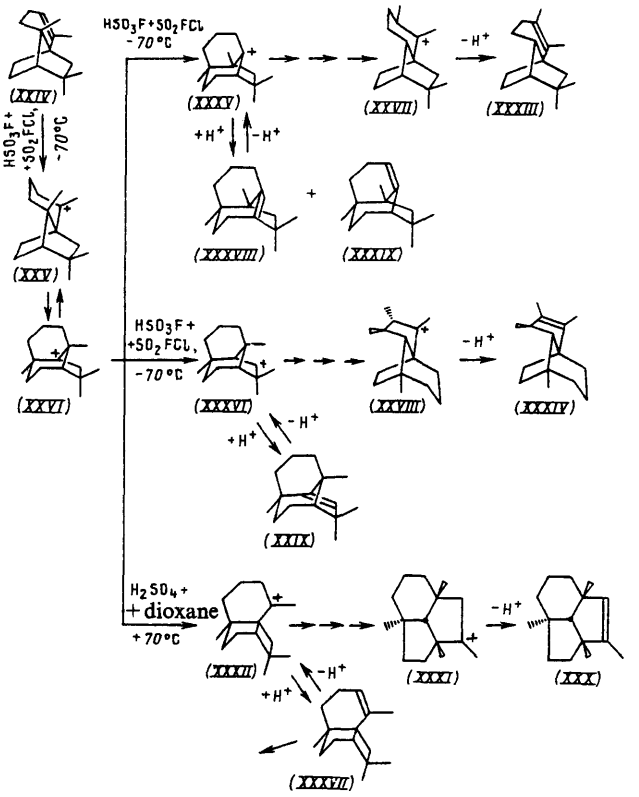
decisive factor is evidently the thermodynamic factor: the heat ΔH of the transannular cyclisation of the cation (XX) is 7.2 kcal mol^{-1}, whereas ΔH for the cyclisation of the ion (XXI) reaches 17.8 kcal mol^{-1}. An attempt may be made to estimate roughly the activation barriers to the cyclisation of the cations (XX) and (XXI) in the following way. We consider the reverse process in the carbonium ions (XXII) and (XXIII)—the dissociation of the corresponding bonds. We assume for simplicity that in the general case the degenernate bond dissociation processes and the Wagner–Meerwein rearrangement begin and proceed similarly, reaching approximately the same transition state as regards energetics. One can then use Eqn. (2) and, having assumed that $\Lambda \simeq$ 5 kcal mol^{-1},[26] the values of ΔG^{+} can be obtained for ring opening in the ions (XXII) and (XXIII)—2.0 and 0.1 kcal mol^{-1} respectively. Hence the activation barriers for the reverse transannular cyclisation in the ions (XX) and (XXI) are 9.2 and 17.9 kcal mol^{-1}.

V. The influence of the medium on the rearrangements

This problem is associated with the general problem of the possibility of predicting the preferred pathway in multistep carbonium ion reactions in the usual acids on the basis of the experimentally observed rearrangements of the carbonium ions generated in superacids from the same precursor. Sorensen[31] published previously data on the carbonium ion rearrangements of monoterpenes in various acid media. He found that, firstly, in superacids and under the conditions of acid catalysis, the sequences in which the barriers ΔG^{+} to the "ion into ion" rearrangements increase are the same and "secondly" that the stability of olefins varies in parallel with the stability of the corresponding carbonium ions. Therefore on the basis of direct observations of the rearrangements of carbonium ions in superacids one can predict the reaction pathway also under the conditions of acid catalysis. Several exceptions to this rule were found subsequently. Thus the mode of reaction in different media can be influenced by the site of the cationic centre[42] and by the nature of the internal nucleophile[43] and also by qualitative changes in the relative rates of competing intramolecular 1,2-shifts[44] and the rates of intermolecular processes.[45]

In a study of the conversion of the sesquiterpene neoclovene (XXIV) in media of different acidity, yet another interesting exception to Sorensen's observation was found.[46] When neoclovene was dissolved in the HSO_3F-SO_2FCl system at −120 °C, the authors observed the appearance of an ion, which, as shown by the application of special methods, involves partial σ-delocalisation of the charge and can be represented by two limiting resonance forms (XXV) and (XXVI) (Scheme 7) as required by the MM method in this instance. When an acid solution of the olefin (XXIV) is heated to −70 °C, the above ion is fully converted into a mixture of the new cations (XXVII) and (XXVIII). As can be seen from Scheme 7, the energy gain expected in the intramolecular conversion of the ion (XXV) into the cations (XXVII) and (XXVIII) in a superacid is 10.7 and 13.0 kcal mol^{-1} respectively.

Scheme 7



Ion/olefin	(XXIV)	(XXV)	(XXVI)	(XXVII)
$\Delta\Delta H_f^0/\Delta H_f^0$, kcal mol^{-1}	−15.6	0.0	3.9	−10.7
s, kcal mol^{-1}	39.0	43.2	52.0	32.9
Ion/olefin	(XXVIII)	(XXIX)	(XXX)	(XXXI)
$\Delta\Delta H_f^0/\Delta H_f^0$, kcal mol^{-1}	−13.0	8.4	−19.7	−2.4
s, kcal mol^{-1}	30.6	63.1	34.9	40.8
Ion/olefin	(XXXII)	(XXXIII)	(XXXIV)	(XXXV)
$\Delta\Delta H_f^0/\Delta H_f^0$, kcal mol^{-1}	6.6	−24.9	−29.8	−11.6
s, kcal mol^{-1}	49.7	30.7	25.8	36.1
Ion/olefin	(XXXVI)	(XXXVII)	(XXXVIII)	(XXXIX)
$\Delta\Delta H_f^0/\Delta H_f^0$, kcal mol^{-1}	2.7	−8.2	8.7	11.4
s, kcal mol^{-1}	38.6	46.6	65.2	45.9

It was shown in the same study[46] that neoclovene (XXIV) is almost fully converted into the olefin (XXX) in a H_2SO_4–dioxane mixture at 70 °C. It is seen from Scheme 7 that the olefin (XXX) is more stable than the initial neoclovene by 4.1 kcal mol^{-1}. The barrier to the conversion of the ion (XXV) into (XXXI) is 18.1 kcal mol^{-1}, the latter being more stable than the initial ion (XXV) to the extent of 2.4-kcal mol^{-1}. [However, experiment showed the opposite situation to be true: at −80 °C in a superacid, the ion (XXXI) is fully converted into the initial ion (XXV)]. It is noteworthy that the pathway leading to the formation of the olefin

(XXX) proceeds via the carbonium ion (XXXII) containing a four-membered ring. This fact conflicts with the postulate[47] that such iosmers be excluded from consideration since they would be very strained.

Thus the pathways in the molecular rearrangements of neoclovene in media of different acidity are completely different. The pathway (XXV)→(XXXI) does not occur in a superacid, because it would lead to a less stable ion. However, it is not clear why the reactions observed in a superacid, which could lead both to more stable ions and more stable olefins (XXXIII) and (XXXIV) than the ion (XXXI) and the corresponding olefin (XXX) actually obtained, do not occur in a usual acid.

If the rearrangements occurred intramolecularly in the usual acids, one would have to expect the same mode of rearrangement in both types of media in conformity with the relative stabilities of the intermediate and final ions. Consequently the process in a usual acid proceeds via the intermolecular protonation–deprotonation pathway. This hypothesis is confirmed by the fact that the reformation of the ion (XXV) from the olefin (XXX), obtained in usual acid, is observed in a superacid (i.e. via an intramolecular pathway). If one considers the "fork" in the rearrangements in different media [Scheme 7, the ion (XXVI)] and attention is turned to the stability of the olefins (XXIX) and (XXXVII)–(XXXIX), whose appearance is possible on deprotonation of the cations (XXXII), (XXXV), and (XXXVI), then it is readily seen that the "normal acid" olefin (XXXVII) is significantly more stable (to the extent of 1.6–19.6 kcal mol^{-1}) than the "superacid", anti-Bredt olefins (XXIX), (XXXVIII), and (XXXIX). Hence one may postulate that the mode of the rearrangements of neoclovene in a usual acid is determined by the relative stabilities of the intermediate olefins. It also follows from Scheme 7 that the principle of the parallel variation of the relative stabilities of carbonium ions and the corresponding olefins, put forward by Sorensen, breaks down in the given instance and the extent to which the variation is antiparallel may exceed 20 kcal mol^{-1}.

In the general case, the rearrangements of carbonium ions in a usual acid are regulated by the competition between several possible intramolecular 1,2-shifts and the protonation–deprotonation reaction. The methods for the estimation of the activation barriers to the intramolecular 1,2-shifts were considered above (see Section III). We shall now examine the protonation–deprotonation equilibrium under the conditions of acid catalysis where the enthalpies of formation of ions and olefins are apparently similar. In this situation, the gas-phase heats of formation calculated by the MM method are unsuitable and we attempted to resort to the concept of the intrinsic strain of the molecule (S) [1] (Scheme 7). It is seen from the values of S that the deprotonation reactions of the carbonium ions (XXVII), (XXVIII), (XXXI), and (XXXII), leading to Bredt olefins, are accompanied by the partial removal of the intrinsic strain (to the extent of 2–6 kcal mol^{-1}). On the other hand, the deprotonation of the ions (XXXV) and (XXXVI) with formation of anti-Bredt olefins increases the intrinsic strain by 10–30 kcal mol^{-1}.

Thus one may expect that the deprotonation processes in a usual acid, accompanied by an appreciable growth of the intrinsic strain in the molecule, would be difficult.

Thus the MM method makes it possible to calculate fairly reliably the stability of carbonium ions with a localised change and to estimate the heights of the activation barriers to the 1,2-shifts of the migrating species. The fruitfulness of the use of the MM method has been demonstrated in predictions of the most probable pathways in the acid-catalysed reactions of terpenoids in media of different acidity.

References

1. U Burkert, N L Allinger *Molecular Mechanics* (Translated into Russian), Mir, Moscow, 1986, 364 pp
2. V G Dashevskii *Konformatsionnyi Analiz Organicheskikh Molekul* (Conformational Analysis of Organic Molecules), Khimiya, Moscow, 1982, 272 pp
3. A I Pertsin, A I Kitaigorodsky *The Atom–Atom Potential Method,* Springer Verlag, Berlin–Heidelberg, 1987, 397 pp
4. T L Hill *J. Chem. Phys.,* 1946, **14** 465
5. V A Koptyug *Arenonievye Iony. Stroenie i Reaktsionnaya Sposobnost'* (Arenonium Ions. Structure and Reactivity), Nauka, Novosibirsk, 1983, 270 pp
6. E M Arnett, N J Pienta *J. Am. Chem. Soc.,* 1980, **102** 3329
7. E Osawa, K Aigami, N Takaishi, et al. *J. Am. Chem. Soc.,* 1977, **99** 5361
8. G J Gleicher, P R v Schleyer *J. Am. Chem. Soc.,* 1967, **89** 582
9. E M Engler, M Farcasiu, A Sevin, et al. *J. Am. Chem. Soc.,* 1973, **95** 5769
10. R P Kirchen, T S Sorensen *J. Am. Chem. Soc.,* 1978, **100** 1487
11. J M Harris, S G Shafer, M R Smith, et al. *Tetrahedron Lett.,* 1979, (23) 2089
12. E M Engler, J D Andose, P R v Schleyer *J. Am. Chem. Soc.,* 1973, **95** 8005
13. G A Olah, G Liang, P R v Schleyer, et al. *J. Am. Chem. Soc.,* 1973, **95** 6829
14. N L Allinger *J. Am. Chem. Soc.,* 1973, **99** 8127
15. P M Muller, J Blanc, J Mareda *Tetrahedron Lett.,* 1984, **25** 1703
16. P M Muller, J Blanc, J Mareda *Helv. Chim. Acta,* 1986, **69** 635
17. P M Muller, J Mareda *Helv. Chim. Acta,* 1987, **70** 1017
18. P M Muller, J Blanc, J Mareda *Chimia,* 1985, **39** 234
19. P R v Schleyer, J Chandrasekhar *J. Org. Chem.,* 1981, **46** 227
20. D Farcasiu *J. Org. Chem.,* 1981, **46** 223
21. T Laube *Angew. Chem. Intern. Ed. Engl.,* 1987, **26** 560
22. T Laube *Angew. Chem.,* 1986, **98** 368
23. T Clark *Computer Chemistry* (Translated into Russian), Mir, Moscow, 1990 p. 186
24. A Nickon, R C Weglein *J. Am. Chem. Soc.,* 1975, **97** 1271
25. N Takaishi, Y Inamoto, K Aigami, et al *J. Org. Chem.,* 1977, **42** 2041
26. V P Gatilova, D V Korchagina, I Yu Bagryanskaya, et al. *Zh. Org. Khim.,* 1985, **21** 7
27. M P Polovinka, V I Mamatyuk, D V Korchagina, et al. *Zh. Org. Khim.,* 1991, **27** 999
28. V P Gatilova, D V Korchagina, T V Rybalova, et al. *Zh. Org. Khim.,* 1989, **25** 320
29. Yu V Gatilov, T V Rybalova, V A Barkhash, et al. *Zh. Org. Khim.,* 1991, **27** 1129
30. V A Bushmelev, M M Shakirov, D M Brauver, et al. *Zh. Org. Khim.,* 1979, **15** 1579
31. T S Sorensen *Acc. Chem. Res.,* 1976, **9** 257
32. R Haseltine, K Ranganaykulu, N Wang, et al. *Can. J. Chem.,* 1975, **53** 1901
33. T W Bently, B Goer, W Kirmse *J. Org. Chem.,* 1988, **53** 3066
34. S V Morozov, V G Shubin, V A Koptyug *Zh. Org. Khim.,* 1989, **25** 889

35. D H Aue, M T Bowers *Gas Phase Ion Chemistry,* Acad. Press, New York, 1979, Vol. 2, p. 346
36. R Heseltine, E Huang, K Ranganayakulu, et al. *Can. J. Chem.,* 1975, **53** 1876
37. H-J Kohler, H Lischka *J. Am. Chem. Soc.,* 1979, **101** 3479
38. V P Gatilova, D V Korchagina, Yu V Gatilov, et al. *Zh. Org. Khim.,* 1991, **27** 3001
39. L E Tatarova, V B Nigmatova, D V Korchagina, et al. *Zh. Org. Khim.,* 1989, **25** 2321
40. S A Osadchii, M P Polovinka, D V Korchagina, et al. *Zh. Org. Khim.,* 1981, **17** 1211
41. V B Nigmatova, L E Tatarova, Yu V Gatilov, et al. *Zh. Org. Khim.,* 1992, **28** 1
42. P F Vlad, N D Ungur, A N Barba, et al. *Zh. Org. Khim.,* 1986, **22** 2519
43. O A Gavrilyuk *Abstract of Candidate's Thesis in Chemical Sciences, Novosibirsk,* 1987, 150 pp
44. M P Polovinka, S A Osadchii, D V Korchagina, et al. *Zh. Org. Khim.,* 1981, **17** 1629
45. T M Khomenko, D V Korchagina, Yu V Gatilov, et al. *Zh. Org. Khim.,* 1990, **26** 2129
46. T M Khomenko, D V Korchagina, Yu V Gatilov, et al. *Zh. Org. Khim.,* 1991, **2** 599
47. D Farcasiu, E Wiskott, E Osawa, et al. *J. Am. Chem. Soc.,* 1974, **96** 4669

Received 22nd April 1992

Translated from *Uspekhi Khimii* **61** 1983–1991 (1992) U.D.C. 548.3

High-temperature X-ray diffraction: experience in the use of samples on a backing plate for studying crystalline phases mixed with the liquid

S K Filatov
St. Petersburg University

ABSTRACT. This review covers the operating procedures for X-ray diffraction studies of materials and processes in the presence of the liquid phase over a wide range of temperatures using standard X-ray diffractometers with a polycrystalline sample on a backing plate. The feasibility of using high-temperature X-ray diffraction to study materials during melting and crystallisation, to construct the supersolidus parts of equilibrium diagrams of systems, to investigate fluid crystalline materials, to find the optimum conditions for preparing materials from a solution in the melt, etc. is demonstrated.

The bibliography comprises 14 references.

Contents

I. Introduction 1085
II. The sample for high-temperature X-ray diffraction 1085
III. Studies of the fusion of materials 1086
IV. Determination of the lattice parameters of crystalline phases in mixtures with the liquid 1087
V. Studies of the supersolidus parts of equilibrium diagrams 1087
VI. Finding the optimum conditions for preparing materials 1088
VII. High-temperature studies of fluid materials (taking rotational crystals—paraffins—as an example) 1089
VIII. Conclusion 1090

I. Introduction

High-temperature X-ray diffraction has in recent decades been used successfully to study crystalline materials at different temperatures. The method has been used to determine the phase composition of a material, its crystal structure, and thermal expansion and to study high-temperature solid state transitions. Results obtained from high-temperature X-ray diffraction studies are used to construct the subsolidus parts of equilibrium diagrams of systems and as a check on the creation of technologies and materials which will function at high temperatures.[1–5]

High-temperature X-ray diffraction can also be used to study samples in the presence of a liquid.[6,7] However this facility is not often used and the results available are therefore not very complete. A choice has to be made between the two main methods of preparing a sample for investigation: packing the powder into a holder or applying the powder to a backing plate. These methods are equally laborious and similar in cost but the second fundamentally expands the potentialities of the method because it enables the material to be examined not only as a solid but also as a mixture of solid and liquid, e.g. during melting of a crystalline material.

The aim of this paper is to review and popularise the practice of using samples on a backing plate for high-temperature X-ray diffraction studies.

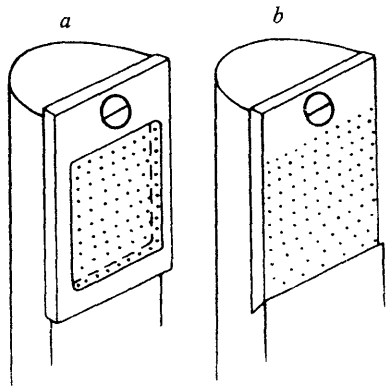


Figure 1. Powder samples for high-temperature X-ray diffraction prepared: *a*, in a holder; *b*, on the surface of a plate.

II. The sample for high-temperature X-ray diffraction

The powdered compound under investigation is usually packed into a holder made of a chemically inert material (Fig. 1*a*). Due to the geometry of the diffractometer the holder is positioned vertically and consequently on heating the material may crumble and slip down and on fusion it may run out of the holder. A more reliable specimen is obtained by depositing a thin layer of the powder on a thick plate, a backing plate,[5–7] which is not the heater (Fig. 1*b*). When this type of sample is heated above the melting point of the compound under investigation the liquid almost always wets the vertical surface of the backing plate and remains on it. An inert material, e.g. platinum, is used for the backing plate.

If the thermal expansion coefficient of the backing plate is known the latter can be used as an "internal" standard by measuring the reflection angles at all the temperatures studied. The risk of the specimen and the standard contaminating each other on heating is then less than when a powdered internal standard is used.

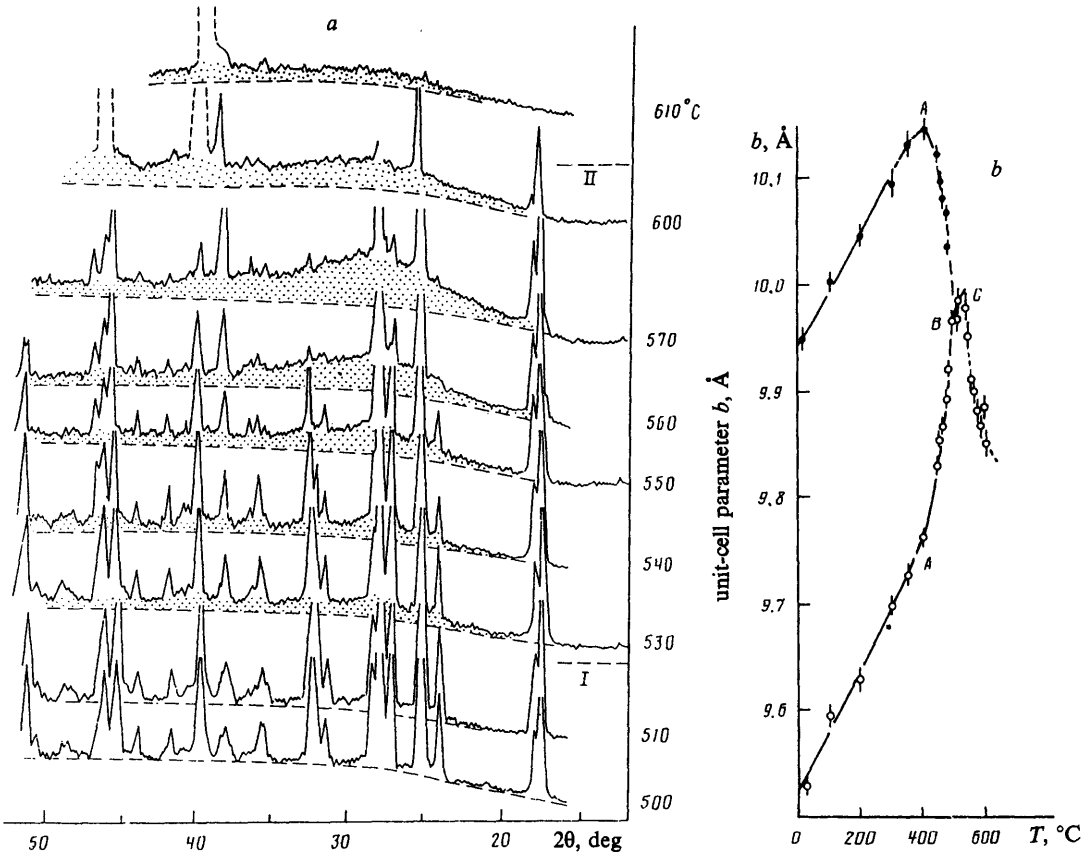


Figure 2. Typical changes with temperature in the X-ray diffraction pattern (*a*) and the unit-cell parameter (*b*) of solid solutions. Specimen composition: 80 mol% $NaVO_3$ + 20 mol% KVO_3, monoclinic phases, diopside structure type; CoK_α radiation.

A uniform thin layer (0.2–0.4 mm) of the powder on the backing plate can be obtained as follows. The plate is laid horizontally, a small quantity of the powder (some tens of milligrams) poured on to it, a few drops of alcohol added, the material levelled out with a thin (ø ≈ 0.1 mm) steel wire and kept in suspension for several minutes until all the alcohol has evaporated. If the material reacts with alcohol or the water present in it another highly volatile liquid must be used.

The thickness chosen for the layer of powder is such that the diffraction peaks from the backing plate (platinum) are completely absorbed. For inorganic compounds a layer of powder 0.2–0.4 mm thick satisfies this condition. However if the peaks from the backing plate are to be used as internal standards a thinner layer of powder is applied.

A very small amount of material is required for this type of sample, the specimen is stable at different temperatures, and solid and liquid phases can be studied concurrently.[5–13]

The representative costs of the labour and materials involved in preparing such a sample are nothing compared with the difficulties of setting up an X-ray diffractometer with a horizontal sample surface because with a geometry of that type the counter would have to rotate in a vertical plane.

III. Studies of the fusion of materials

Determinations using the halo due to the amorphous phase. Using X-ray diffraction, melting is defined by the disappearance of the diffraction maxima belonging to the crystalline phase and the appearance of a halo due to an amorphous phase (see, for example, Fig. 2*a*, 610 °C).

Melting of part of the material may be indicated by the appearance of a halo and substantial changes in the relative intensities and positions of the diffraction maxima taking place due to recrystallisation of the solid phase in the melt with a change in its chemical composition and the possible emergence of texture; compare, for example, Fig. 2*a*, 510 °C (before melting) and 560 °C (after partial melting).

If some of the melt runs off the vertical surface of the specimen holder the diffraction peaks due to the backing plate material may appear or be intensified in the diffraction pattern (see broken lines in Fig. 2*a*, 600° and 610 °C).

For a sample from the $NaVO_3$–KVO_3 system (4:1) (Fig. 2*a*) melting as defined by the criterion described starts in the region of 530 °C (line *I*) and is complete at 605 °C (line *II*).

As the halo is normally detected when there is a sufficiently large amount of the melt, there is an appreciable threshold in the sensitivity of this method to the appearance of the melt (10%).

Determinations based on the lattice parameters. The variation of the crystal lattice parameters with temperature is often a more sensitive "indicator" of melting. The onset of melting is marked by pronounced changes in the relationship. For example, for the 4:1 specimen in the $NaVO_3-KVO_3$ system melting, as defined by this criterion, starts at 535 °C (point *C* in Fig. 2*b*) and is complete at 610 °C. The detection of melting from the changes in the unit-cell parameters *b*, β, and the unit-cell volume *V* give consistent results within a few degrees.

IV. Determination of the lattice parameters of crystalline phases in mixtures with the liquid

The unit-cell parameters of a crystalline phase mixed with the liquid can be determined using a sample on a backing plate. The first such determination was made in a study of the $NaVO_3-KVO_3$ system.[12] As an example, the temperature dependence of the unit-cell parameter *b* of a 4:1 specimen from this system is shown in Fig. 2*b*. The specimen consists of two monoclinic phases of the diopside type. When these are heated, up to a certain temperature (400 °C, point *A* in Fig. 2*b*) they undergo only thermal expansion but between points *A* and *B* (~400–500 °C) the phases are homogenised, then on the section *BC* (500–530 °C) the homogeneous solid solution undergoes thermal expansion, and at point *C* (530 °C) it starts to melt.[5]

V. Studies of the supersolidus parts of equilibrium diagrams

High-temperature X-ray diffraction is widely used together with thermal analysis to study the equilibrium diagrams of systems, mainly because it is advantageous for the interpretation of transitions and identification of the phases.

It is usually used to study the subsolidus part of an equilibrium diagram. When using the method in its standard version, the formation of a liquid phase makes further investigation impossible because the material runs off the vertical plane of the sample.

Using a sample on a backing plate enables not only the solid state transformations but also the solidus and liquidus lines to be studied, i.e. a complete high-temperature X-ray diffraction study of the equilibrium diagram of a system to be made.[5,10,12,13]

Solidus and liquidus lines (plotted at various compositions). The methods described above (see Section III) are used to determine the temperatures of the commencement and termination of melting for specimens with different chemical compositions and then the solidus and liquidus lines are plotted.

Solidus line (plotted at a single composition). This is achieved using the unit-cell parameters of solid solutions. The variation of the unit-cell parameters with temperature and chemical composition is studied. The unit-cell parameters of the crystalline phases are measured at various temperatures. The dependence of these parameters on temperature and composition is used to calculate the chemical composition of the solid solutions at each temperature at which measurements are made. The points obtained are plotted on the equilibrium diagram and the interphase boundaries (solidus, binodal decomposition curve) are constructed from them.

The variation of the parameter *b* of the monoclinic solid solutions $K_xNa_{2-x}V_2O_6$ in the $NaVO_3-KVO_3$ system with temperature (*T*, °C) and potassium content (at.%) is described by the equation:

$$b = 9.478 + 0.55 \cdot 10^{-3} T + 0.0117x.$$

Part of the equilibrium diagram of the system, obtained by studying a specimen with an Na:K atomic ratio of 4:1, is shown in Fig. 3. When the temperature is raised above the solidus line this specimen breaks down into a liquid phase which is richer in potassium and a solid solution richer in sodium. In this case heating leads not only to the customary thermal expansion but also to a change in the chemical composition of the solid solution. Consequently, as is clear from Fig. 2*b*, on heating beyond point *C* the replacement of potassium ions by the smaller sodium ions leads to a marked contraction of the structure in spite of the thermal expansion that is taking place.

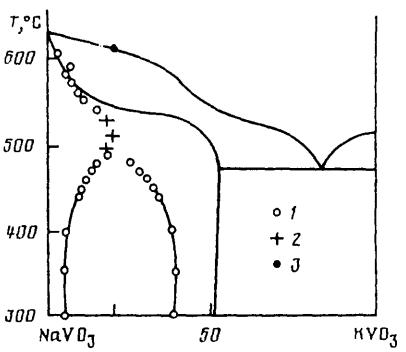


Figure 3. Construction of the equilibrium diagram of the $NaVO_3-KVO_3$ system. The experimental points were obtained using the parameter *b* for two-phase specimens (*1*) and single-phase specimens (*2*) and from the disappearance of peaks due to a crystalline phase (*3*).

The eutectic. Aspects of the X-ray diffraction study of melting in the region of the eutectic (475 °C, 83 mol% KVO_3) are illustrated in Fig. 4. When a specimen containing 80 mol% KVO_3 is heated, initially the peaks belonging to one phase (shown hatched in Fig. 4) disappear and a halo due to the liquid phase appears. There are no marked changes in the positions of the peaks belonging to the other phase or in its unit-cell parameters above the eutectic temperature (because there is no appreciable isomorphous miscibility) right up to the liquidus line, at which point these peaks disappear (*cf.* the melting of the solid solution, Fig. 2).

For compositions lying to the left of the eutectic, the diffraction peaks belonging to the right-hand phase disappear first and for those lying to the right of the eutectic, the peaks due to the left-hand phase disappear first. The composition of the eutectic is taken to be the mean between the two closest compositions at which different phases disappear. The melting point of the eutectic is the temperature at which one of the phases in the eutectic mixture

disappears. The closer the chemical composition of the specimen to that of the eutectic mixture the more melt is formed at the eutectic temperature (and hence the stronger the halo).

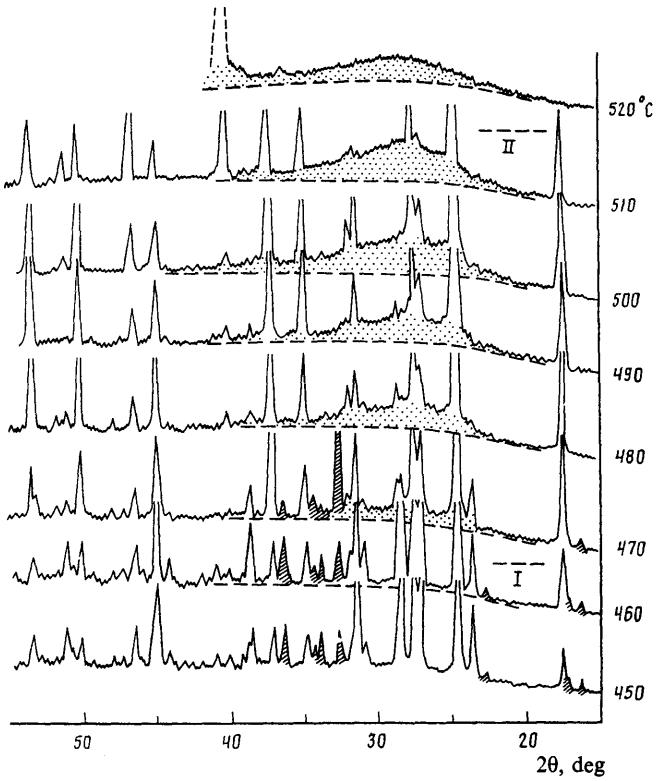


Figure 4. Typical changes in the X-ray diffraction pattern of a eutectic mixture with temperature. Specimen composition: 20 mol% $NaVO_3$ + 80 mol% KVO_3; the KVO_3 peaks are hatched and those due to $KNaV_2O_6$ are not; CoK_α radiation.

High-temperature X-ray diffraction gives some unexpected results in studies of the melting of eutectic systems. Note in particular that in the example we have been discussing (Fig. 4) the first phase disappears at a temperature (475 °C) which is 20° above (and hence later than) the appearance of the halo due to the liquid (455 °C), rather than simultaneously. Insufficiently studied premelting processes may be the cause of this.

High-temperature X-ray diffraction makes it possible to observe phases and processes at different temperatures directly and to identify them objectively. It is therefore advisable to use this method of studying equilibrium diagrams in conjunction with other methods of thermal investigation.

VI. Finding the optimum conditions for preparing materials

Reactions between substances are more rapid in the melt than between solid phases. For this reason it is helpful to introduce an easily fusible component into the mixture.

For example, in order to prepare anorthite $CaAl_2Si_2O_8$, $CaCl_2$ (m.p. 777 °C) was mixed with dickite $Al_2Si_2O_5(OH)_4$ in a 1:1 ratio, the mixture was heated, and X-ray diffraction patterns recorded at various temperatures (Fig. 5).[5] In the pattern recorded at 600 °C the diffraction peaks belonging to $CaCl_2$ are hatched. On reaching 700 °C the peaks belonging to dickite disappear due to dehydration and conversion to a metakaolinite that is amorphous to X-rays (thermographic and quenching data). The diffraction pattern recorded at 800 °C contains no peaks belonging to $CaCl_2$ either, indicating that the metakaolinite phase is in a $CaCl_2$ melt. This state also persists at 900 °C (Fig. 5).

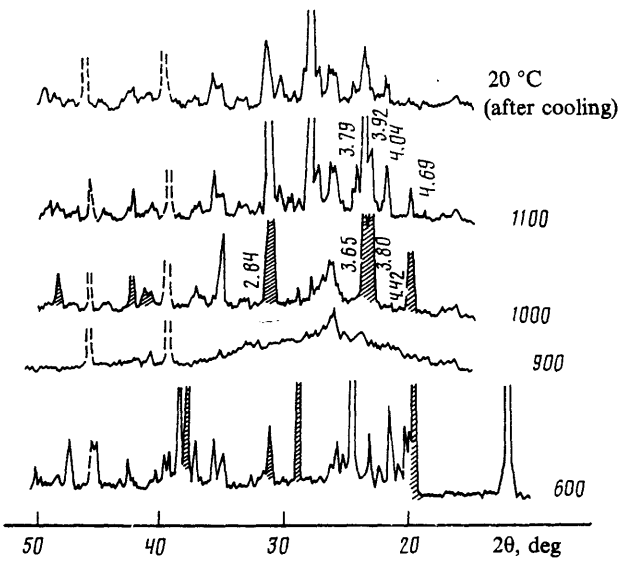


Figure 5. Preparation of anorthite: X-ray diffraction patterns of dickite mixed with $CaCl_2$ (the peaks at 600 °C due to the latter are hatched) and the products obtained by heating them (CuK_α radiation).

At 1000 °C a new structure (a layer type anorthite with the interplanar spacings d = 4.42, 3.80, 3.65, and 2.84 Å) is found in the products and when the temperature is raised to 1100 °C this is transformed to a framework modification of anorthite (with d = 4.69, 4.04, 3.92, and 3.79 Å) which is retained on cooling to room temperature.

In this experiment the film of liquid was kept on the vertical backing plate by surface adhesion forces (see Fig. 5, 900 °C). This permitted direct "observation" of the synthesis of anorthite involving the liquid phase, determination of the synthesis temperature, and the discovery that a layer-type modification of anorthite is formed initially (at 950 ± 50 °C) and is irreversibly converted to the more stable framework modification of this compound at 1050 ± 50 °C.

VII. High-temperature studies of fluid materials (taking rotational crystals — paraffins as an example)

Certain crystalline compounds display considerable fluidity, especially at temperatures near the melting point. High-temperature studies of fluid materials are not feasible on standard X-ray diffractometers with the sample packed into a vertical holder but no technical difficulties are encountered if the sample is placed on a backing plate.

Let us take as an example the normal paraffins C_nH_{2n+2}. At low temperatures these have normal crystal structures with three-dimensional periodicity but on heating they change, due to rotation of the linear molecules around their axes, to rotational crystals which have one-dimensional periodicity and finally melt, losing the periodicity. In all these states paraffins can be retained safely on the vertical surface of a sample for high-temperature X-ray diffraction.

The polymorphism of paraffins. The diffractometer traces in Fig. 6 show that the low-temperature orthorhombic modification of the paraffin with $n = 23$ changes at 40 °C to the (comparatively) high-temperature hexagonal rotational modification (the 200 and 110 peaks merge together) which melts at 47 °C. X-Ray diffraction studies of other members of the homologous series show that, contrary to the accepted opinion, the paraffins with n odd and less than 23 melt without reaching the hexagonal state.[11]

Ranges [of existence] of paraffin solid solutions. Both in nature (as concomitants of petroleum, coverings of plants) and in industries (packaging, food, electronic, and other branches) paraffins usually occur as a mixture of many homologues. For this reason studies have been made of the ranges of existence of solid solutions of different paraffins and the effect of the formation of solid solutions on polymorphism, melting, and other properties of paraffin compositions.[14]

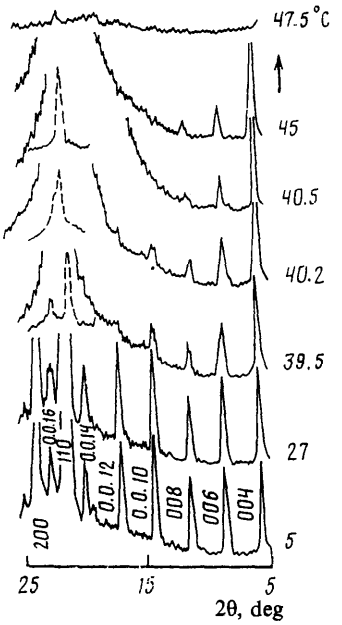


Figure 6. X-Ray diffraction patterns of the paraffin with $n = 23$ at different temperatures.[11] The peaks shown by broken lines were re-recorded using an anode current 10 times smaller; CuK_α radiation.

The data plotted in Fig. 7 show that when a homogeneous orthorhombic solid solution with the composition $C_{21}H_{44}:C_{23}H_{48} = 1:5$ is heated it breaks down at 30 °C to give two orthorhombic solid solutions, then at 34 °C the mixture of phases becomes homogeneous again, and close to 39 °C it changes to the hexagonal

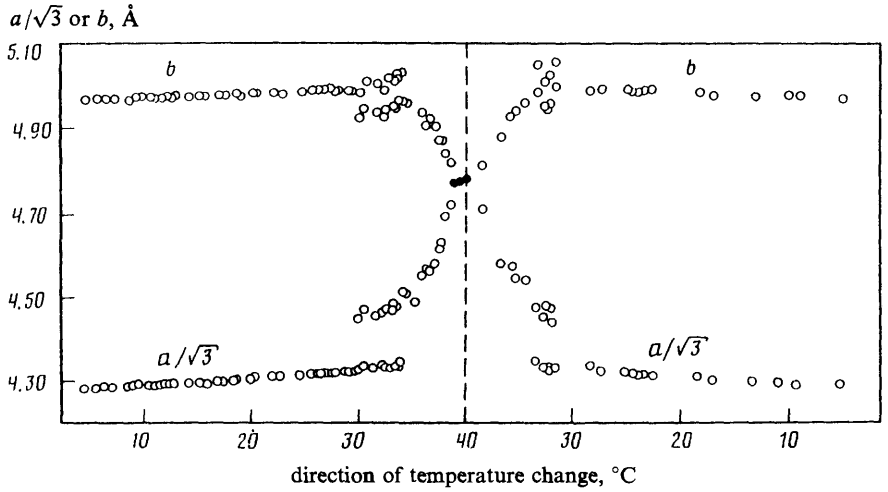


Figure 7. Variation with temperature (both heating and cooling) of the parameters $a/\sqrt{3}$ and b of the orthorhombic and hexagonal unit cells of a paraffin solid solution with the composition $C_{21}H_{44}:C_{23}H_{48} = 1:5$. The dark points relate to the hexagonal modification.

phase. On cooling these changes are repeated in the reverse sequence. This is the only example we know of where the range of the solid solution contracts on raising the temperature. It is evidently connected with the rotation of the molecules.

When the solid solution is heated the shorter aliphatic chains in the paraffin with $n = 21$ reach critical amplitudes of swinging, and possibly complete rotation around their axes, at an earlier stage and they escape from the structure of the homogeneous solid solution; at a temperature a few degrees higher when the longer molecules with $n = 23$ reach a comparable degree of oscillation or rotation, all the molecules again become comparable in energy and the mixture becomes homogeneous again.[14]

VIII. Conclusion

The high-temperature X-ray diffraction of polycrystalline samples is an objective method of studying the qualitative and quantitative phase composition of crystalline materials during a variety of solid-state thermal changes.

Using a standard X-ray diffractometer with a polycrystalline sample in the form of a thin layer of material on an inert backing plate also enables us to study crystalline materials in contact with the liquid phase, i.e. to study fusion, crystallisation, and recrystallisation processes. This provides opportunities for the complete high-temperature X-ray diffraction study of the equilibrium diagrams of systems, including their supersolidus part, and also for investigating the processes of the formation of crystalline materials from the liquid, and modelling magma and other processes involving the liquid phase.

The experience in the use of samples on a backing plate built up in the Department of Crystallography of St. Petersburg University over a period of twenty-five years shows that films of melts of various chemical compositions can be maintained on the vertical surface of a platinum backing plate by adhesion forces, so making it possible to carry out the high-temperature X-ray diffraction studies that have been described.

We can be confident that this experience will promote a wider application of high-temperature X-ray diffraction, especially with the use of a sample on a backing plate, for solving problems in crystal chemistry, physical chemistry, materials science, etc.

I am grateful to my colleagues, especially R S Bubnova and E N Kotel'nikova, for the joint research which I have quoted in this review.

References

1. S P Clark, Jr. (Editor) *Handbook of Physical Constants* (The Geological Society of America, Memoir 97) (Translated into Russian), Mir, Moscow, 1969, 543 pp
2. R S Krishnan, R Srinivasan, S Devanarayanan *Thermal Expansion of Crystals*, Pergamon Press, Oxford, 1979, 305 pp
3. R M Hasen, L W Finger *Comparative Crystal Chemistry*, London, 1982, 231 pp
4. D Taylor *Br. Ceram. Trans. J.*, 1984, **83** 5–9 (I), 32–37 (II), 92–98 (III), 129–133 (IV); 1985, **84** 9–14 (V), 121–127 (VI), 149–153 (VII), 181–188 (VIII); 1986, **85** 111–114 (IX), 147–155 (X); 1987, **86** 1–6 (XI); 1988, **87** 39–45 (XII), 88–95 (XIII); 1991, **90** 64–69 (XIV)
5. S K Filatov *Vysokotemperaturnaya Kristallokhimiya* (High-Temperature Crystal Chemistry), Nedra, Leningrad, 1990, 288 pp
6. S K Filatov *Kristallokhimiya i Termostoikost' Dvuokisi Tsirkoniya* (The Crystal Chemistry and Thermal Stability of Zirconium Dioxide), Thesis for the Degree of Candidate of Geological and Mineralogical Sciences, Leningrad State University, Leningrad, 1969, 184 pp
7. S K Filatov *Krist. und Techn.*, 1971, **6** 777–785
8. *Rukovodstvo po Rentgenovskomu Issledovaniyu Mineralov* (Manual on the X-Ray Diffraction Study of Minerals), Nedra, Leningrad, 1975, 400 pp
9. S K Filatov *Voprosy Geneticheskoi i Strukturnoi Kristallografii* (Problems in Generic and Structural Crystallography), Izd. Leningrad. Gos. Univ., Leningrad, 1978, pp 18–21
10. S K Filatov, R S Bubnova *Apparatura i Metody Rentgenovskogo Analiza* (Apparatus and Methods for X-Ray Diffraction Analysis), Mashinostroenie, Leningrad, 1983, No. 31, pp 180–183
11. S K Filatov, E N Kotelnikova, E A Aleksandrova *Z. Kristal.*, 1985, **172** 35–43
12. R S Bubnova, S K Filatov, R G Grebenshchikov *Dokl. Akad. Nauk SSSR*, 1987, **292** 107–111
13. R S Bubnova, S K Filatov, R G Grebenshchikov *Dokl. Akad. Nauk SSSR*, 1989, **306** 1148–1151
14. S K Filatov, E N Kotelnikova, I E Rastorgueva *Z. Kristal.*, 1991, **194** 253–260

Received 13th December 1991

Translated from *Uspekhi Khimii* **31** 1992–2039 (1992) U.D.C. 547.345

Silicon-containing 1,3-alkenynes and more unsaturated compounds

M D Stadnichuk, T I Voropaeva
The Technological Institute, St. Petersburg

ABSTRACT. The methods of synthesis and characteristic features of the reactivity of silicon-containing alkenynes are treated systematically and surveyed for the first time. It is shown that the carbon–carbon double bonds are reactive in the reactions of silahydrocarbons and their functional derivatives containing the $\equiv Si-C\equiv C-C=C<$ fragments. Only aluminium, boron, and tin hydrides as well as certain weak electrophiles add preferentially or exclusively to the triple bond. The absence of a dependence of the mode of addition on the polarity of the unsaturated compound and the other reactant indicates orbital control in the reactions investigated.

Studies of the dependence of the mode of reaction (addition, desilylation, reactions of functional groups) on the structure of the silicon-containing alkenynes, the nature of the other reactant, and the experimental conditions served as a basis of the development of methods for the introduction of functional groups into the alkenynes and of a silyl protecting group method in the chemistry of acetylenic compounds and have demonstrated the extensive possibilities of the application of these procedures in the stereocontrolled synthesis of natural products and their synthetic analogues.

The bibliography includes 346 references.

Contents

I.	Introduction	1091
II.	Synthesis of 1-triorganosilylalk-3-en-1-ynes	1091
III.	Chemical properties of silicon-containing alk-3-en-1-ynes	1100

I. Introduction

The highly unsaturated compounds containing a conjugated double and triple bond and an organosilyl group attached to a multiply bound carbon atom exist in the form of three isomers differing in the position of the silicon-containing substituent:

$R^1_3Si-C\equiv C-CR^2=CR^3R^4$ (A)

$R^1_3Si-CR^2=CR^3-C\equiv CR^4$ (B)

$R^2R^3C=C(SiR_3)-C\equiv C-R^4$ (C)

Representatives of all these types have now been synthesised, but compounds of type (A) are historically the first and have been most thoroughly investigated. Hundreds of original articles have been devoted to the methods of their synthesis and chemical properties, but there are no reviews on the problem.

Compounds of types (B) and (C) have not been studied systematically. The communications published on this problem were devoted to the development of the methods of their synthesis and are as a rule non-systematic in character.

In the first stage, the chemistry of 1-triorganosilylalk-3-en-1-ynes (A) was indissolubly linked to the study of fundamental problems of theoretical organic chemistries such as conjugation, including $d_\pi-p_\pi$ conjugation, the relation between reactivity and structure, and the redistribution of the π-electron density of conjugated multiple bonds under the influence of the organosilicon substituent. A considerable proportion of studies in the first stage were therefore devoted mainly to the synthesis of 1-trialkylsilylalk-3-en-1-ynes and to the study of their properties. Such investigations (UV,[1] IR,[2–8] and photoelectron spectra,[9] molecular refraction,[10,11] quantum-chemical calculations,[12,13] ^1H[14] and ^{13}C[13,15–17] NMR spectra, dipole moments,[18–20] and mass spectra[21]) yield direct or indirect information about the magnitude and sign of the induction and mesomeric constants of the silicon-containing groups. The results have demonstrated unambiguously that the triorganosilyl groups attached to the triple bond exhibit an overall electron-donating effect, which is somewhat smaller than that of the hydrocarbon groups with the corresponding structures, while the basic (π-donor) properties of the triple bond in the 1,3-enyne silahydrocarbons are weaker than those of the hydrocarbons having similar structures. The spectroscopic parameters (IR, ^1H NMR, and mass spectra) have been recommended for analytical purposes in the determination of the structures of highly unsaturated organosilicon compounds.

Interest in the chemistry of enyne organosilicon compounds of type (A) increased appreciably after the development of mild desilylation methods (the removal of the triorganosilyl substituent stabilising the triple bond) as well as methods for the stereocontrolled synthesis of functional derivatives of 1-triorganosilylalk-3-en-1-ynes and the possibility of using them as synthetic units in fine organic synthesis was demonstrated.

II. Synthesis of 1-triorganosilylalk-3-en-1-ynes

The methods of synthesis of 1-triorganosilylalk-3-en-1-ynes and their carbofunctional derivatives known at present include procedures such as silylation of complete 1,3-enyne hydrocarbons and their derivatives, the creation of enyne structures as a result of β-elimination reactions of the derivatives of the corresponding acetylenic silylhydrocarbons or reactions involving the addition of silicon-containing diynes, the isomerisation (including reactions with ring opening) of unsaturated organosilicon compounds, as well as the creation of alkenyne structures as a result of the cross-coupling of silicon-containing acetylenes with the corresponding alkenes or

their precursors. As a rule, these fundamental approaches to the synthesis of a specific compound are intertwined and may involve simultaneously the formation of a double bond and the construction of the carbon skeleton and silylation.

1. Silylation of alkenynes

The most important methods for the laboratory synthesis of silicon-containing alkenynes and their derivatives is organometallic synthesis involving the interaction of the corresponding Iotsich complex with trialkylchlorosilane. 3-Methyl-1-triethylsilylpent-3-en-1-yne, the first representative of silicon-containing vinylacetylenes, was synthesised by this method in 1946:[1]

$$Et_3Si{-}Cl + CH_3CH{=}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{-}C{\equiv}CMgBr \longrightarrow$$

$$\longrightarrow Et_3Si{-}C{\equiv}C{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{=}CHCH_3.$$

The Iotsich reagents derived from the simplest vinylacetylenic (vinyl-,[22–24] isoalkenyl-,[25–29] alkenyl-,[25–30] and cycloalkenyl-acetylenes[25,27,28]) and more unsaturated hydrocarbons[31–34] were initially made to react with trialkylchloro- and dialkyldichloro-silanes. Trialkyl-, dialkylaryl-, and alkyldiaryl-chloro-silanes, entered into this reaction. With increase in the number of aryl groups at the silicon atom, the yield of the condensation products fell.[23,24] The attempts obtain 1-triphenylsilylbut-3-en-1-yne by the reaction of chlorotriphenylsilane and vinylethynylmagnesium bromide was unsuccessful.[23] The corresponding silylhydrocarbon was synthesised only by the reaction of the Iotsich complex with fluorotriphenyl-silane.[24] However, tri-*p*-chlorophenylsilylvinylacetylene was obtained by the reaction of the corresponding chlorosilane with the Iotsich complex, but it was necessary to heat the reaction system to a high temperature—the temperature of boiling dibutyl ether.[24]

The vinylacetylenic hydrosilanes $R_2HSi{-}C{\equiv}C{-}CH{=}CH_2$ and $RHSi(C{\equiv}C{-}CH{=}CH_2)_2$ were synthesised by the reaction of chlorohydrosilanes with vinylethynylmagnesium bromide.[23]

There are data showing the trialkyliodosilanes give rise to the corresponding vinylacetylenic silylhydrocarbons in higher yields than trialkylchlorosilanes.[25]

Alkoxysilanes, siloxanes, alkoxychlorosilanes, and triflates can be used as the silicon-containing component:

$$R^1_{4-n}(R^2O)_nSi + CH_2{=}CH{-}CMgBr \rightarrow R^1_{4-n}Si(C{\equiv}C{-}CH{=}CH_2)_n$$

(Refs. 23, 35, 36),

$$(R^1R^2SiO)_x + CH_2{=}CH{-}C{\equiv}CMgBr \rightarrow HO(R^1R^2)SiC{\equiv}C{-}CH{=}$$

$$={=}CH_2 \quad \text{(Refs. 37, 38)},$$

$$(RO)_3SiCl + CH_2{=}CH{-}C{\equiv}CMgBr \rightarrow (RI)_3SiC{\equiv}C{-}CH{=}CH_2$$

(Refs. 39, 40),

$$R_3SiCTf + CH_2{=}CH{-}C{\equiv}CMgBR \rightarrow R_3SiC{\equiv}CH{=}CH_2 \text{ (Ref.41)}.$$

A method based on the reaction of a mixture of the enyne hydrocarbon and chlorotrimethylsilane with butyllithium in hexane, presupposing the formation of lithium vinylacetylide, was developed for the synthesis of alkenyl-1-trimethylsilyl-, isoalkenyl-1-trimethyl-silyl-, and cycloalkenyl-1-trimethylsilyl-acetylenes:[30,42–44]

$$R^2CH{=}CR^1{-}C{\equiv}CH \xrightarrow[2.\ Me_3SiCl]{1.\ LiBu} Me_3SiC{\equiv}C{-}CR^1{=}CHR^2.$$

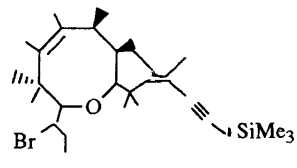
When isopropenylacetylene is treated with a mixture of butyllithium and potassium t-butoxide, the corresponding organo-potassium compound reacts with the chlorosilane:[43]

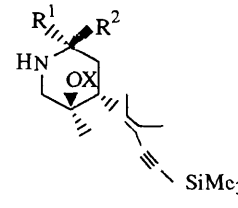
$$\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH_2{=}C{-}C{\equiv}CH}} \xrightarrow{BuLi;\ t\text{-}BuOK} \underset{\displaystyle CH_2K}{\overset{\displaystyle |}{CH_2{=}C{-}C{\equiv}CK}} \xrightarrow{Me_3SiCl} \underset{\displaystyle CH_2SiMe_3}{\overset{\displaystyle |}{CH_2C{-}C{\equiv}}}$$

$$\equiv CSiMe_3.$$

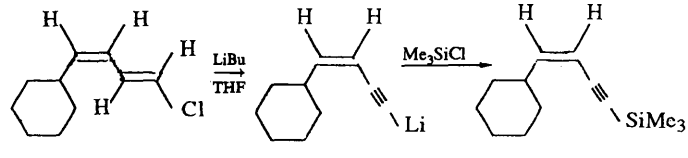
Subsequently the method of synthesis of lithium acetylides was simplified and reduced to the single-stage interaction of metallic lithium with vinylacetylene in tetrahydrofuran (THF).[45,46] Sodium vinylacetylide was obtained similarly.[47] The use of lithium and sodium acetylides makes it possible to increase the yield of the target products by 30–40% compared with the reactions of Iotsich complexes having analogous structures.[45–47]

The organolithium, organosodium, and organomagnesium syntheses of silicon-containing alkenynes can be used also for the preparation of functional derivatives of hydrocarbons subject to the condition that the functional group does not interact with the organometallic compound. Silicon-containing vinylacetylenic alcohols,[48–51] ethers,[52–54] sulphides,[55] acetals,[56,57] ketals,[41] tertiary amines,[30,42,58–60] and more complex organic compounds[61,63] were obtained in this way, for example:





An unusual version of this method involves a procedure employed in the synthesis of (*Z*)-4-cyclohexyl-1-trimethylsilylbut-3-en-1-yne:[64]



and 3-ethoxy-1-trimethylsilylbut-3-en-1-yne:[65]

$$CH{\equiv}CF + CH_2{=}C(Li)OEt \longrightarrow \underset{\displaystyle OEt}{\overset{\displaystyle |}{CH_2{=}C}}{-}C{\equiv}CLi \xrightarrow{Me_3SiCl}$$

$$\longrightarrow \underset{\displaystyle OEt}{\overset{\displaystyle |}{CH_2{=}C}}{-}C{\equiv}CSiMe_3.$$

The method involving the direct silylation of vinylacetylene with iodosilatrane was developed by Voronkov et al.:[66]

$$CH_2{=}\,CH{-}C{\equiv}CH + ISi(OCH_2CH_2)_3N \longrightarrow$$

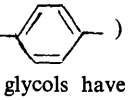
$$\longrightarrow CH_2{=}CH{-}C{\equiv}CSi(OCH_2CH_2)_3N.$$

The same vinylethynylsilatrane was obtained by the transalkylation of triethoxyvinylethnylylsilane with triethanolamine.[67]

2. β-Elimination reactions

(a) Dehydration of silicon-containing acetylenic alcohols

This method was successfully used for the first time in the synthesis of silicon-containing alkenynes in 1957. Distillation of dimethyl(trimethylsilylethynyl)carbinol in the presence of catalytic amounts of potassium hydrogen sulphate afforded 3-methyl-1-trimethylsilylbut-1-yne in a satisfactory yield.[68] Phosphorus pentoxide,[69,70] adipic acid,[71,72] boric acid,[72] toluene-*p*-sulphonic acid,[70–75] and phosphoryl chloride[76] began to be used later as dehydrating agents.

The method yields positive results not only in the synthesis of the corresponding silylhydrocarbons[68–78] but also of their derivatives,[70,74,76] as well as bisalkenylsilanes. In the latter case, the corresponding glycols of the type $Me_2Si[C{\equiv}C{-}C(CH_3)_2OH]_2$ and $[HO(CH_3)_2C{-}C{\equiv}C{-}SiR_2]_2A$ (A = $-CH_2CH_2-$ or ) were dehydrated.[79–83]

Oxygen-containing tertiary acetylenic alcohols and glycols have also been dehydrated. The attempts to dehydrate a secondary alcohol with potassium hydrogen sulphate failed to give positive results.[84]

One should evidently note the unusual dehydration, contrary to Zaitsev's rule, of a diacetylenic ketoalcohol, which led to the formation of a "stable" enol:[74]

$$Me_3SiC{\equiv}C{-}\,C(OH)CH_3CH_2COC{\equiv}\,CSiMe_3 \xrightarrow[-H_2O]{H^+}$$

$$\longrightarrow Me_3SiC{\equiv}C-\underset{\underset{CH_2}{\|}}{C}-CH=\underset{\underset{OH}{|}}{C}-C{\equiv}\,CSiMe_3.$$

The stereochemistry of the dehydration has not been studied in most cases but there are indications that water is split off stereospecifically.[85,86]

(b) Base-catalysed elimination of hydrogen halides and other acids

The dehydrohalogenation method, widely used in the chemistry of alkenes, has been scarcely employed in the synthesis of silylhydrocarbons owing to the low hydrolytic stability of the silicon–carbon bond: the elimination of hydrogen halides is as a rule accompanied by desilylation. For example, treatment of 1,4-dibromo(bromochloro)-1-trimethylsilylbuta-1,2-diene with an alcoholic solution of alkali involves dehydrohalogenation and desilylation even in the cold with formation of the corresponding α-halovinylacetylenes:

$$Me_3SiCX{=}C{=}CHCH_2Br \xrightarrow[EtOH]{KOH} XC{\equiv}C{-}CH{=}CH_2;$$

X = Cl (Ref.87), Br (Ref.25).

The data on the dehydrobromination of silicon-containing acetylenic bromoethers are contradictory; whereas according to the data of Komarov and co-workers dehydrobromination without the cleavage of the silicon–carbon bond occurs only when triethylamine is used as the base and dehydrosilylation takes place in the presence of alkali,[88] according to Shchukovskaya and Kapustyanskaya[89] the dehydrobromination of bromoethers can be carried out also in the presence of solid potassium hydroxide:

$$R_3SiC{\equiv}C{-}\underset{\underset{OR'}{|}}{CH}CH_2Br \begin{cases} \xrightarrow[EtOH]{KOH} CH{\equiv}C-C(OR'){=}CH_2\ ; \\ \xrightarrow[\text{or KOH}]{Et_3N} R_3SiC{\equiv}C-C(OR'){=}CH_2\ . \end{cases}$$

Dehydrohalogenation without appreciable cleavage of the silicon–carbon bond has been used successfully in the synthesis of 1-trimethylsilylalk-3-ene-1,5-diynes[90] and 1,8-bis(trimethylsilyl)octa-3,5-diene-1,7-diyne.[33]

The dehyodrohalogenation (X = Cl, Br, I) of silicon-containing acetylenic and alka-1,2-diene sulphones by tertiary amines takes place particularly readily and with virtually quantitative yields (the reactions occurs at room temperature):[91–94]

$$R_3SiC{\equiv}C{-}CR'XCHR''SO_2Ar \xrightarrow[C_6H_6]{Et_3N} R_3SiC{\equiv}C{-}CR'{=}CR''SO_2Ar.$$

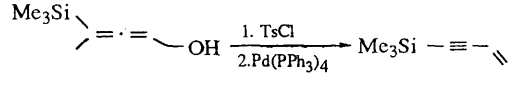
The study of the IR and ^1H NMR spectra as well as the dipole moments of the sulphones formed indicates their exclusive *trans*-structure.[20,91–93]

It has been shown in relation to the dehydroiodination of silicon-containing iodonitroacetylenes that mercury [lead?] acetate may be used as a weak base which does not cleave the silcon–carbon bond:[95]

$$R_3SiC{\equiv}\,CCHICH_2NO_2 \xrightarrow[AcOH,\ 30-40^\circ C]{Pb(OAc)_2} R_3SiC{\equiv}C-CH{=}CHNO_2.$$

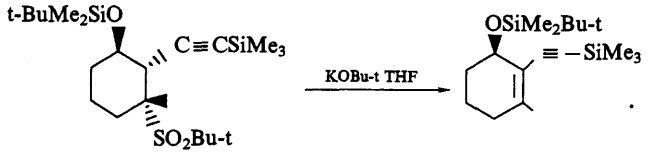
The reaction takes place stereospecifically with formation of compounds having the *trans*-configuration.

The data presented permit the claim that the base-catalysed dehydrohalogenation can serve as a convenient preparative method of synthesis of 1,3-enyne silylhydrocarbons and their derivatives but in each specific instance the solvent and base must be selected empirically. The method involving the base-catalysed (pyridine, diazabicycloundecyne) β-elimination of toluene-*p*-sulphonic acid proved to be successful in the synthesis of 1,3-enyne silylhydrocarbons and their derivatives.[85,86] Tosylates have been obtained from the corresponding secondary silicon-containing acetylenic alcohols and glycols. 4-Trialkylsilylbuta-2,3-diene-1-yl tosylate gives rise to a satisfactory yield of 1-trimethylsilylbut-2,3-en-1-yne on treatment with triphenylphosphine or the palladium complex $Pd(PPh_3)_4$:[96]



The base-catalysed cleavage of acetylenic sulphones, sulphoxides, selenoxides, and other reagents with elimination of H–X, where X = PhSO,[97] PhSeO,[98] t-$BuSO_2$,[99] and $(EtO)_2P(O)O$ [100] respectively, can also be included in this group of methods. It is of interest that

the elimination of 2,2-dimethylethanesulphonic acid on treatment with potassium t-butoxide in the example below is not accompanied by the cleavage of the silicon–carbon bond:[99]



3. Synthesis from 1-trialkylsilylalka-1,3-diynes

The 1,3-diyne silicon-containing compounds, which are available under laboratory conditions, are convenient "starters" for the synthesis of two types of the corresponding silylalkenynes containing a silicon atom attached to the triple or double bond: $R_3SiC{\equiv}C{-}CX{=}CYR'$ and $R_3SiCX{=}CY{-}C{\equiv}CR'$, which can be obtained by adding the reagent XY to one of the triple bonds of the diyne.

(a) Reduction of 1,3-diynes

The catalytic reduction of silicon-containing diacetylenic hydrocarbons was first achieved in 1964.[101] It was established that the reaction proceeds with a high chemoselectivity in relation to the triple bond remote from the silicon atom:

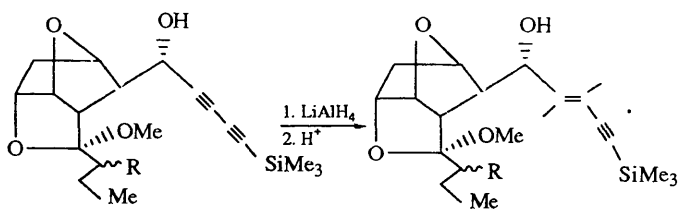
$$R_3SiC{\equiv}C-C{\equiv}C-R' + H_2 \xrightarrow{Pd/CaCO_3} R_3SiC{\equiv}C-CH{=}CHR'.$$

The stereochemistry of the process was not investigated.

The protecting effect of the trialkyl(aryl)silyl groups was used later by other investigators for the selective catalytic hydrogenation of triple bonds "unprotected" by silicon-containing groups in the synthesis of 1,3-enyne silicon-containing hydrocarbons. These studies served as the experimental basis of the method involving the "silyl protection" of the triple α,β-bond in catalytic reduction reactions, the method being widely used in organic synthesis.[102] It has been established that, regardless of the nature of the catalyst (palladium on calcium carbonate or sulphate,[32,101,103] Lindlar's platinum[104,105]) the reaction is chemoselective and stereospecific: the 1-trialkylsilylalk-3-en-1-ynes formed have the (*Z*)-configuration.

The reduction of silylalkadiynes with metallic zinc in ethanol proceeds similarly, i.e. it involves the bond remote from the heteroatom, with the preferential formation of (*Z*)-enynes.[106] The reaction takes place when zinc is activated with lithium dibromocuprate and 1,2-dibromoethane or with 1,2-dibromoethane alone.

(*Z*)-Alkenynes have been obtained exclusively also in the reduction of bis(trimethylsilyl)buta-1,3-diyne with lithium tetrahydroaluminate in THF.[107] On the other hand, the reduction of diacetylenic alcohols with lithium tetrahydroaluminate takes place stereo-specifically in the *trans*-position:[108–110]

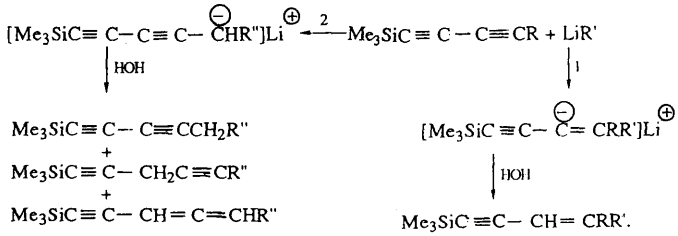


Enyne silicon-containing hydrocarbons with the exclusive (*E*)-configuration are formed in high yields (more than 90%) when lithium trialkylaluminates are used as the reducing agents:[111,112]

$$Me_3SiC{\equiv}C-C{\equiv}CR + Li[AlH(iso\text{-}Bu)_2Bu] \xrightarrow{E} Me_3SiC{\equiv}C-\underset{\displaystyle E}{\underset{|}{C}}{=}C-R.$$
$$\qquad\qquad\qquad

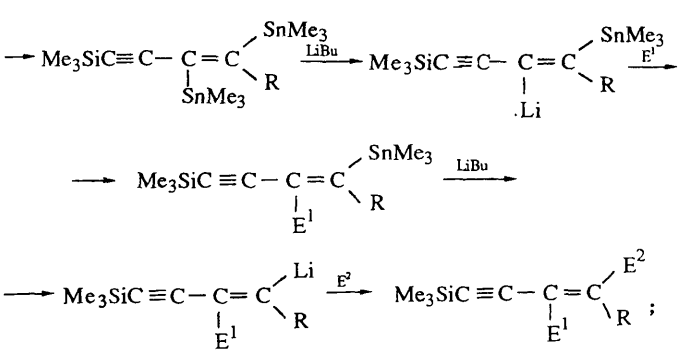
(c) Interaction with organometallic compounds

Organolithium compounds add to the triple bond of 1-trialkylsilylalka-1,3-diynes remote from the silicon atom. After the demetallation of the lithium-containing adducts with water, the corresponding vinylacetylenic silyl-substituted hydrocarbons were obtained in satisfactory yields:[119,120]



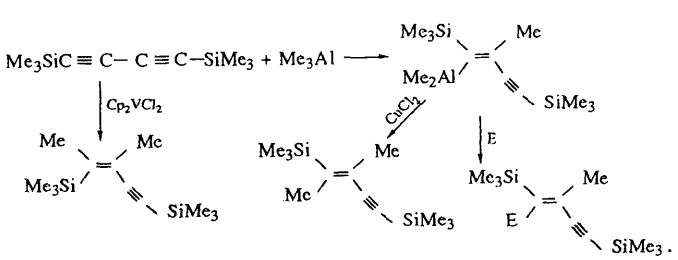
The addition reaction is accompanied by the isomerisation of the initial diacetylenes (pathway 2). Appreciable amounts of the isomerisation products were obtained in reactions of 1-trialkylsilylpenta-1,3-diyne with lithium alkyls.

The silicon-containing alkenynes $Me_3SiC{\equiv}CE^1C{=}CE^2R$ are obtained from the corresponding diacetylenic silicon-containing hydrocarbons by the successive treatment of the diyne with trimetylstannyl cuprate and the corresponding electrophile E in accordance with the scheme[121]



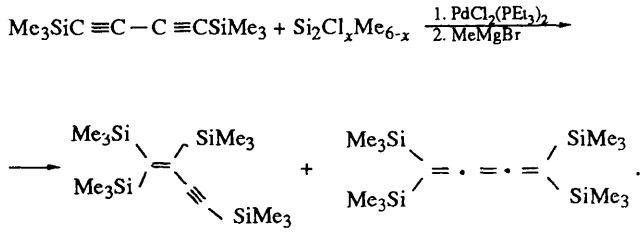
E^1 and E^2 = AlkBr.

The addition of trialkylaluminium and subsequent treatment of the alumnium-containing adducts with an electrophile E can also be recommended as a preparative method of synthesis of silicon-containing alkenynes:[122,123]



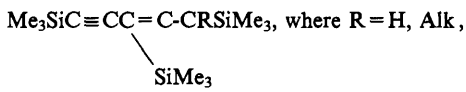
The reaction is regio- and stereo-specific and takes place only in the presence of catalysts. In the series Cp_2ZrCl_2, Cp_2TiCl_2, and Cp_2VCl_2, the best yields were obtained with the zirconium catalyst.

An interesting method of synthesis of persilylated butenynes is based on the catalytic silylation of bis(trimethylsilyl)buta-1,3-diyne with alkylchlorodisilanes[124]



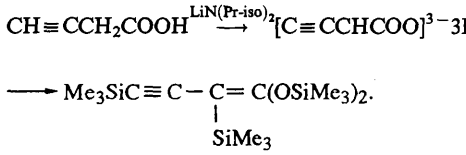
The yield and the rate of the isomeric 1,2- and 1,4-adducts are determined by the structure of the disilane as well as the temperature and duration of the experiment.

Mono- and poly-silylated alkadienynes of the type



where R = H or alkyl, are formed in the reaction of the anions or polyanions obtained from alka-1,2-diynes with chlorotrimethylsilane.[125–128]

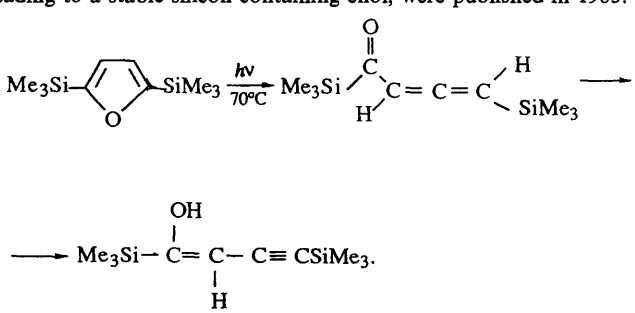
Polysilylated alkenynes have also been obtained by treating the trianion of but-3-ynoic acid with chlorotrimethylsilane:[129]



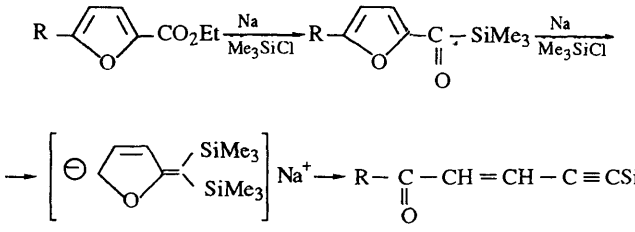
The reaction involving the addition[130–134] or cycloaddition (the Diels–Alder reaction)[135] of the corresponding reagents (bromine,[133,134] thiols,[130,131] hydrazine,[132] hydroxylamine[132]) to one of the triple bond of 1-trialkylsilylalka-1,3-diyne may be recommended as a method of synthesis of halogen-, sulphur-, and nitrogen-containing derivatives of silylalkenynes.

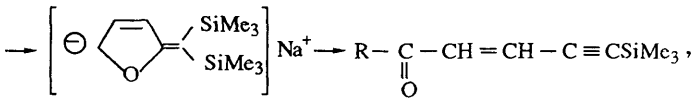
(4) Isomerisation reactions

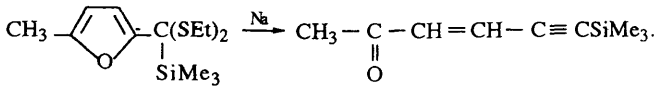
Oxygen containing functional derivatives of 1-trialkylsilylalk-3-en-1-ynes can be obtained as a result of the specific cleavage reaction of silylated furans and their sulphur and selenium analogues. Thus the results of an unusual photoinitiated opening of the furan ring, leading to a stable silicon-containing enol, were published in 1983:[136]



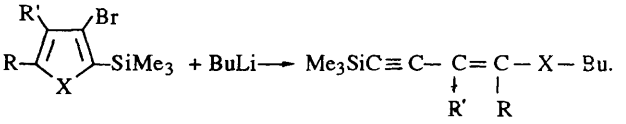
Ethyl furoates[137] and thioketals of the furan series[138] are converted into vinylacetylenic silicon-containing ketones on treatment with metallic sodium:



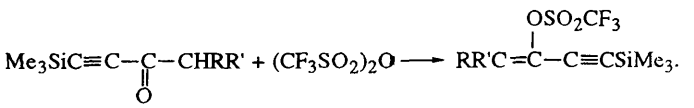




Silylated 3-bromothiophenes and 3-bromoselenophenes give rise to silicon containing alkenyne thio- and seleno-ethers with a (*Z*)-configuration in satisfactory yields on reaction with butyl-lithium:[139]



Silicon-containing triflates with alkenyne fragments are readily obtained from acetylenic ketones and the anhydride of trifluoromethanesulphonic [triflic] acid:[140–143]



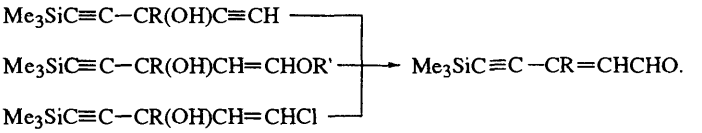
The kinetics of this reaction were investigated.[141]

Carbofunctional derivatives of 1-trialkylsilylalk-3-en-1-ynes (alcohols, aldehydes, ethers, esters, amides, etc.) are formed in satisfactory yields as a result of the acid-catalysed isomerisation of the corresponding non-conjugated vinylethynyl and diethynyl alcohols (the Claisen rearrangement). The nature of the functional group and the configuration of the substances obtained under these conditions are determined by the nature of the donor of the anion introduced into the reaction mass:[144–148]

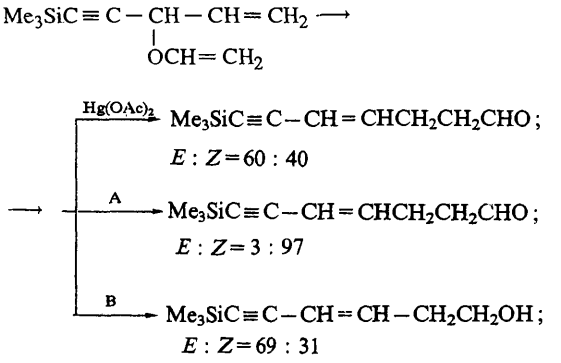
The availability of the initial vinylethynyl alcohols and the high preparative yields of the target products make this reaction one of the promising and stereocontrolled processes in the synthesis of derivatives of 1,3-enyne silicon-containing hydrocarbons.

The isomerisation of secondary alcohols proceeds stereospecifically and the reactions of tertiary alcohols afford mixtures of the (*E*) and (*Z*)-isomers, the isomers in which the substituent R is in the *trans*-position relative to the functional group predominating under these conditions.[144]

The isomerisation of diacetylenic alcohols[145] and alcohols containing substituted vinyl groups[146,149] leads to the formation of the corresponding aldehydes:

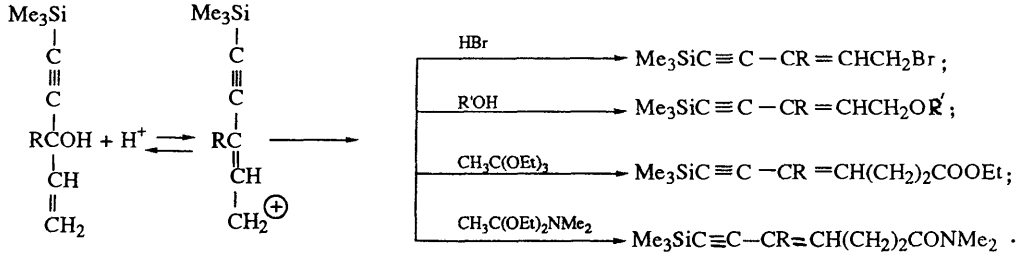


The rearrangement of the vinyl ethers (the Cope–Claisen rearrangement) also leads to the corresponding vinylacetylenic alcohols or ethers. The nature of the functional group and the configuration of the substances obtained are determined by the nature of the catalyst:[150,151]

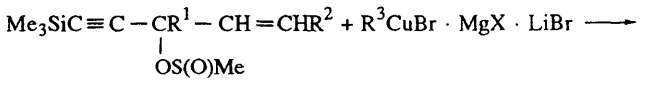


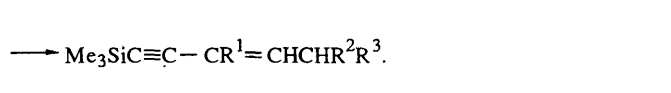
A = [2,6-(t-Bu)$_2$–4-BrC$_6$H$_2$]$_2$MeAl; B = [2,4-Ph$_2$-C$_6$H$_3$]$_2$MeAl.

Similar reactions occur also when the sulphinate of a silicon-containing vinylethynylcarbinol is treated with alkyl or aryl cuprates [the ratio of the (*E*) and (*Z*)-isomers is (4–10) : (96–89)]:[152]

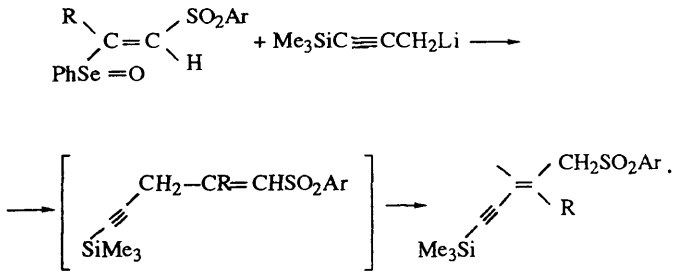


R' = H, Me, Et, Ac.

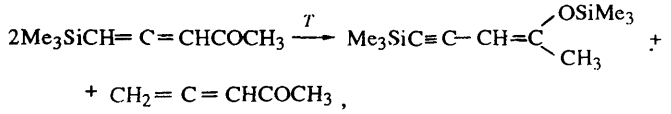




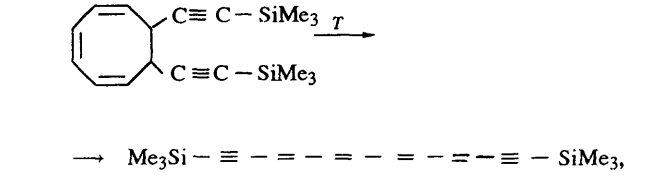
A protropic isomerisation apparently also takes place in the synthesis of vinylacetylenic sulphones by the condensation of a selenoxide with trimethylsilylpropargyllithium:[153]



The method of synthesis of silicon-containing enyne enols by the thermal disproportionation of silicon-containing allenyl ketones,[154] i.e.



and of bis(trimethylsilyl)cyclooctatetraene,[155] i.e.



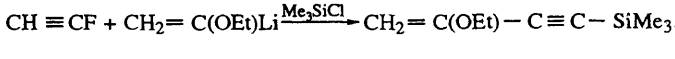
can be formally assigned to the same group of reactions (isomerisation).

5. Construction of enyne structures from block-synthons

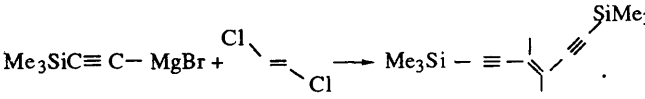
In the construction of enyne structures from block-synthons, use is made of methods based on the transition metal complex-catalysed reactions of organometallic compounds, condensations of the type of the Knoevenagel reaction, and the Wittig reaction and its phosphonate (the Horner–Emmons reaction) and silyl (the Petersen reaction) modifications. An obligatory feature of these methods is the formation of new single or multiple carbon–carbon bonds.

(a) Organometallic synthesis

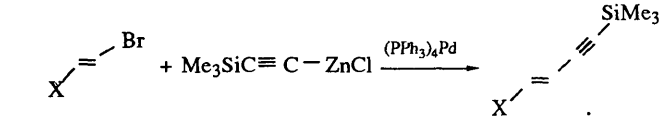
The possibilities in the synthesis of silicon-containing alkenynes from organolithium compounds have been demonstrated solely in relation to the condensation of fluoroacetylene with α-ethoxyvinyllithium:[65]



Trimethylsilylethynylmagnesium bromide condenses with *trans*-1,2-dichloroethylene only in the presence of the nickel catalyst $NiCl_2.Ph_2P(CH_2)_3PPh_2$:[156]

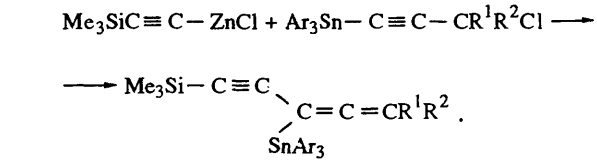


The best results were obtained in the reaction of haloalkenes with acetylenic organozinc compounds. The reactions take place only when palladium complexes are used as the catalyst.[157–162] It has been noted that *cis*- and *trans*-haloalkenes give rise to only alkenynes in these reactions:

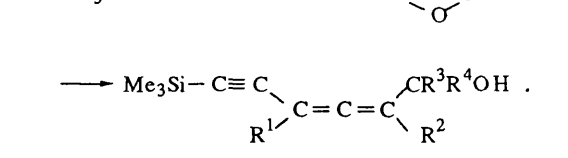


However, it has been reported[163] that the interaction of trimethylsilylethynylzinc bromide with *cis*- and *trans*-1-iodoalkenes afforded individual *cis*- and *trans*-1-trimethylsilyldec-3-en-1-ynes respectively in 74 and 75% yields.

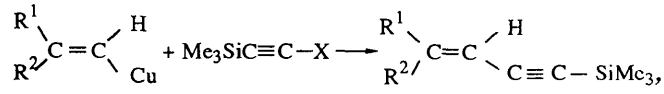
Alkenyne structures were formed somewhat unexpectedly in the reaction of trimethylsilylethynylzinc chloride with tertiary chlorides of the propargyl type.[164,165] The reaction is described by the following scheme:



The reaction of zinc acetylides with acetylenic epoxides proceeds similarly under the condition of catalysis by palladium:[166,167]



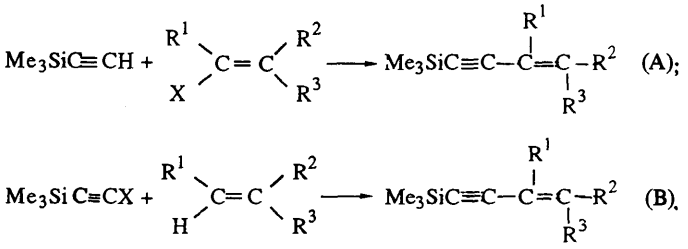
Alkenyne silicon-containing structures can be obtained by condensing silicon-containing halides (bromides, iodides) with alkenyl cuprate:[166,168–171]



where X = Br or I and R^2 and R^1 are alkyl and alkenyl groups, including groups with functional substitutents.

The cross-coupling of organic halides with an unsaturated hydrocarbon, catalysed by compounds of platinum group metals, occupies a special place in the synthesis of organosilicon alkenynes.

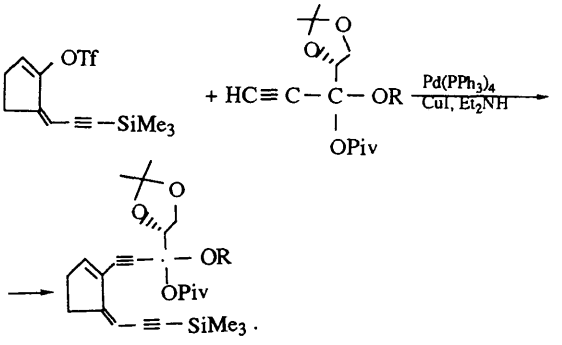
It can be achieved in two ways:



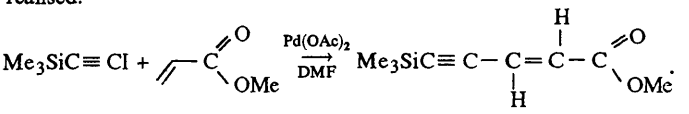
The availability of the starting compounds and the higher stereoselectivity of the processes make it possible to use method (A) on a wide scale in fine organic synthesis, including the synthesis of complex natural products and their synthetic analogues.[36,149,172–190]

$Pd(PPh_3)_4$ [149,175,176,178–180,182,186,187,189–191] or $PdCl_2(PPh_3)_2$ [36,174,175,177,183–185,188] are used as catalysts. It has been noted that *trans*-1,2-dichloro(dibromo)alkenes are much less reactive in this reaction than their *cis*-isomers.[175]

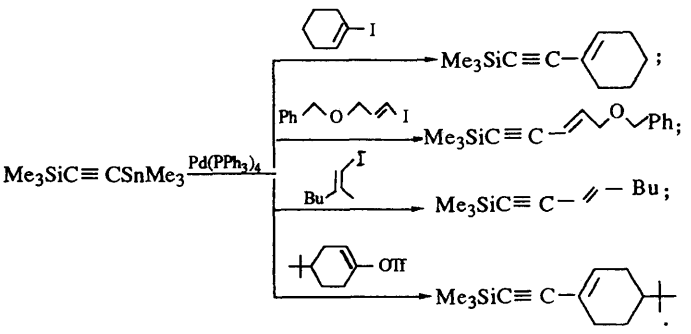
Cases are known where the corresponding triflate is made to enter into the palladium-catalysed cross-coupling reaction instead of the vinyl halide:[192–194]



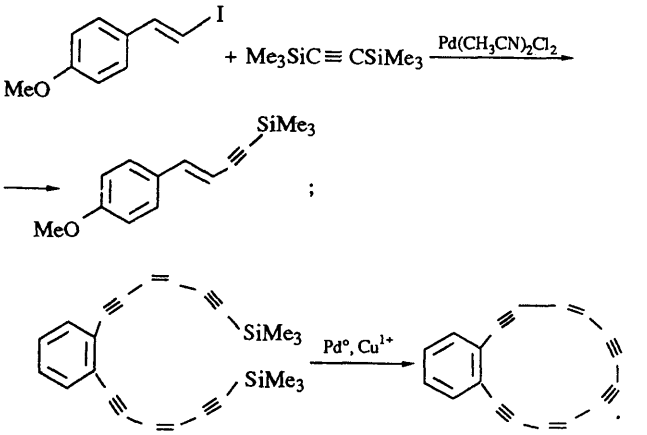
There have been only isolated instances where scheme (B) was realised:[195]



The method of synthesis of silicon-containing alkenynes by the stereospecific alkynylation of alkenyl halides[196,197] or triflates[198–200] with trialkylstannylacetylenes catalysed by a palladium complex was developed significantly during the last decade.



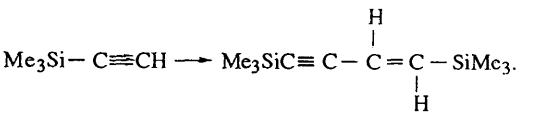
Silicon-containing acetylenes can also serve as alkynylating agents:[184,201]



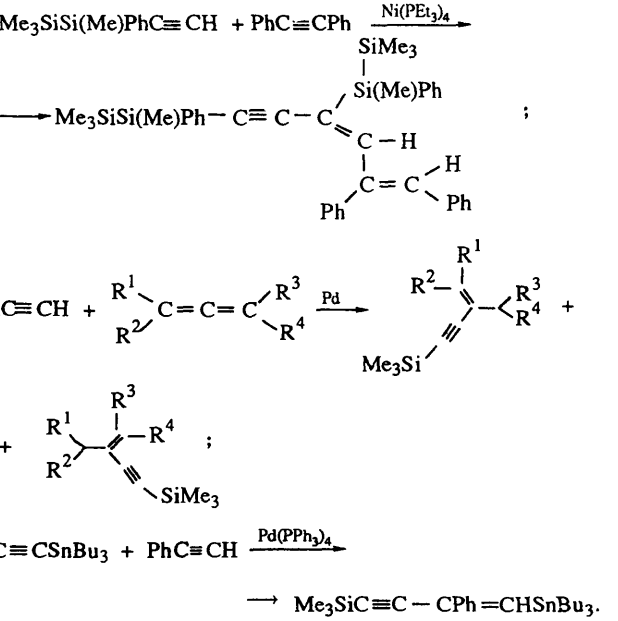
The silicon–carbon bonds are dissociated in these reactions.

(b) Dimerisation of silylacetylenes catalysed by transition metal complexes

Under the influence of the nickel complexes $Ni(acac)_2PPh_3$ [202,203] and $Ni(PEt_3)_4$,[204] the palladium complex $Pd(PPh_3)_4$,[205] the rhodium complex $RhCl(PPh_3)_3$,[206] or the titanium complex $(\eta^5\text{-}C_5H_5)TiCl_2.RMgX$ [207] as catalysts, silylacetylenes are readily dimerised with formation of the corresponding bissilylated alkenynes. The satisfactory yields (up to 90%) and controlled stereochemistry make it possible to recommend these reactions as convenient preparative methods of synthesis of alkenynes:



Under the conditions of metal complex catalysis, it is possible to carry out the codimerisation reactions of trialkylsilylacetylenes with other acetylenes or allenes:[204,208,209]



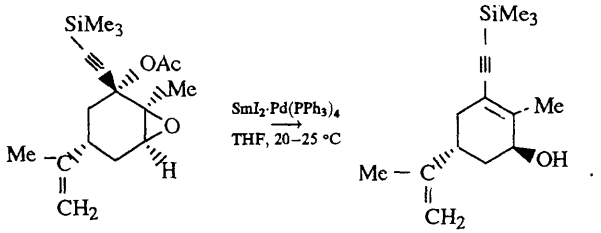
An unusual reaction involving alkynylation with silylacetylenes was described in 1978 by Japanese investigators,[210] who established that alkynylamines add to electron-deficient acetylenes with formation of silylated alkenynes containing a silicon atom attached to the double bond:

$$R^1_{R^2}\!\!>N-C\equiv C-SiR_3 + YC\equiv C-COOMe \longrightarrow$$

$$\longrightarrow R^1_{R^2}\!\!>N-C\equiv C-\underset{\displaystyle SiR_3}{\overset{\displaystyle Y}{\underset{|}{\overset{|}{C}}}}=C-COOMe\ ;$$

Y = H or COOMe.

(3*S*, 5*R*)-3-Hydroxy-5-isopropenyl-2-methyl-1-(2-trimethylsilylethynyl)-1-cyclohexene — a key compound in the synthesis of $\Delta^{9(11)}$-unsaturated vitamin D — was obtained from the corresponding epoxide using a palladium catalyst:[211]



(c) The Wittig reaction and its modifications

Silicon-containing alkenynes can be synthesised in two ways using phosphoranes: (1) by the reaction of a silicon-containing acetylenic phosphorane with a carbonyl compound:

$$Me_3SiC\equiv C-CH=PPh_3 + O=C\!<^{H(R^2)}_{R^1} \longrightarrow$$

$$\longrightarrow Me_3Si-\equiv-\underset{\displaystyle H}{\overset{\displaystyle H(R^2)}{\underset{|}{\overset{|}{\diagup\!\!\diagdown}}}}-R^1\ ; \qquad (1)$$

(2) by the reaction of a silicon-containing acetylenic aldehyde with the corresponding phosphorane:

$$Me_3SiC\equiv C-CH=O + Ph_3P=CHR^1 \longrightarrow$$

$$\longrightarrow Me_3Si-\equiv-\underset{\displaystyle |}{\overset{\displaystyle |}{\diagup\!\!\diagdown}}-R^1 \qquad (2)$$

The silicon-containing acetylenic phosphorane $Me_3SiC\equiv C-CH=PPh_3$ was first obtained by Belyaev, Stadnichuk, and Petrov in 1972.[212,213] By condensing it with cyclohexanone or benzaldehyde, it was shown that it can be used in the synthesis of silicon-containing alkenynes.[212]

Somewhat later Corey et al.[64] and then Eiter et al.[214] again described the silicon-containing propargyl-substituted phosphorane and confirmed the possibility of using it in the synthesis of the simplest vinylacetylenic hydrocarbons[64] and more complex compounds.[215] The silicon-containing propargyl-substituted phosphorane $Me_3SiC\equiv C-CH=PPh_3$ has come to be widely used in studies by other investigators.[216–223] In all these investigations, complex polyfunctional organic compounds containing the aldehyde group were employed as the carbonyl component. The condensation was stereospecific or highly stereoselective with formation of the corresponding (*E*)-alkenynes containing the trimethylsilyl protecting group at the triple bond.

The silicon-containing alkenyne-substituted phosphorane $Me_3SiC\equiv C-CH=CH-CH=PPh_3$ is frequently used in the synthesis of more unsaturated compounds, for example lipoxin[49,50] and leukotriene antagonists.[224]

The synthesis of 1-trialkylsilylalk-3-en-1-ynes and their derivatives using the second variant of the Wittig reaction was first achieved by Belyaev, Stadnichuk, and co-workers:[213,225]

$$Me_3SiC\equiv C-CH=O + Ph_3P=CHX \longrightarrow Me_3SiC\equiv C-CH=CHX;$$

X = $COOCH_3$, $COCH_3$, CN.

The stereoselectivity of the reaction depends on the structure of the phosphorane and the nature of the solvent.[225,226] The replacement of ether or THF by hexane not only increases the yield of the target products but also promotes the formation of the (*E*)-isomer in the mixture.

The phosphonate modification of the Wittig reaction (the Horner–Emmons reaction) is as a rule characterised by a greater *trans*-stereoselectivity in the synthesis of alkenes. The available data on the use of the phosphonate methods in the synthesis of silicon-containing alkenynes[49,227] agree on the whole with this claim:

$$Me_3SiC\equiv C-CH=O + (EtO)_2P(O)CH_2X \xrightarrow{Na}$$

$$\longrightarrow Me_3SiC\equiv C-CH=CHX\ ;$$

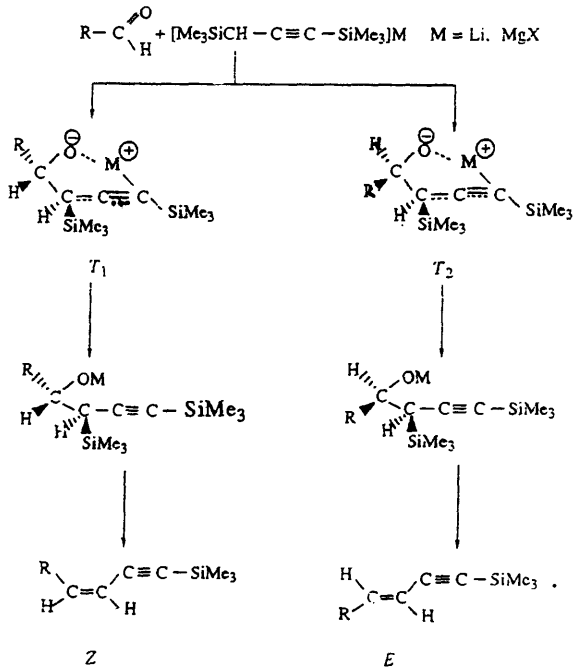
X = COOR, CN.

It is interesting that the synthesis of vinylacetylenic nitriles by the Horner–Emmons reaction produces better results (yield, stereoselectivity) than the Wittig reaction, while in the synthesis of carbonyl compounds the Wittig reaction is preferable.[213,225–227]

The conversion into silylalkenes or alkenes by the Peterson method is frequently regarded as one of the variants of the Wittig method. This procedure presupposes attack by the silicon-containing anions on the carbonyl carbon atom of the substrate. The reaction is distinguished by a high stereoselectivity. An advantage of the method (compared with the Wittig and Horner–Emmons reactions) is the fact that the hexamethyldisiloxane produced as a result of the reaction is volatile (T_b = 100 °C) and can be readily removed.

The Peterson reaction was first applied in the synthesis of silylalkenyls by a group of Japanese workers[228] in 1981 in relation to the interaction of certain aldehydes and ketones with the allene

carbanion obtained by treating 1,3-bis(trimethylsilyl)propyne with organolithium or organomagnesium compounds:



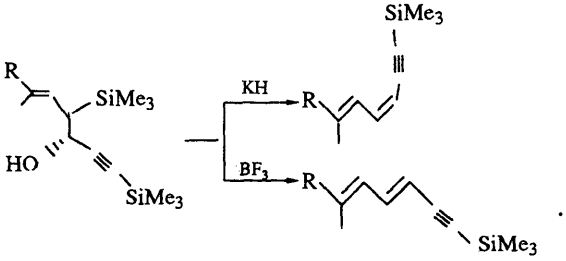
In conformity with the proposed scheme of the possible interaction pathways, the reactions of the bis(trimethylsilyl)propargyl anion with aldehydes give rise to mixtures of the (*E*)- and (*Z*)-isomers, with the latter predominating.[228–230] Judging from the yields (80–90%) and the ratio of the (*E*)- and (*Z*)-isomers, this reaction should be regarded as a convenient preparative method of synthesis of (*Z*)-alkenynes.

It follows from the available data[228–230] that the fraction of the (*Z*)-isomer increases with increase in the bulk of the SiR_3 group and also when lithium is replaced by magnesium. The replacement of magnesium by titanium[229,230] hardly affects the stereochemical result of the reaction. The authors are inclined to explain this by the steric destabilisation of the transition state T_2 compared with T_1 with increase in the bulk of the SiR_3 group.

The low level of stereoselectivity in the reactions with benzaldehyde[228,230] canot be explained. As regards the role of the counterion, the principal idea used in its explanation reduces to the fact that the ability of the cation to form the transition state T_1, possibly with the allene structure, increases in the series Li < Mg < T_1. In this transition state, the steric repulsion increases to a maximum (T_1 is more favourable on energy grounds than T_2). Therefore the allene carbanion attacks the carbonyl carbon atom preferentially, which leads to the formation of the energetically more favourable transition state T_1.[229,230]

In 1982 Corey and Ruecker[231] repeated the experiments of the Japanese workers and also showed that the reaction of lithiated 1,3-bis(trimethylsilyl)propyne with cyclohexanecarbaldehyde and trimethylacetaldehyde in THF results in the formation of the corresponding alkenynes in a satisfactory yield and with the ratio *E*:*Z* = 20:1 (as in the study of Yamakado et al.[228]). However, when the reaction is carried out in a THF–hexamethylphosphoramide (HMPA) mixture, the corresponding alkenynes are formed in proportion of 1:2.[231] The preferential formation of the (*E*)-isomer (*E*:*Z* = 7:1) when the reaction is carried out in a THF–HMPA mixture has also been observed by other workers.[232] The lithium derivative of 1-triisopropylsilyl-3-trimethylsilyl-1-propyne does not react with aldehydes under these conditions.[231] It has been suggested that the lithium derivative of bis(triisopropylsilyl)propyne exists in THF in the form of an allene, to which corresponds the energetically most favourable cyclic transition state T_1. This promotes the formation of the (*Z*)-isomer. In a more polar solvent (a mixture of THF and HMPA), an acyclic transition state is formed, promoting the formation of the (*E*)-isomers.[231]

The stereoselectivity of the elimination of trimethylsilanols also depends on the nature of the catalyst (KH or BF_3):[233]



Judging from the available data, the Peterson rection constitutes a convenient preparative method of synthesis of silicon-containing alkenynes with the (*Z*)-configuration.[234–237]

Trialkylsilylpropynals react with C–H acids (the Knoevenagel reaction) to form the corresponding derivatives of silicon-containing alkenyne hydrocarbons:[238]

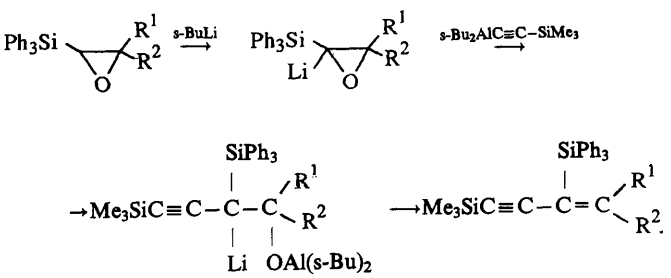
$$Me_3SiC{\equiv}C{-}CHO + CH_2XY \longrightarrow Me_3SiC{\equiv}C{-}CH{=}CXY;$$

X = Y = CN, CO_2Et; X = Ac, Y = CO_2Et; X = NO_2, Y = H.

5-Trimethylsilylbut-2-en-4-ynoic acid was obtained on hydrolysis of the diester and heating the resulting acids:

$$Me_3SiC{\equiv}C{-}CH{=}C(CO_2Et)_2 \xrightarrow[H^+]{HOH} Me_3SiC{\equiv}C{-}CH{=}C(CO_2H)_2 \xrightarrow{T} Me_3SiC{\equiv}C{-}CH{=}CHCOOH.$$

The method involving the elimination of lithium aluminate in the concluding stage, described recently,[239] can be also included formally in this group of methods:



III. Chemical properties of silicon-containing alk-3-en-1-ynes

Among the chemical reactions of silicon-containing alkenynes, three large groups can be distinguished.

1. Reactions occurring with participation of multiple bonds. They lead as a rule to the synthesis of new types of functional derivatives of alkynes or alka-1,3-dienes and alka-1,2-dienes.

2. Reactions in which the trialkylsilyl group is replaced by a proton (removal of the silyl group protecting the triple bond) or another atom or radical (halogen, acyl, etc.)—desilylation reactions.

3. Reactions with participation of the functional groups of derivatives of silicon-containing alkenynes.

1. Addition reactions

The addition of reagents of different nature of 1-trialkylsilylalk-3-en-1-ynes and their carbofunctional derivatives constitutes the most thoroughly investigated type of reactions of compounds of this class. However, their rigorous classification in terms of reaction mechanisms is impossible, since in most cases such mechanisms have not been investigated. The known types of reactions have therefore been classified in this review in terms of the type of reagent. Despite the fact that the same reagent adds via different mechanisms depending on the experimental conditions and the proposed classification principle cannot therefore be maintained throughout, this approach appears to be most acceptable at the present stage.

(a) Interaction with electrophiles

The study of the addition of electrophiles to compounds with multiple carbon–carbon bonds traditionally with the analysis of data on their reactions with hydrogen halides. Unfortunately, it is merely stated in the literature that 1-trimethylsilylbut-3-en-1-yne combines with two moles of hydrogen chloride. The structure of the reaction products was not demonstrated. The reaction could not be stopped at the stage involving the formation of monoadducts.[23]

Bromination of 1-trialkylsilylalk-3-en-1-ynes and their derivatives. Whilst describing the simplest reactions of vinylacetylenic silicon-containing hydrocarbons, Petrov, Sadykh-zade, and Egorov[22,23] noted that the addition of the first mole of bromine to 1-trimethylsilylbut-3-en-1-ynes takes place exclusively at the triple bond. However, it was later established that the bromination of silicon-containing alkenynes takes place non-chemoselectively, while the relative amounts of the dibromo-derivative formed are determined by the structure of the initial silicon-containing hydrocarbons and the conditions in the isolation and purification of the dibromo-derivatives. In the reactions of silylalkenynes in which the alkenyne fragment has the normal structure, the main products are 1,4-dibromo-derivatives, while bromination of compounds with a branched structure affords acetylenic dibromo-derivatives. Dibromo-derivatives of 1,3-dienes are either not formed at all or are present only in trace amounts.[26]

On heating, the 1,4-dibromo-derivatives readily isomerise to the bromo-derivatives of 1,3-dienes. Alkenyldimethylsilylbut-3-en-1-ynes are also brominated non-selectively,[31] the main product formed in the case of 1-dimethylvinylsilylbut-3-en-1-yne being dibromoallene. 1-Allyldimethylsilylbut-3-en-1-yne combines with the first molecule of bromine preferentially at the double bond which is not conjugated with the triple bond.

Bromine adds essentially only to the double bond also in the bromination of 1,6-bis(trimethylsilyl)oct-4-ene-1,7-diyne.[33] These data[25,26,31,33] agree well with the rule according to which bromine adds to double bonds at a rate approximately an order of magnitude higher than that of its addtion to the triple bond.[240]

The study of the dependence of the rate of bromination on the structure of the silicon-containing alkenyne[241] and the polarity of the solvent[242] and also data on the way in which 1-trimethylsilylbut-3-en-1-yne reacts with bromine in a saturated solution of lithium chloride in acetic acid[87] enabled the authors to claim that bromination, whose rate is described by a second order equation, is a two-step electrophilic process. The bromine molecule and (or) the complex Br_3^- functions as the electrophile.[242]

The functional derivatives of vinylacetylenic silicon-containing hydrocarbons $Me_3SiC{\equiv}C-CH=CH-X$, where X = NMe_2, $COCH_3$, $COOCH_3$,CN, or NO_2,[59,95,243] combines with bromine exclusively[59,95] or preferentially[243] at the triple bond regardless of the donor–acceptor properties of the substituents X. 1,4-Adducts were never detected.

The bromination of nitroalkenynes takes place only in highly polar solvents in the presence of lithium bromide and most probably via a nucleophilic mechanism.[241,244] One cannot rule out the possibility that the isotypical mode of addition of bromine to alkenynes containing the electron-donating dimethylamino-group and the electron-accepting carbonyl, carboxy-, cyano-, and nitro-groups is determined by the fact that the corresponding complexes of the reagents with bromine of the type

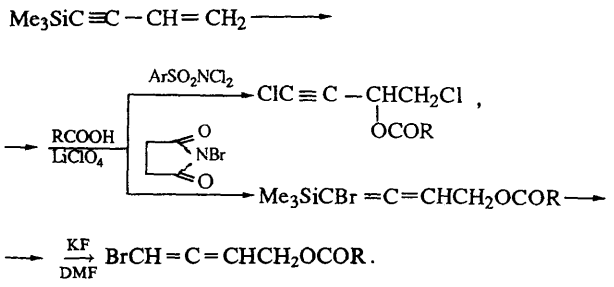
$$[R_3SiC{\equiv}C{-}CH{=}CHNMe_2{\cdot}Br]^+Br^-$$

enter into the bromine reaction.[245]

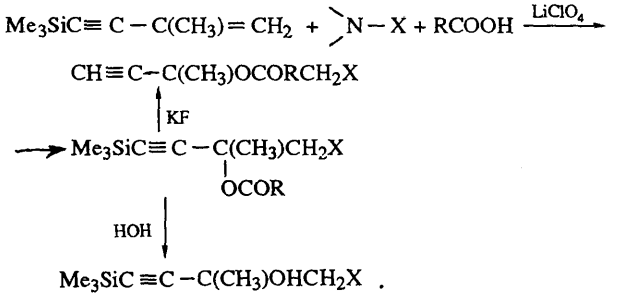
Hydroxy-, alkoxy-, and acyloxy-halogenation. The coupled hypohalogenation of silylalkenynes, where the nucleophilic solvent (water, alcohols, carboxylic acids) is involved in the concluding stage of the reaction, has not been studied systematically. It has only been stated that, when 1-trimethylsilylbut-3-en-1-yne was treated with the dichloroamide of *p*-chlorobenzenesulphonic acid or *N*-bromosuccinimide in methanol, a mixture of positional isomers of the corresponding dihalo-derivatives containing chloro- or bromo-ethers was obtained in low yields (5–10%).[246] 3-Methyl-1-trimethylsilylbut-1-yne reacts with the dichloroamide of *p*-chlorobenzenesulphonic acid and 85% formic acid to form the corresponding chlorohydrin in a satisfactory yield:[247]

$$Me_3SiC{\equiv}CC(CH_3){=}CH_2 + ArSO_2NCl_2 \xrightarrow[LiClO_4]{H_2O\ +\ HCOOH} Me_3SiC{\equiv}CC(CH_3)CH_2Cl.$$
$$\qquad\qquad\qquad

interaction of 1-trimethylsilylbut-3-en-1-yne with a dichloroamide in formic and acetic acid takes place with desilylation:

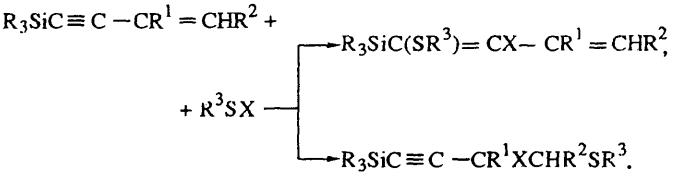


1-Trimethylsilylbut-3-en-1-yne reacts with *N*-bromosuccinimide in both acetic and formic acid to form the products of coupled 1,4-addition, uncharacteristic of the given type of reactions, with the electrophilic bromine being attached to the α-carbon atom of the triple bond. 3-Methyl-1-trimethylsilylbut-3-en-1-yne reacts with chloro- and bromo-amides to form only the products of acyloxyhalogenation at the double bond:



There is no acceptable explanation of the inversion of the electrophilic attack (at the triple bond in 1-trimethylsilylbut-3-en-1-yne in reactions with chloro- and bromo-amides and at the double bond in the reactions of an isopropenylacetylenic compound).

Interaction with the acid halides of sulphenic acids and their selenium containing analogues. The halides of sulphenic acids RSX are known to add to multiple carbon–carbon bonds via an electrophilic mechanism. These reagents belong to the category of weak electrophiles and their electrophilicity can be varied by altering the nature of the organic group. In conformity with the rule that, in reactions with electrophiles, the double bond is more reactive approximately by an order of magnitude than the triple bond, vinylacetylene[248] combines with methanesulphenyl chloride via the double (90%) and triple (10%) bonds, while its homologue 5,5-dimethylhex-1-en-3-yne combines with the above reagent exclusively via the double bond.[249,250] In contrast to hydrocarbons, their silicon-containing analogues $R_3SiC{\equiv}CCR^1{=}CHR^2$ combine with the halides of alkane- and arene-sulphenic acids exclusively or preferentially via the triple bond:[249–251]



The mode of reaction is independent of the nature of the solvent (CH_2Cl_2, $CHCl_3$, CH_3COOH, and the $CH_3COOH-LiClO_4$ mixture) and is determined by the structure of the reactants. The fraction of the minor acetylenic adduct increases with increase in the bulk of R and R^3, on passing from acid chlorides to bromides, and on passing from compounds with R^1 = H to compounds with R^1 = CH_3, and also as the electron-accepting properties of R^3 are enhanced. It has been established in relation to derivatives of vinylacetylenic silicon-containing hydrocarbons with nitro-,[252] acetyl, ethoxycarbonyl, and cyano-groups[253] in the alkenyne fragments that the introduction of electron-accepting groups increases sharply the chemoselectivity of the addition of the halides of sulphenic acids to the triple bond.

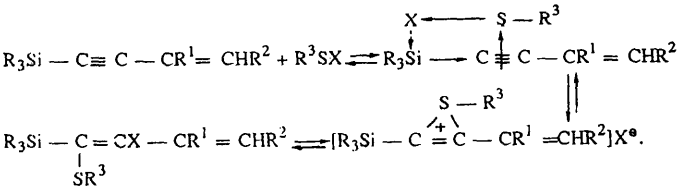
The study of the kinetics of the addition of methanesulphenyl chloride to derivatives of vinylacetylenic silicon-containing hydrocarbons[254] shows that the rate of addition to hydrocarbon and silylhydrocarbon derivatives with similar structures decreases as the electron-accepting properties of the group R^2 weaken in the sequence COR > COOR > CN, which agrees with an electrophilic mechanism of the addition reaction. This conclusion is supported also by the formation of a certain amount of solvoadducts when arenesulphenyl chlorides add to acetic acid in the presence of lithium perchlorate.[249]

However, silicon-containing alkenynes are more reactive in this reaction than the hydrocarbon derivatives of similar structure.[254] It is appropriate to recall here that hydrocarbons are more reactive approximately by an order of magnitude in electrophilic bromination reactions than their silicon-containing analogues: owing to the $d_\pi-p_\pi$ interaction, organosilicon substituents have weaker electron-donating properties than the hydrocarbon groups of similar structure.[255]

In the presence of anhydrous aluminium chloride, methanesulphenyl chloride adds to 1-trimethylsilylbut-3-en-1-yne preferentially at the double bond.[256]

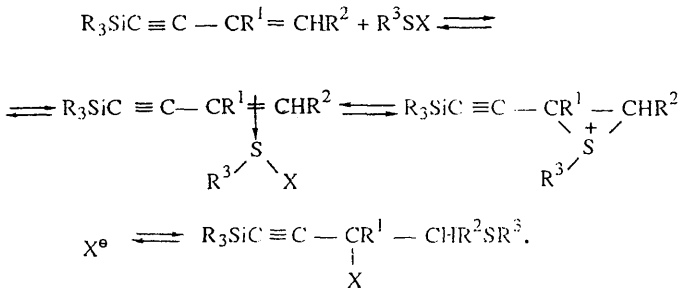
The results of the studies of the reactions of alkane(arene)sulphenyl halides with 1,3-alkenynes, their silicon-containing analogues, and their functional derivatives, examined above, made it possible to conclude that the unusual mode of reaction is due to the characteristic features of the donor–acceptor reagent–substrate interaction, in which the silicon atom with its unoccupied orbitals (a soft acid as defind by Pearson) interacts with the electron-donating end of the polar molecule of the sulphenyl halide:[249–254,256,257]

Scheme 1



This reaction should compete with the donor–acceptor interaction leading to the formation of a π-complex, which is characteristic of electrophilic addition:

Scheme 2



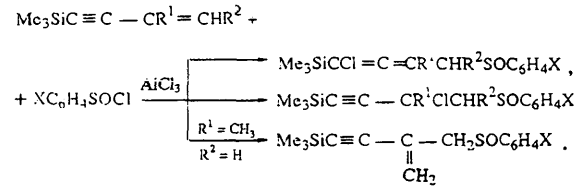
Evidently a greater bulk of R and X (the *d* orbitals are less accessible), a lower effective electronegativity of the alkenyne fragment (a smaller partial positive charge on the heteroatom), and more pronounced electron-accepting properties of R^3 (a low basicity of X) entail a greater difficulty of the realisation of Scheme 1, which presupposes the specific solvation of the substrate by the reagent, and a smaller probability of the addition of the reagent to the triple bond. The formation of molecular associated species with participation of the unoccupied *d* orbitals of silicon should facilitate the addition of the electrophile to the triple bond.[254]

The addition to 1-trialkylsilylalk-3-en-1-ynes and areneselenyl chlorides takes place similarly, i.e. preferentially to the double bond, and apparently for the same reason.[257–259] Data on the addition of sulphenyl and selenyl halides to vinylacetylenic germyl-[250,257] and stannyl-hydrocarbons[260] are satisfactorily consistent with the proposed scheme, which involves the reagent–substrate intermolecular association stage as one determining the chemoselectivity of the addition. The availability of the *d* orbitals of the heteroatoms increases in the series of silicon, germanium, and tin compounds, which is the reason for the increase in the fraction of the products of the addition to the triple bond almost to 100%.[250,257,260] It is of interest that 1-dimethylvinylsilylbut-3-en-1-yne (one of the double bonds and the triple bond are in the α,β-positions relative to the silicon atom) combines with methanesulphenyl chloride via the vinyl group non-conjugated with the triple bond:

$$CH_2{=}CH(CH_3)_2SiC{\equiv}C-CH{=}CH_2 + CH_3SCl \longrightarrow$$
$$\longrightarrow CH_3SCH_2CHCl(CH_3)_2SiC{\equiv}C-CH{=}CH_2.$$

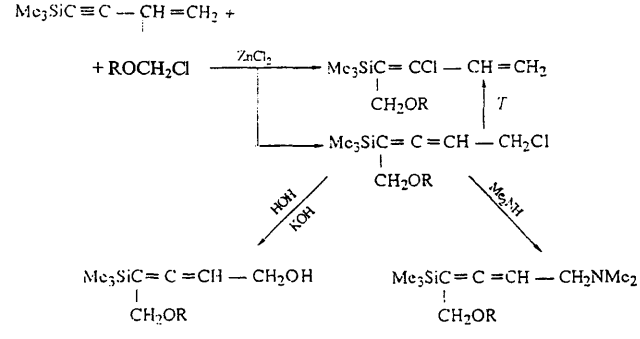
Under identical conditions, the double bond is more reactive in reactions with an electrophile.

Interaction with the halides of sulphinic acids. It has been established in relation to the interaction of the chlorides of arenesulphinic acids with 1-trialkylsilylbut-3-en-1-ynes that, in the absence of catalysts and also in the presence of zinc chloride, the reaction does not occur. In the presence of anhydrous aluminium chloride, the mode of reaction is determined by the structure of the silicon-containing alkenyne: compounds with an unbranched structure of the alkenyne fragment give rise to a mixture of the products of the addition to the double bond and in the 1,4-positions, while alkenynes having the iso-structure give rise to the products of substitutional sulphinylation:[261,262]



The corresponding vinylacetylenic hydrocarbons behave similarly in reactions with sulphinyl chlorides.[262] The chlorides of arenesulphonic acids containing electron-accepting substituents (chloro- and nitro-groups) in the aromatic ring do not react. Chlorine-containing adducts are not dehydrochlorinated when they are treated with triethylamine.[262]

Interaction with α-haloethers. There exists only one communication devoted to this problem. According to the data of Vartanyan and Tosunyan,[263] chloromethyl methyl, chloromethyl ethyl, and chloromethyl isopropyl ethers add to 1-trimethylsilylbut-3-en-1-yne at the triple bond and in the 1,4-positions in the presence of zinc(II) chloride:



It is also striking that in such cases the electrophile attacks the α-carbon atom of the triple bond, which is not characteristic of alkenynes.

(b) Interaction with radical reagents

Interaction with triphenylmethyl radicals. This was investigated in relation to their addition to 1-trimethylsilylbut-3-en-1-yne and its closest homologues — 1-trimethylsilylpent-3-en-1-yne and 3-methyl-1-trimethylsilylbut-3-en-1-yne. It was established that the introduction of the methyl group into the alkenyne fragment not only hinders the addition reaction but also alters its mode: 1-trimethylsilylbut-3-en-1-yne combines with triphenylmethyl radicals at the double bond, 3-methyl-1-trimethylsilylbut-3-en-1-yne combines with them in the 1,4-positions, and 1-trimethylsilylpent-3-en-1-yne combines with them at the triple bond.[264]

Interaction with thiols. The tertiary butyl peroxide-initiated addition of alkanethiols to 1,3-alkenyne silicon-containing hydrocarbons $R_3SiC{\equiv}C-CR^1{=}CHR^2$ (R = Me, Et: R^1 and R^2 = H or CH_3) via a free-radical mechanism involves preferentially the double bond (80–90%), the thiyl radical being attached to the α-carbon atom of the double bond and the content of allene adducts in the mixture not exceeding 15%. 1,3-Diene adducts were not

detected in the reactions of silicon-containing alkenynes. The sharp decrease in the reactivity of the alkenynes after the introduction of methyl groups at the α- and β-carbon atom of the double bond is striking.

Interaction with *N,N*-dichloroamides of arenesulphonic acids. It was noted above that treatment of silicon alkenynes with haloamides in hydroxylated solvents leads to the formation of the products of coupled halogenation. In aprotic solvents (chloroform, methylene chloride, etc.), arenesulphonic acid dichloroamides add to the double bond and in the 1,4-positions in trialkylsilylbutenynes,[246,268] which affords the compounds $Me_3SiC{\equiv}C-CR^1ClCHR^2NClSO_2Ar$ and $Me_3SiCCl=C=CR^1CHR^2NClSO_2Ar$.

On treatment with bisulphite, the adducts form the corresponding amides which are readily converted into *N*-arenesulphenylaziridines;

$$\left.\begin{array}{l} Me_3SiC{\equiv}C-CR^1ClCHR^2NHSO_2Ar \\ Me_3SiCCl=C=CR^1CHR^2NHSO_2Ar \end{array}\right\} \xrightarrow{KOH} CH{\equiv}C-CR^1(N\!<\!SO_2Ar)-CR^2$$

In all cases, the addition of the dihalo-derivative to the multiple bonds of the silicon-containing alkenynes is accompanied by side reactions involving chlorination.[246,268]

Oxidation. The oxidation of 1,3-alkenyne silicon-containing hydrocarbons and their derivatives can involve the multiple bonds or the functional groups.

The oxidation of silylalkenynes with peracids (they are usually obtained by treating the anhydrides of the corresponding carboxylic acids with concentrated hydrogen peroxide or with urea peroxide in the presence of a base) takes place chemoselectively at the double bond with formation of the corresponding acetylenic oxirans $R^1_3SiC{\equiv}C-CR^2(O)-CHR^3$.[27-29,269-273] Examples of the stereo-oxidation of *cis*- and *trans*-1-trimethylsilyldec-3-en-1-ynes have been described.[163] The oxidation of silicon-containing alkenynes with participation of functional groups was examined in subsection 2.

(c) Reactions with nucleophiles

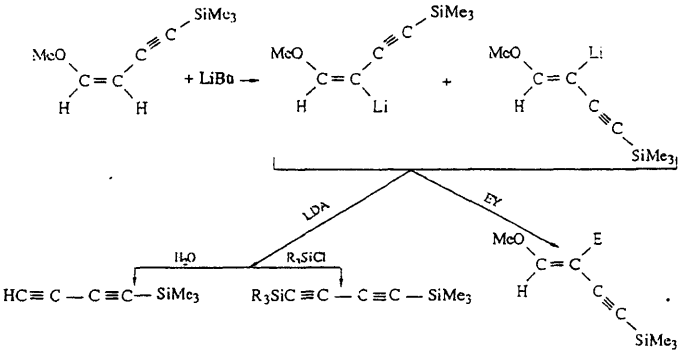
Interaction with organolithium compounds. The interaction of organolithium compounds with trialkylsilylalkenynes was first mentioned by Petrov et al.[23] According to their data, methyllithium and butyllithium add to 1-trialkylsilylbut-3-en-1-ynes exclusively at the double bond with formation, after demetallation with water, of the corresponding acetylenic silylhydrocarbons. It was later shown[274,275] that trialkylsilylalkenynes combine with organolithium compounds non-selectively at the double bond and in the 1,4-positions. The introduction of methyl groups at the α- and β-carbon atoms of the double bond hinders the addition reaction and lowers the yield of the products. It is noteworthy that 1,4-disubstituted alkenynes isomerise under these conditions with migration of the triple bond to the end of the chain.[276]

The ratio of the isomeric acetylenic and allene silylhydrocarbons depends little on the structure of the starting materials. A change in the structure of the demetallating agents also hardly affects the ratio of the isomeric reaction products: when lithium-containing adducts are treated with chlorotrimethylsilane, aldehydes, or ketones, the corresponding allene and acetylene derivatives are formed in proportions of approximately 1 : 1:

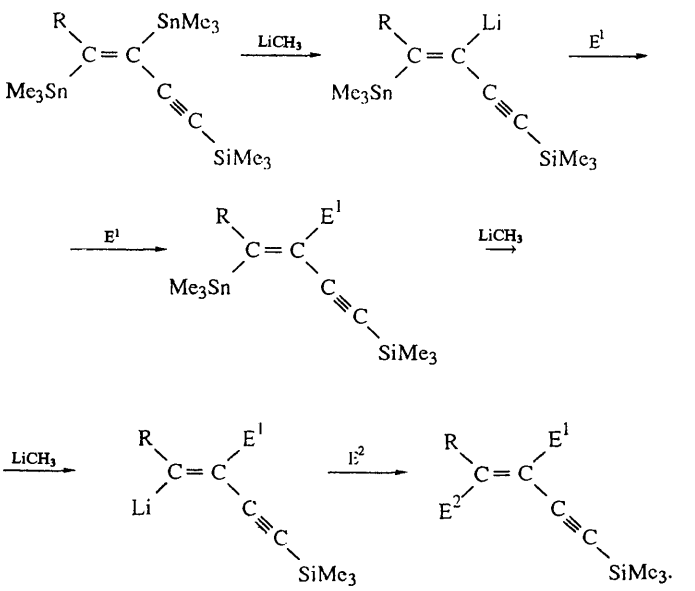
$$[R_3SiC{\equiv}C-\overset{\ominus}{C}HCH_2R']Li^{\oplus} + E^+Y^- \rightarrow \begin{cases} R_3SiCE=C=CHCH_2R' \\ R_3SiC{\equiv}C-CHECH_2R' \end{cases}$$

E — Y = Me_3SiCl; $R^2R^3C{=}O$.

1-Methoxy-4-trialkylsilylbut-1-en-3-ynes are metallated on treatment with lithium alkyls, a mixture of the *cis*- and *trans*-lithiated silylalkenynes being formed from the *cis*-ether.[53] On interaction with electrophiles, the lithiated silylalkenynes form the corresponding derivatives with the *trans*-configuration,[53] while their interaction with nucleophiles[54] affords the lithiated derivatives of 1-trialkylsilylbutadiyne:



3,4-Bis(trialkylstannyl)-1-trimethylsilylalk-3-en-1-ynes are trans-metallated on interaction with organolithium compounds. The organolithium compounds formed on treatment with the corresponding electrophiles afford derivatives of silicon-containing alkenynes in satisfactory yields:[121]



Judging from the structure of the reaction products after demetallation with water, the methyl ester of 5-trimethylsilylpent-2-en-4-ynoic acid combines with triphenyl lithiotrithioformate exclusively at the double bond (most probably via the 1,4-addition to the $-C=C-C=O$ fragment):[48]

$$Me_3SiC\equiv C-CH=CH-\underset{\displaystyle OMe}{\underset{|}{C}}=O + LiC(SPh)_3 \xrightarrow{HOH}$$

$$\longrightarrow Me_3SiC\equiv C-\underset{\displaystyle C(SPh)_3}{\underset{|}{CHCH_2COOMe}}$$

The interaction of the silicon-containing vinylacetylenic ketone with metallic sodium in chlorotrimethylsilane apparently proceeds as 1,4-addition of trimethylsilylsodium:[138]

$$Me_3SiC\equiv C-CH=CH-\underset{\displaystyle Me}{\underset{|}{C}}=O \xrightarrow[2.\ HOH]{1.\ Na + Me_3SiCl}$$

$$\longrightarrow Me_3SiC\equiv C-\underset{\displaystyle SiMe_3}{\underset{|}{CHCH_2}}-\underset{\displaystyle Me}{\underset{|}{C}}=O\ .$$

Treatment of an alkenynyl chloride with a mixture of metallic lithium and chlorotrimethylsilane followed by the demetallation of the reaction products with water afforded a vinylallene. Its formation presupposes the 1,4-addition of trimethylsilyllithium to the conjugated system of multiple bonds and dehydrochlorination:[46]

$$Me_3SiC\equiv C-\overset{CH_3}{\overset{|}{C}}=CHCH_2Cl \xrightarrow[2.\ HOH]{1.\ Li + Me_3SiCl}$$

$$\longrightarrow \begin{matrix} Me_3Si \\ \diagdown \\ \quad C=C=C \\ \diagup \qquad \diagdown \\ Me_3Si \qquad\quad CH=CH_2 \end{matrix} \begin{matrix} \\ \\ \diagup \\ \\ \\ CH_3 \end{matrix} .$$

In the absence of chlorotrimethylsilane, treatment of 1-trialkylsilylbut-3-en-1-yne with lithium and then water leads to a mixture of diacetylene and diallene hydrodimerisation products. Cross-coupling products (the corresponding allenylacetylenes) were not detected.[277]

Interaction with organomagnesium, organocalcium, and organobarium compounds. Organomagnesium compounds (Grignard reagents) are less reactive: silicon-containing alkenynes do not react with the Grignard reagent obtained beforehand under standard conditions.[278,279] However, at the instant of their formation, such reagents add fairly vigorously to 1-trimethyl- and 1-triethyl-silylbut-3-en-1-ynes,[278–280] affording, after demetallation with water, mixtures of the corresponding acetylene and allene silylhydrocarbons in proportions of 10:1 (yield about 10–15%) and oligomers.

Tris(trimethylsilyl)allene is apparently formed via the same mechanism in the reaction of 1-trimethylsilylbut-3-en-1-yne with a mixture of metallic magnesium and chlorotrimethylsilane.[46,281]

It has been shown for the reactions with phenylmagnesium bromide that silicon-containing alkenynes combine with organomagnesium compounds at the double bond in the presence of nickel(II) halides. The yield of the corresponding acetylenic hydrocarbons is 30–35%.[282] It can be increased by using other catalysts—$Fe[CH(COMe)_2]_3$, $Ni[CH(COR)_2]_2$; R = Me, Ph.[283]

Organocalcium and organobarium compounds RMI (M = Ca, Ba) add to silicon-containing alkenynes also in the absence of catalysts and, as in the reactions with organolithium compounds, mixtures of allene and acetylene silylhydrocarbons are formed after the demetallation of the adducts with water. Whereas in the reactions with organocalcium compounds the ratio of the isomers formed is 70:30,[284] in those with organobarium compounds the ratio is approximately 1:1.[285,286] Organozinc compounds (investigated in relation to the interaction of allylzinc bromide with 3-methyl-1-trimethylsilylbut-3-en-1-yne[287]) add chemo- and regio-selectively (95% *trans*) to the triple bond.

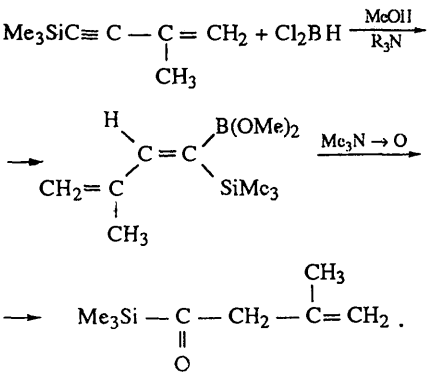
Interaction with organoaluminium compounds. Trialkylaluminium interacts with 1-trialkylsilylalk-3-en-1-ynes only under severe conditions. The reaction takes place chemoselectively at the triple bond with formation of a mixture of (*E*,*E*)- and (*E*,*Z*)-2-alkyl-1-trialkylsilylalka-1,3-dienes. The addition of bimetallic complexes of trialkylaluminium and dialkylmagnesium also takes place chemoselectively to the triple bond but much more readily:[288,289]

$$Me_3SiC\equiv C-CH=CH-C_6H_{13} + Alk_3Al\cdot Bu_2Mg \xrightarrow{H^+}$$

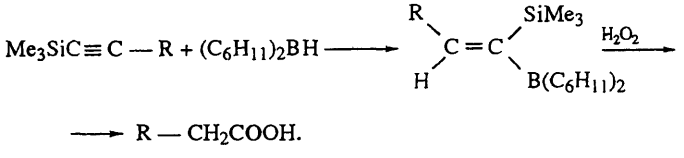
$$\longrightarrow \begin{matrix} Me_3Si \\ \diagdown \\ \quad C=C \\ \diagup \qquad \diagdown \\ H \qquad\quad C=C \\ \qquad\quad \diagup \qquad \diagdown \\ \qquad\quad H \qquad\quad C_6H_{13} \end{matrix} \begin{matrix} Alk \\ \diagup \\ H \\ \\ \\

On interaction with electrophiles, the adducts formed corresponding silylhydrocarbons or their derivatives.

Hydroboration of unsaturated compounds. This most probably proceeds via a molecular quasi-cyclic mechanism. However, it is formally analogous to hydroalumination. The first studies on the hydroboration of alkenynes were undertaken in order to develop an effective method of synthesis of silicon-containing ketones by oxidising the corresponding boron-containing adducts. It was found that the hydroboration of silylalkenynes proceeds chemo-, regio-, and *cis*-stereo-specifically at the triple bond.[292–294] The adducts formed isomerise to the *trans*-isomer on irradiation. Oxidation of the adduct with *N*-oxides leads to the formation of unsaturated silicon-containing ketones in good yields:

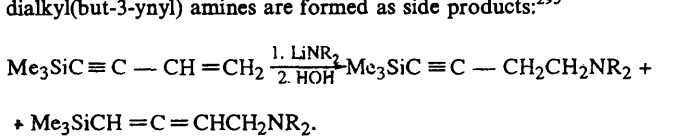


Dicyclohexylborane also adds stereo- and regio-selectively to the triple bond in silylalkenynes.[294] The adducts formed are oxidised in an alkaline medium with hydrogen peroxide to the corresponding unsaturated acids:



This method was subsequently used successfully in the synthesis of *cis*- and *trans*-6-phenyl-3-hexenoic and 5-amino-6-(4-t-butoxyphenyl)-3-hexenoic acid—key compounds in the synthesis of enkephalin analogues.[218,219]

Interaction with amines and amides. In the absence of a basic catalyst, primary and secondary amines do not interact with silylalkenynes. However, lithium dialkylamides, obtained beforehand, add under mild conditions to 1-trimethylsilylbut-3-en-1-yne with formation of a mixture of silicon-containing alkynyl- and allenyl-amines after demetallation with water. Silicon-free dialkyl(but-3-ynyl) amines are formed as side products:[295]

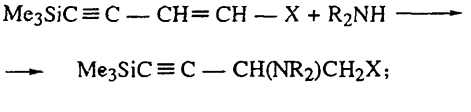


Desilylation most probably proceeds mainly at the stage involving the decomposition of the metal-containing adduct.[295] The fraction of the silicon-free alkynylamines depends on the structure of the amine: in the reaction with dimethylacetamide, they were detected only spectroscopically, while in the reaction with piperidine the yield of *N*-butynylpiperidine is 21%.

The same mixtures of silicon-containing amines derived from acetylenes and allenes are formed when an ethereal solution of the amine and 1-trimethylsilylbut-3-en-1-yne is heated to boiling in the presence of catalytic amounts of metallic sodium.[296] Desilylation products were not detected under these conditions.

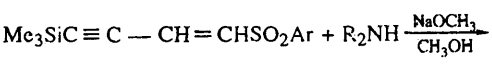
According to the results of Perveev and Afonina,[297] the silicon-containing nitriles $R_3SiC{\equiv}C-C(CH_3)=CH-CN$ are desilylated on interaction with primary and secondary amines. The nitrile of the alkenynoic acid formed combines with amines at the triple bond under these conditions. However, it was noted that, in experiments with methylamine and the nitrile of 3-methyl-1-trimethylsilylpent-3-en-4-ynoic acid, it was also possible to isolate small amounts of the product of the addition of the amine to the double bond.

Systematic study of the characteristic features of the addition of secondary amines to silyl derivatives of vinylacetylenes containing electron-accepting substituents X at the double bond showed that vinylacetylene nitriles, esters, ketones, and sulphones combine with secondary amines chemo- and regio-selectively at the double bond:[95,298–300]



In aprotic solvents (dimethyl ether of ethylene glycol), the addition takes place only after prolonged heating of the reactants at temperatures of the order of 100 °C.[298,299] In the absence of a solvent with an excess of the amine the reaction proceeds under appreciably milder conditions, ketones and ethers combining with amines even at room temperature. A decrease in temperature and reaction time in the interaction of amines with nitriles can be achieved only in proton-donating solvents (120 °C and 12 h without a solvent or 25 °C and 12 h in methanol[299]). The observed dependence of the relative reactivities of the alkenynes investigated in relation to amines has been explained by autocatalysis caused by the acid–base reagent–substrate interaction.

Silicon-containing vinylacetylenic sulphones do not combine with secondary amines in the presence of alcohols. Nor were any of the reactions of the reactants observed when their mixtures in methanol were allowed to stand in the presence of sodium methoxide at room temperature. However, on heating in the presence of methoxide, desilylation and the addition of the amine to the terminal bond take place:[300]



Reactions with thiols and thiolates. As already mentioned,[265–267] the free-radical addition of thiols to 1-trialkylsilylalk-3-en-1-ynes initiated by peroxides proceeds non-regioselectively. The attempts to add alkanethiols to silylalkenynes under the conditions of base catalysis did not yield positive results. In the interaction of 1-trimethylsilylbut-3-en-1-yne with ethanethiolate in methanol, an exothermic reaction takes place, as soon as the reactants are mixed and leads to the formation of sulphides with and without silicon in

proportions of 1 : 5.[301] The silicon-containing sulphides are products of 1,4-, 3,4-, and 1,2-addition in proportions of 4 : 1 : 2, while the sulphides without silicon constitute a mixture of 4-ethylthiobut-1-yne (12%), 1-ethylthiobuta-1,3-diene (34%) and 4-ethylthiobuta-1,2-diene (54%). Since the thiolate-catalysed addition of ethanethiol to vinylacetylene in an alcoholic solution results in the formation of only 1-ethylthiobuta-1,3-diene,[302] the formation of a mixture of silicon-free sulphides in the reaction analysed is most probably due to the desilylation of free-containing adducts.

As was to be expected, the introduction of electron-accepting groups ($COCH_3$, $COOCH_3$, CN, NO_2, SO_2Ar) into the alkenyne fragment increases significantly the rate of addition of thiols. However, when the reaction is carried out in methanol, only silicon-free products are formed from silylalkenyne derivatives even at −10 to −50 °C in the presence of thiolate:[301,303–305]

$$Me_3SiC{\equiv}C-CH=CHX + RSH \xrightarrow[CH_3OH]{RSNa} RSCH=CH-CH=CHX.$$

It has been established empirically that the silylalkenynes investigated can be made to undergo an addition reaction without appreciable cleavage of the silicon–carbon bond, provided that it is carried out in benzene or a 3 : 1 benzene–methanol mixture. Ethanethiol adds to the alkenyne both in benzene and in its mixture with methanol, while the less nucleophilic thiophenol adds only in the mixed solvent:[304]

$$Me_3SiC{\equiv}C-CH=CHX+RSH \xrightarrow[C_6H_6+CH_3OH]{RSNa} Me_3SiC{\equiv}C-CH(SR)CH_2X;$$

$R = C_2H_5$, C_6H_5.

The reaction is chemo- and regio-specific.

The silyl derivatives of vinylacetylenes investigated combine with alkane- and arene-thiols under very mild conditions, which agrees well with the nucleophilic mechanism proposed for these reactions. However, attention has been drawn to the fact[300,304,305] that the corresponding ketones react most readily, while the nitriles and sulphones react with the greatest difficulty. The antiparallel variation of the reactivity with the electron-accepting properties of the substituents X can be explained, according to the authors, by the fact that autocatalysis due to the acid–base reagent–substrate interaction plays a significant role in the reactions:

$$Me_3SiC{\equiv}C-CH=CH-\underset{\displaystyle R'}{\underset{|}{C}}=O + RSH \rightleftharpoons$$

$$\longrightarrow Me_3SiC{\equiv}C-CH=CH-\underset{\displaystyle R'}{\underset{|}{C}}=O\ldots H-SR.$$

Such interaction intensifies the polarisation of the multiple bonds and promotes the addition of the reagent to the double bond with attachment of the alkyl(aryl)thio-group to the β-carbon atom of the double bond. Aprotic solvents decompose such associated species and hinder the addition reaction, whilst proton-donating solvents themselves form associated species with the substrate and promote the addition reaction. This mechanism explains satisfactorily the decrease in the rate of addition on passing from thiophenol to ethanethiol and also the finding that in the presence of an excess of the reagent thiophenol adds to vinylacetylenic esters and ketones (X = $COOCH_3$ and $COCH_3$) at room temperature with 100% conversion in 10–15 min in the absence of a base.[305]

Interaction with arenesulphinates. This has been investigated only in relation to the reaction of 1-nitro-4-trimethylsilylbut-1-en-3-yne with sodium toluene-*p*-sulphinate. According to the available data, the addition proceeds chemo- and regio-selectively but only in the presence of an equivalent amount of acetic acid:[306]

$$Me_3SiC{\equiv}C-CH=CHNO_2 + p\text{-}CH_3C_6H_4SO_2Na \xrightarrow[CH_3OH]{CH_3COOH}$$

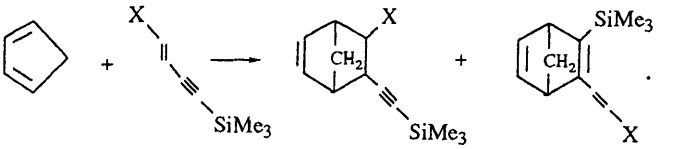
$$\rightarrow Me_3SiC{\equiv}C-\underset{\displaystyle SO_2C_6H_4CH_3\text{-}p}{\underset{|}{CH}}CH_2NO_2.$$

The silicon-containing vinylacetylenic sulphones, containing groups with weaker electron-accepting properties do not combine with sulphinates under these conditions.[307]

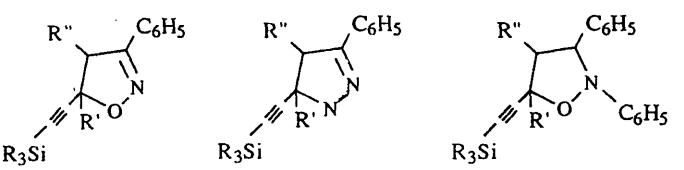
(d) Cycloaddition and cyclisation reactions

This section deals with reactions completed by the formation of carbocyclic and heterocyclic compounds as a result of intermolecular or intramolecular addition regardless of their mechanism. Shostakovskii et al.[308] showed for the first time that 1-triethylbut-3-en-1-yne is an active dienophile in condensation with hexachloropentadiene.

It has also been shown that interaction of cyclopentadiene with functional silyl-substituted derivatives of vinylacetylenes also involves the formation of a mixture of *endo,endo*, and *exo,exo*-isomers. Significant amounts of products of addition to the triple bond have been detected only in the reactions of cyclopentadiene with 1-cyano–4-trimethylsilylbut-1-en-3-yne:[309,310]

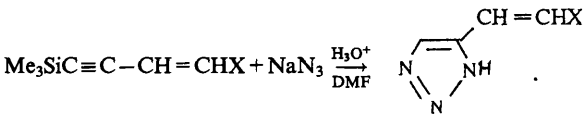


The reactions of 1,3-dipolar reagents (benzonitrile *N*-oxide, diphenylnitrile imine, α,*N*-diphenylnitrone, *C*-ethoxycarbonyl-*N*-phenylnitrile imine, 3-phenylsydnone, and sodium azide) with 1-trialkylsilylalk-3-en-1-ynes and some of their functional derivatives proceed in different ways depending on the structure of the alkenyne and the dipolar compound. Silicon-containing hydrocarbons combined in all cases with Huisgen's 1,3-dipoles at the double bond with formation of the corresponding trialkylsilylethynyl-substituted isoxazolines (I), pyrazolines (II), and isoxazolidines (III):



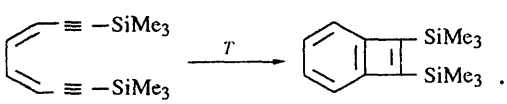
It was shown by the method of competing reactions that silylhydrocarbons are more reactive in their reactions with 1,3-dipoles than silicon-free hydrocarbons with similar structures.[311]

Sodium azide does not react with 1-trialkylsilylalk-3-en-1-ynes. However, their derivatives containing electron-accepting groups at the double bond combine with sodium azide at the triple bond on heating in dimethylformamide (DMF) at 90–95 °C. Demetallation of the adducts with water involves desilylation with formation of substituted triazoles:[312,313]

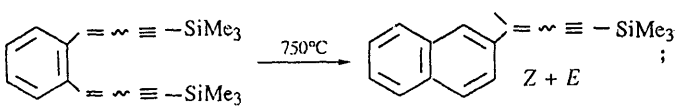


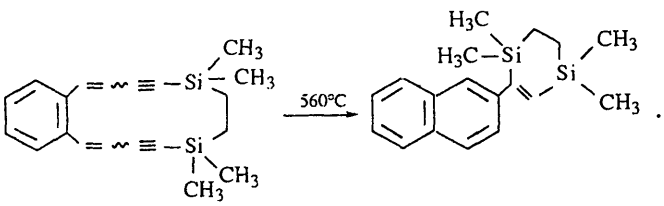
The attempts to add aryl- and trialkyl-silyl azides to silylalkenynes and their derivatives failed.[313]

The first reports concerning the intramolecular cyclisation of organosilicon compounds containing a conjugated double and triple bond appeared recently. It was shown that pyrolysis of 1,8-bis(trimethylsilyl)octa-3,5-diene-1,7-diyne *in vacuo* affords [8]annulene, which is very sensitive to atmospheric oxygen:[314]

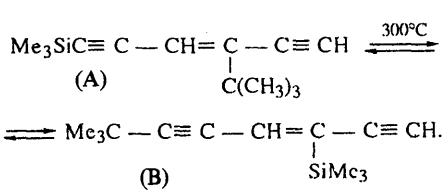


It has been established[315] that the structural analogues of 1,8-bis(trimethylsilyl)octa-3,5-diene-1,7-diyne form the corresponding naphthalene derivatives:

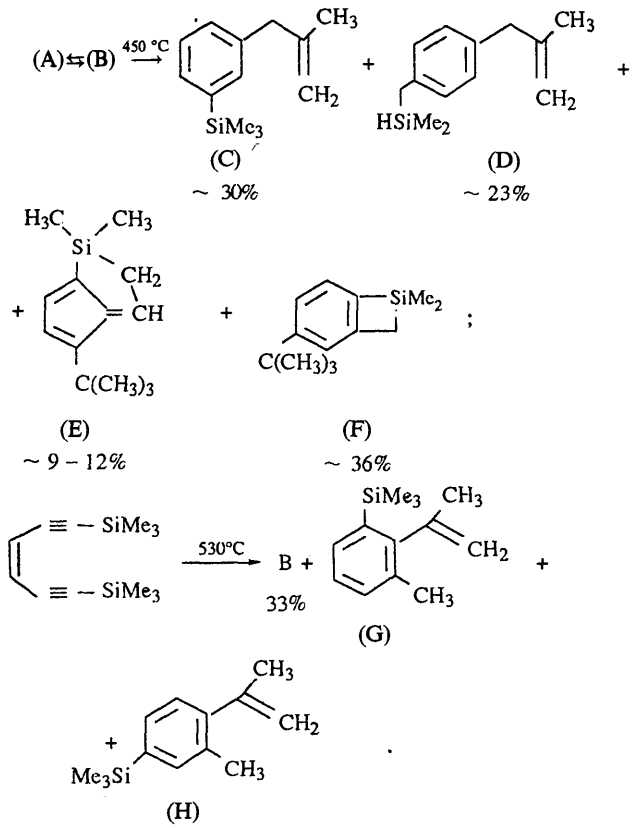




t-Butyltrimethylsilylpent-3-ene-1,4-diynes isomerise to a mixture of isomers containing only 1% of the structure (B):[90]



When a mixture of compounds (A) and (B) or each isomer separately is heated, four isomeric silyhydrocarbons are formed in an overall yield in excess of 90% regardless of the configuration (*E* or *Z*):

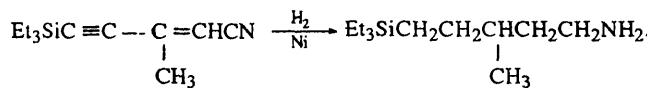


It is difficult to cyclise the disilylated alkenediyne containing the bulky trimethylsilyl groups in the 1,6-positions. The reaction takes place at an appreciable rate only at 530 °C with formation of compounds (C), (G), and (H).

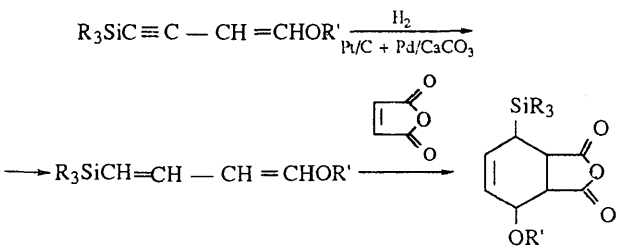
(e) Metal-catalysed homogeneous and heterogeneous reactions

Homogeneous and heterogeneous catalysis by transition metal compounds is one of the most important procedures for the activation of multiple bonds. Their characteristic feature, regardless of the mechanisms of the particular reactions occurring, is the involvement of the unsaturated ligand in intracomplex reactions of the ligands, which is as a rule the reason for a particular stereochemical result.

Catalytic hydrogenation. The catalytic hydrogenation of silicon-containing alkenynes up to complete saturation has been usually carried out in the presence of the Raney nickel catalyst,[70,78,79] the aim being to synthesise the corresponding saturated silylhydrocarbons and their derivatives. It has been noted that the nitrile of the acid derived from vinylacetylene is reduced under these conditions to the corresponding amine:[70]



Incomplete hydrogenation with the aim of determining the relative reactivities of the double and triple bonds of 1-trialkylsilylalk-3-en-1-ynes in relation to catalytically activated hydrogen was carried out by Petrov and co-workers[22,23] in the presence of a palladium catalyst. Since bands characteristic of the double bond were found in the Raman spectrum of the products obtained after hydrogenation and by analogy with data on the catalytic hydrogenation of vinylacetylene and its homologues (see, for example, Bal'yan et al.[316]), it was concluded that the first molecule of hydrogen adds to the triple bond of 1-trialkylsilylalk-3-en-1-ynes. Shostakovskii et al.,[52] who studied the hydrogenation of 4-ethoxy-1-trialkylsilylbut-3-en-1-ynes, arrived at the same conclusion:



The yield of the corresponding cyclic adduct with maleic anhydride reached only 25%. It has also been noted[52] that silicon-containing alkenyl ethers were not hydrogenated in the presence of only platinum on charcoal or palladium on calcium carbonate.

A more thorough investigation of the catalytic hydrogenation of silicon-containing alkenynes[26,244,317] showed that, in contrast to the alkenynes themselves, their silicon-containing analogues are hydrogenated non-selectively. In all cases the reaction products were mixtures of the initial silylhydrocarbon and the products of its hydrogenation in proportions of 1 : 1 (~90%) and the products of more extensive hydrogenation (5%). The products of the addition of the first molecule of hydrogen consisted of a mixture of alkyne, 1,3-diene, and allene isomers $R_3SiC{\equiv}C-CHR'CH_2R''$, $R_3SiCH=CH-CR'=CHR''$, and $R_3SiCH=C=CR'CH_2R''$ in proportions of approximately 60 : 35 : 5.[244]

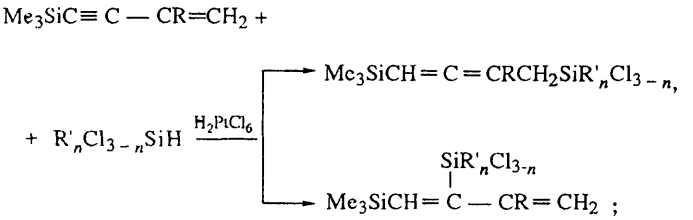
The ratio of the isomeric silylhydrocarbons varies within fairly wide limits depending on the nature of the substituents at the double bond and the silicon atom. The formation in all cases of appreciable amounts of silylallenes is striking. Their maximum amount is observed in the hydrogenation of 3-t-butyl-1-trimethylsilylbut-3-en-1-yne.[26] The addition of hydrogen in the 1,4-positions was not observed in th catalytic hydrogenation of vinylacetylenes.

It is also noteworthy that the rate of catalytic hydrogenation of silicon-containing alkenynes depends greatly on the bulk of the substituents at the silicon atom and in the alkenyne fragment.

Judging from the available data[31] allyldimethylsilylbut-3-en-1-yne is also hydrogenated in the vinylacetylene fragment, the ratio of the isomeric hydrogenation products being approximately the same as in the hydrogenation of 1-trialkylsilylbut-3-en-1-ynes.[244,317]

The data examined show that the trialkyl(aryl)silyl group at the α-carbon atom of the triple bond of the alkenyne hinders the addition of the first molecule of hydrogen to the triple bond and renders the process non-chemoselective.

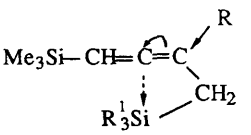
Hydrosilylation of 1-trialkylsilylalk-3-en-1-ynes. This was investigated solely in relation to the interaction of trialkyl- and alkylchloro-hydrosilanes with 1-trimethylsilylbut-3-en-1-ynes[318,319] and 3-methyl-1-trimethylsilylbut-3-en-1-yne[320] in the presence of Speier's catalyst. Chlorosilanes are more reactive in this process than trialkylsilanes and the mode of reaction depends on the structure of the alkenyne and the hydrosilane. 1-Trimethylsilylbut-3-en-1-yne combines with trimethyl- and triethyl-silanes preferentially in the 1,4-positions, while the chlorosilanes CH_3Cl_2SiH, $C_2H_5Cl_2SiH$, and Cl_3SiH combine with the above alkenyne at the triple bond:



n = 0, 1, 3; R = H, CH_3; R' = CH_3, C_2H_5.

On heating in the presence of a catalyst of the addition reaction or copper(I) chloride in an acid medium, the allene adducts isomerise almost wholly to the 1,3-diene adducts.

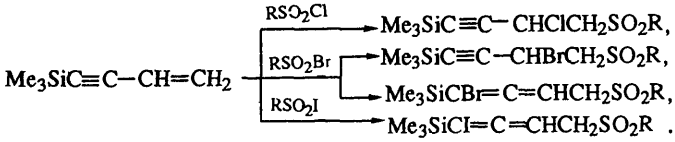
Regardless of the nature of the hydrosilane, 3-methyl-1-trimethylsilylbut-3-en-1-yne forms predominantly 1,3-diene adducts.[320] The authors suggest that the addition takes place in all cases in the 1,4-positions as an intramolecular reaction of the ligands. The ability of silicon-containing alkenynes to form "allene" complexes with platinum group metals has been demonstrated experimentally.[321,322] The allene adduct formed isomerises via a quasi-cyclic complex to the 1,3-diene adduct with migration of the trialkylsilyl group R^1_3Si:[320]



By inducing a partial positive charge on the silicon atom, the electron-accepting substituents R^1 (in the given instance chlorine) should promote the same type of isomerisation as that promoted by the introduction of a methyl group in the 3-position (R = CH_3), which increases the electron density on the C^2 carbon atom. The electron-donating substituents R^1 should hinder isomerisation. The observed dependence of the structure of the reaction products on the nature of the substituents at the silicon atom[318,320] as well as the data obtained for the hydrosilylation of 1,2,3-tris(trimethylsilyl)but-1-en-yne[117] are explained satisfactorily by the proposed mechanism. The hydrosilylation of alkenynes by trialkylsilanes is regarded[117] as a new effective preparative method of synthesis of allenes.

Intereaction with sulphonic acid halides. The relative reactivities of organic sulphonic acid halides in reactions with 1-trialkylsilylalk-3-en-1-ynes depend on the halogen; whereas acid iodides add exothermically merely on mixing the reactants, the bromides react on heating or in the presence of a catalyst, while the chlorides react only in the presence of the Asscher–Vofsi catalyst [a mixture of copper(I) halide, triethylamine hydrochloride, and acetonitrile[323]]. There are no literature data for the addition of these reagents to 1,3-alkenynes in the presence of aprotic Lewis acids.

The addition of the chlorides of alkane- and arene-sulphonic acids catalysed by copper(I) halides proceedes chemoselectively at the double bond:[91,92,94]



Regardless of the conditions (catalytic or thermal addition), the acid bromides add regioselectively to the alkenynes investigated with formation of a mixture of acetylene and allene adducts in proportions of approximately 1 : 1. In the absence of a catalyst, the acid iodides add exclusively in the 1,4-positions. The addition of the Asscher–Vofsi catalyst does not affect the mode of reaction.[93] It is of interest that t-butylvinylacetylene combines under these conditions with the acid chlorides, bromides, and iodides only at the double bond.[91,95] The introduction of a methyl group in the 3- or 4-position greatly hinders the reaction and impairs its selectivity. The chlorine-containing adducts formed in these reactions in low yields (20–30%) are mixtures of products of the addition to the double bond and in the 1,4-positions.[92]

It is also noteworthy that finely dispersed copper can be used instead of copper(I) chloride (bromide). Copper(II) hydroxide and copper oxide are inactive in the reaction.[324] It has been suggested that the reactions of the acid chlorides and bromides in the presence of copper salts proceed as intracomplex redox-initiated interaction of the ligands.[325]

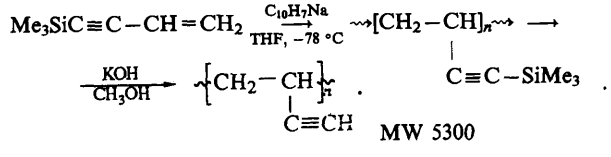
Chlorine-, bromine-, and iodine-containing products obtained in the reactions are readily dehydrohalogenated with triethylamine to form the corresponding *trans*-ethynylvinyl sulphones $R^1_3SiC{\equiv}CCR^2{=}CHR^3SO_2R^4$ in almost quantitative yields.[20]

(f) Polymerisation and copolymerisation

Trialkylsilylbut-3-en-1-ynes are known to polymerise spontaneously even at room temperature with formation of brittle vitreous masses.[23] On heating in the presence of benzene peroxides, the process proceeds at a much higher rate.[23,326] The relatively high rate of the peroxide-initiated polymerisation of dialkylhydroxysilylbut-3-en-1-yne has been pointed out.[38] There are data on the copolymerisation of 1-dimethylphenylsilylbut-3-en-1-yne with methyl methacrylate and certain physicochemical properties of the copolymers have been published.[326] The data on the structure of the polymers and copolymers obtained have not been discussed.[38,326]

In the presence of azobisisobutyronitrile, bisvinylethynylsilanes polymerise even at room temperature. The homopolymer formed under these conditions (most probably with a three-dimensional structure) is stable on heating to 400 °C.[327] The copolymerisation of bisvinylethynylsilanes with methyl methacrylate takes place at 60 °C. The influence of the ratio of the monomers on the yields, dielectric constants, and solubilities of the copolymers has been studied.

Japanese workers[328,329] have patented an effective method of synthesis of the vinylacetylene homopolymers by the naphthyl-sodium-initiated polymerisation of 1-trimethylsilylbut-3-en-1-yne and subsequent disilylation of the polymer with alkali:



Similar results were obtained using naphthyl- or butyl-lithium as polymerisation initiators.[329]

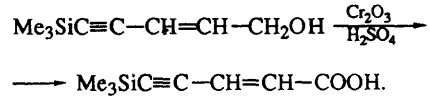
Two stages have been found in the polymerisation of 1-trimethylsilylbut-3-en-1-yne under the influence of γ-radiation: the formation of a linear polymer and the formation of three-dimensional structures in the polymer.[330] It was established that the replacement of the acetylene hydrogen by the trimethylsilyl group promotes the first stage and hinders the second.

A method has been patented for the preparation of materials for gas-permeable contact lenses from substances obtained by the polymerisation and copolymerisation of organosilicon vinylacetylene monomers of the type $CH_2{=}CR^1C{\equiv}CSiR^2R^3OSiR^4R^5R^6$ [331] or $CH_2{=}CR^1C{\equiv}CSiR^2R^3R^4$ and $[CH_2{=}CMeC{\equiv}C]_2SiMe_2$.[332]

2. Reactions with participation of functional groups

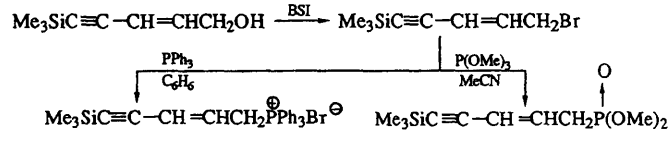
This type of chemical reaction of functional derivatives of silicon-containing alkenynes has been least investigated. However, it is known that the oxidation of silicon-containiing alkenynes with active manganese dioxide[145,186] or nickel peroxide[51] leads to the formation of the corresponding aldehydes in satisfactory yields. It has been noted that the oxidation of the (*Z*)-isomer proceeds without change in the configuration. Dimethyl sulphoxide can also be used as the oxidant.[179]

The oxidation of silicon-containing (*E*)- and (*Z*)-vinylacetylen alcohols with the Jones reagent leads to the corresponding acids, which have been converted, without purification, into methyl esters by treatment with diazomethane[48] or methanol in the presence of concentrated sulphuric acid[51]

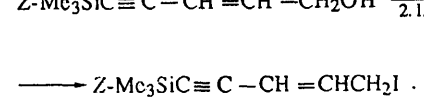


When the (*Z*)-carbinol is treated with the chlorides of acetic and (*E*)- or (*Z*)-2-methylbut-2-enoic acids,[51] the corresponding esters are produced. The configuration of the alkenyl fragments does not change under these conditions.

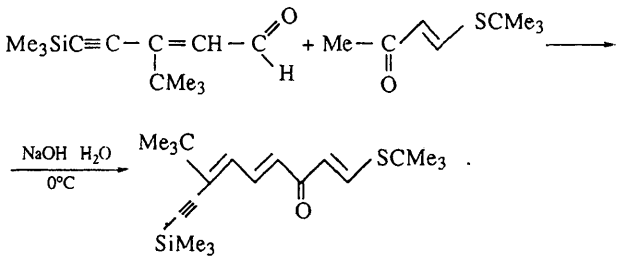
The interaction of 5-trimethylsilylpent-2-en-4-yn-1-ol with bromosuccinimide (BSI) afforded the corresponding bromide, which is readily converted into phosphoranes or phosphonates—key compounds in the synthesis of lipoxin A,[49,50,333,334,335] numerous dehydroannulenes (see Nakagawa[336] and the references quoted therein and Nakagawa and co-workers[337,338]) as well as other natural products and their synthetic analogues:[186,220,339]



A method has been developed for the synthesis of (*Z*)-1-iodo-5-trimethylsilylhex-2-en-4-yne which is used in the total synthesis of (±)-penacene:

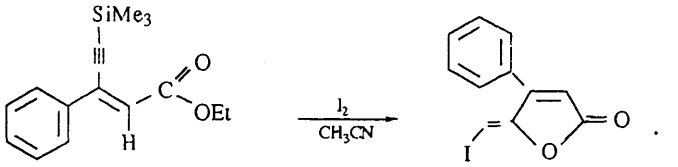


It has been shown for 3-t-butyl-5-trimethylsilylpent-2-en-4-yn-1-al[140,340] that silicon-containing aldehydes of the alkenyne series enter into aldol and crotonic condensations without the cleavage of the silicon–carbon bond:

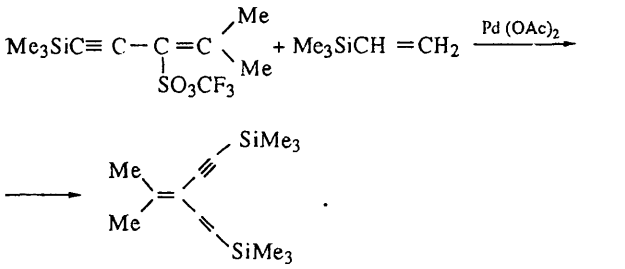


They also interact with organometallic compounds, affording the corresponding alcohols.[336,341,342]

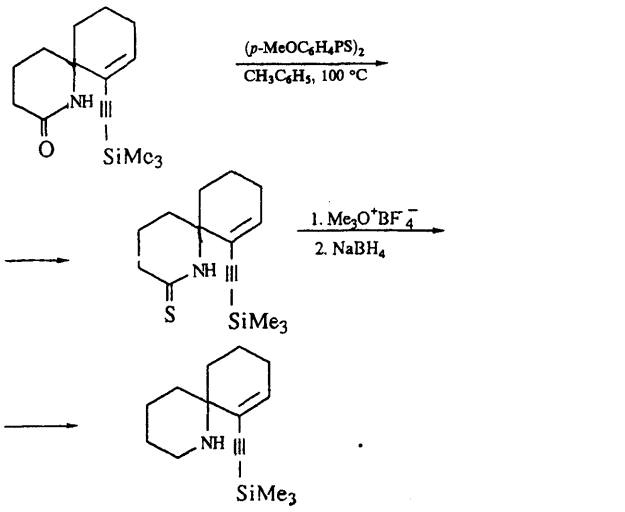
Iodolactonisation also takes place with participation of functional groups:[85]



It has been shown that 1,3-alkenyne silicon-containing triflates are capable of undergoing the palladium-catalysed cross-coupling reaction. The trimethylsilyl group is not then involved:[343,344]

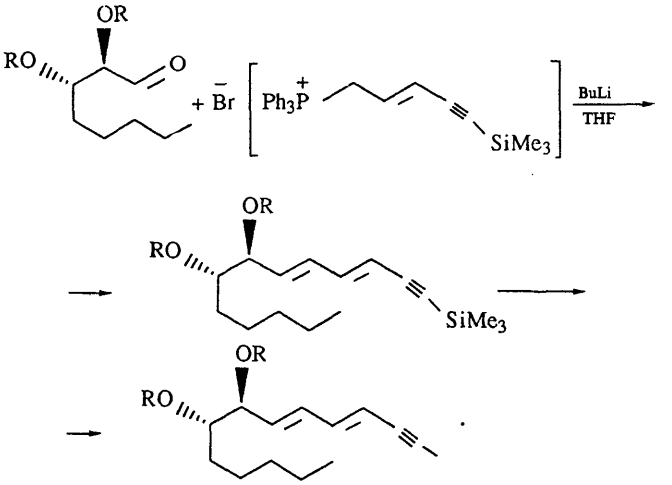


The reactions of an organosilicon lactam, described by Bultin et al.,[178] proceed with participation of functional groups:



3. Reactions with participation of the silicon–carbon bond

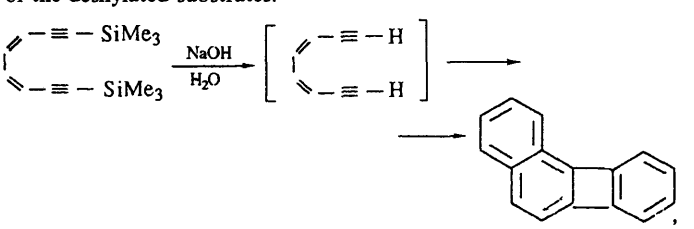
The introduction of a trialkyl(aryl)silyl group at the terminal carbon atom of the triple bond is known to increase significantly the stability of alkynes, alkenynes, and more unsaturated derivatives. The silyl protecting group is therefore used widely in the synthesis of natural products containing conjugated alkenyl fragments. As an example, one may quote the scheme for the preparation of the synthetic block (A)—the key compound in the synthesis of the four possible isomers of lipoxin B:[333,334]



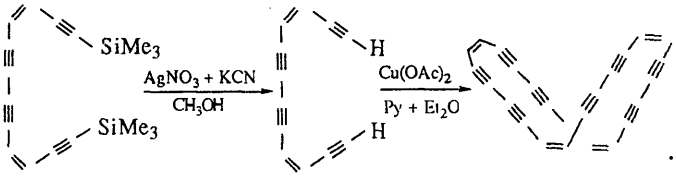
(A)

The triorganosilyl (most often trimethylsilyl) group is usually removed by the reaction of the corresponding silicon-containing acetylene with an alcoholic solution of an alkoxide,[169,170,206] an aqueous[33,85,120,155] or alcoholic[73,76,166,169,344] solutions of alkali, an aqueous solution of sodium carbonate[178] or potassium carbonate,[183] an alcoholic or aqueous alcoholic solution of a mixture of silver nitrate and potassium cyanide,[32,34,50,97,105,145,174,216,234,344] or the same reagents in a 1:1:1 ethanol–tetrahydrofuran (THF)–water mixture.[49,187,333] Desilylation takes place also when silylacetylenes are treated with methyllithium.[36,206,345] The fluorides of potassium,[30,112,141,158,159,172,201,215,224,235] sodium,[62] and tetrabutylammonium[103,104,113,173,176,182,232] have become particularly popular desilylating agents in recent years. Tetrahydrofuran, alcohol, and dimethylformamide are used as solvents in such cases. The reactions proceed as a rule at room temperature or with slight heating. The yields of the desilylation products are nearly quantitative. A method has been developed for the desilylation of silylalkenynes using phase transfer catalysts.[346] For example, the method helps to cleave the silicon–carbon bond under mild conditions without affecting the oxiran ring.

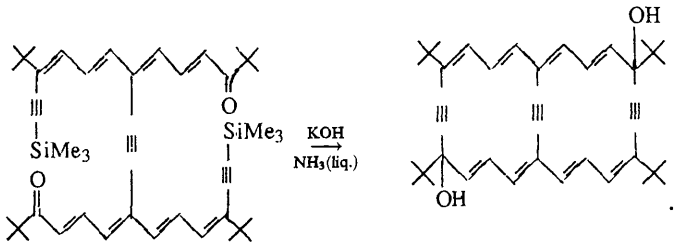
Reactions in which the removal of the silyl protecting group is completed with the formation of a new carbon–carbon bond are extremely interesting. Such processes may be due to the low stability of the desilylated substrates:[33]



or they can take place on treatment with new reagents:[34]



Japanese workers[340] developed a single-stage desilylation-alkynylation method involving the reaction of 1-trialkylsilylalk-1-ynepolyene aldehydes and ketones with alkalies in liquid ammonia. The method presupposes intramolecular or intermolecular nucleophilic attack on the carbonyl carbon atom by the acetylide anion formed on heterolysis of the silicon–carbon bond:



Subsequently this method was used widely in the synthesis of dehydroannulenes with a wide variety of structures (see, for example, Nagakawa[336] and the references quoted therein as well as Yoshikawa et al.[342]).

The reactions involving the acylation of silicon-containing alkenynes catalysed by aprotic acids,[73,107] i.e.

$$R-C(=O)Cl + Me_3SiC\equiv C-CR'=CHR'' \xrightarrow{MCl_x} R-C(=O)-C\equiv C-CR'=CHR'',$$

$$M = Al^{3+}, Ti^{4+}, Zn^{2+},$$

or by zerovalent palladium compounds are especially interesting as a method for the formation of a new carbon–carbon bond. The best yields of the corresponding ketones have been obtained using titanium chloride as the catalyst.[107] Judging from the available data,[73] the formation of ketones derived from acetylenes, which possess fungicidal activity, is also possible in the absence of a catalyst.

The heterolysis of a silicon–carbon bond can be carried out also in the presence of protic acids (perchloric, hydriodic[122]).

Desilylation of acetylenes with an aqueous alcoholic solution of silver nitrate followed by iodination leads to the synthesis of iodoacetylene:[51]

$$Z\text{-}Me_3SiC\equiv C-CH=CH-CH_2OR \xrightarrow[H_2O+EtOH]{AgNO_3+I_2} Z\text{-}IC\equiv C-CH=CH-CH_2OR.$$

Analysis of the data presented in this review permits the following conclusions:

1. The development of numerous methods for the stereospecific synthesis of readily desilylated organosilicon compounds containing the $\equiv Si-C\equiv C-C=C\lessdot$ fragments makes silicon-containing alkenynes unique synthons in the fine organic synthesis of natural products and their synthetic analogues, including sila-analogues.

2. Detailed study of the reactions involving the introduction of functional groups into 1-trialkylsilylalk-3-en-1-ynes has shown that the chemo-, regio-, and stereo-selectivities of the reactions are independent of the polarity of the reagents and substrates in all the cases investigated. The results indicate orbital control in the test reactions and to a first approximation may be generalised within the framework of the model of acid–base interaction.

References

1. K Bowden, A Braude, E R H Jones *J. Chem. Soc.*, 1946, 948
2. T V Yakovleva, A A Petrov, M D Stadnichuk *Opt. Spektrosk.*, 1961, **11** 588
3. M F Shostakovskii, N I Shergina, G I Kagan, N V Komarov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1964, 189
4. E A Gastilovich, D N Shigorin, K V Zhukova, et al. *Opt. Spektrosk.*, 1968, **25** 769
5. M F Shostakovskii, N I Shergina, N N Chipanina, N V Komarov *Primenenie Molekulyarnoi Spektroskopii v Khimii. Sbornik Dokladov Sibirskogo Soveshchaniya po Spektroskopii, Krasnoyarsk, 1964* (Chemical Applications of Molecular Spectroscopy. Collected Reports at the Siberian Conference on Spectroscopy, Krasnoyarsk, 1964), Nauka, Moscow, 1966, p. 180
6. G A Razuvaev, A N Egorochkin, S E Skobelewa, et al. *J. Organomet. Chem.*, 1981, **222** 55
7. M G Voronkov, N I Shergina *Zh. Obshch. Khim.*, 1985, **55** 2338
8. N I Shergina, L V Sherstyannikova, R G Mirskov, et al. *Zh. Obshch. Khim.*, 1980, **50** 602
9. N V Villem *Uch. Zap. Tartu. Univ.*, 1981, **12** 133
10. A D Petrov, Yu P Egorov, V F Mironov, et al. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1956, 50
11. V F Mironov, G I Nikishin *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1958, 1080
12. Y Apeloig, A Stanger *J. Org. Chem.*, 1982, **47** 1462
13. N N Belyaev, V Ya Komarov, E V Komissarova, M D Stadnichuk *Zh. Obshch. Khim.*, **52** 679
14. A Petrov, V B Lebedev *Zh. Obshch. Khim.*, 1962, **32** 657
15. A G Proidakov, G A Kalabin, R G Mirskov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 94
16. M T W Hearn *J. Magn. Reson.*, 1976, **22** 521
17. M T W Hearn *Aust. J. Chem.*, 1976, **29** 2315
18. A A Petrov, K S Mingaleva, M D Stadnichuk, I A Maretina *Zh. Obshch. Khim.*, 1961, **31** 3521
19. K S Mingaleva, T R Boronoeva, N N Belyaev, et al. *Zh. Org. Khim.*, 1975, **11** 1581
20. K S Mingaleva, N N Tanaskov, M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1977, **47** 2278
21. A A Polyakova, K I Zimina, A A Petrov, R A Khmel'nitskii *Dokl. Akad. Nauk SSSR*, 1960, **134** 833
22. A D Petrov, S I Sadykh-Zade *Dokl. Akad. Nauk SSSR*, 1952, **85** 1297

23. A D Petrov, S I Sadykh-Zade, Yu P Egorov *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1954, 722
24. A D Petrov, S I Sadykh-Zade, V M Vdovin *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1955, 181
25. M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1961, **31** 411
26. M D Stadnichuk *Zh. Obshch. Khim.*, 1963, **33** 1421
27. M S Malinovskii, A G Yudasina, N G Krivosheeva *Zh. Obshch. Khim.*, 1968, **38** 1829
28. M S Malinovskii, N G Krivosheeva, V G Dryuk, et al. *Zh. Obshch. Khim.*, 1971, **41** 1760
29. M S Malinovskii, A G Yudasina, N G Krivosheeva *Zh. Obshch. Khim.*, 1967, **37** 1666
30. W Farrell, M T W Hearn, V Thaller *J. Chem. Soc., Perkin Trans. 1*, 1978, 1485
31. M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1962, **32** 3522
32. H M Schmidt, J F Arens *Rec. Trav. Chim. Pays-Bas*, 1967, **86** 1138
33. G H Mitchel, F Sondheimer *J. Am. Chem. Soc.*, 1969, **91** 7520
34. R M McQuilkin, P J Garratt, F Sondheimer *J. Am. Chem. Soc.*, 1970, **92** 6682
35. USSR P. 202 142; *Byull. Izobret.*, 1967, (14) 34
36. G Arsequell, F Camps, G Fabrias, A Guerrero *Tetrahedron Lett.*, 1990, **31** 2739
37. M F Shostakovskii, N V Komarov, Yu V Maroshin *Dokl. Akad. Nauk SSSR*, 1961, **139** 913
38. N V Komarov, Yu V Maroshin, A D Lebedeva, L N Astaf'eva *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1963, 97
39. M G Voronkov, O G Yarosh, T D Burnashova et al. *Zh. Obshch. Khim.*, 1975, **45** 2631
40. S E Orlova, A S Atavin, B A Trofimov, E P Vyalykh *Khimiya Atsetilena* (The Chemistry of Acetylene) (Edited by M F Shostakovskii), Nauka, Moscow, 1968, p. 252
41. I Rubin, S S Lin, C B Knobler, et al. *J. Am. Chem. Soc.*, 1991, **113** 6943
42. French P. 2 498 604; *Chem. Abs.*, 1983, **98** 54196k
43. P A A Klusener, W Kulik, L Brandsma *J. Org. Chem.*, 1987, **52** 5261
44. G Zweifel, W Lewis *J. Org. Chem.*, 1978, **43** 2739
45. O N Florensova, L I Volkova, Yu V Maroshin, Yu G Kryazhev *Zh. Obshch. Khim.*, 1973, **43** 1992
46. J-P Dulcere, J Grimaldi, M Santelli *Tetrahedron Lett.*, 1981, **22** 3179
47. USSR P. 263 596; *Byull. Izobret.*, 1970, (8) 22
48. Europ. P. 21.883; *Chem. Abs.*, 1981, **95** 98321k
49. K C Nicolaou, C A Veale, S E Webler, H Katerinopouls *J. Am. Chem. Soc.*, 1985, **107** 7515
50. K C Nicolaou, S E Webler *J. Chem. Soc., Chem. Commun.*, 1985, 297
51. A Kobayashi, S Kouya, K Yamashita *Agric. Biol. Chem.*, 1976, **40** 2257
52. M F Shostakovskii, E P Gracheva, L A Kayutenko *Dokl. Akad. Nauk SSSR*, 1960, **132** 153
53. G Zweifel, S Rajagopolan *J. Am. Chem. Soc.*, 1985, **107** 700
54. E C Stracker, G Zweifel *Tetrahedron Lett.*, 1990, **31** 6815
55. M F Shostakovskii, N V Komarov, T D Burnashova, I S Akchurina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 625
56. M Iyoda, M Nakagawa *Bull. Chem. Soc. Jpn.*, 1978, **51** 3363
57. M Iyoda, M Nakagawa *Tetrahedron Lett.*, 1973, 4743
58. M V Shostakovskii, N V Komarov, T D Burnashova *Khimiya Atsetilena* (The Chemistry of Acetylene), Nauka, Moscow, 1968, p. 167
59. A A Petrov, I A Maretina, K S Mingaleva *Zh. Obshch. Khim.*, 1965, **35** 1720
60. USSR P. 175 956; *Byull. Izobret.*, 1965, (19) 17
61. A Fukuzawa, I Takasugi, A Murai *Tetrahedron Lett.*, 1991, **32** 5597
62. A G Gonzalez, J D Martin, V S Martin, et al. *Tetrahedron*, 1982, **38** 1009
63. S C Carey, M Aratani, Y Kishi *Tetrahedron Lett.*, 1985, **26** 5882
64. E J Corey, R A Ruden *Tetrahedron Lett.*, 1973, 1495
65. R Sauvetre, J F Normant *Tetrahedron Lett.*, 1982, **23** 4325
66. M G Voronkov, L P Petukhov, V I Rakhlin, et al. *Zh. Obshch. Khim.*, 1986, **56** 964
67. M G Voronkov, L V Shchukina, S N Tandura, et al. *Zh. Obshch. Khim.*, 1979, **49** 614
68. A D Petrov, L L Shchukovskaya, S I Sadykh-Zade, Yu P Egorov *Dokl. Akad. Nauk SSSR*, 1957, **115** 522
69. I A Shikhiev, M F Shostakovskii, L A Kayutenko *Dokl. Akad. Nauk Azerb. SSR*, 1958, 687
70. F Ya Perveev, I I Afonina *Zh. Obshch. Khim.*, 1970, **40** 1096
71. USSR P. 427 941; *Byull. Izobret.*, 1974, (18) 59
72. M F Shostakovskii, N V Komarov, I I Kuznetsova, I I Igonina *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1961, 699
73. O A Malchenko, N P Soboleva, N V Zotchik, et al. *Khim.-Farm. Zh.*, 1974, **8** 6
74. N A Buchkova, N V Zotchik, I A Rubstov *Zh. Obshch. Khim.*, 1984, **54** 1574
75. L Birkofer, A Ritter, H Uhlenbrauck *Chem. Ber.*, 1963, **96** 3280
76. S Ya Panchenko, N A Buchkova, G P Yurevich, et al. *Zh. Org. Khim.*, 1982, **18** 2489
77. N P Smetankina, V P Kuznetsova, V Ya Oprya *Zh. Obshch. Khim.*, 1963, **33** 2281
78. V P Kuznetsova, N P Smetankina, G N Egorova *Zh. Obshch. Khim.*, 1963, **33** 2123
79. I A Shikhiev, M F Shostakovskii, L A Kayutenko *Zh. Obshch. Khim.*, 1959, **29** 2137
80. I A Shikhiev, E M Isaev, I I Aslanov, G F Askerov *Uch. Zap. Azerb. Gos. Univ., Ser. Khim.*, 1968, 91
81. V P Kuznetsova, N P Smetankina, V Ya Oprya, G N Goreva *Zh. Obshch. Khim.*, 1964, **34** 1846
82. V P Kuznetsova, N P Smetankina *Zh. Obshch. Khim.*, 1965, **35** 913
83. V P Kuznetsova, N P Smetankina *Intern. Symp. Organosilicon Chem. Sci. Commun.*, Prague, 1965, p. 17
84. M D Stadnichuk, Candidate's Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1962, 197 pp
85. M J Sofia, J A Katzenellenbogen *J. Med. Chem.*, 1986, **29** 230
86. S Holand, R Epsztein *Bull. Soc. Chim. Fr.*, 1975, 1367
87. M D Stadnichuk, N N Belyaev *Zh. Obshch. Khim.*, 1968, **38** 1658
88. N V Komarov, O G Yarosh, L P Bakhrushev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, 2579
89. L L Shchukovskaya, A M Kapustyanskaya *Zh. Obshch. Khim.*, 1971, **41** 609
90. G C Johnson, J J Stofko, T P Lockhart, et al. *J. Org. Chem.*, 1979, **44** 4215

91. T B Kryukova, M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1972, **42** 470
92. T B Kryukova, M D Stadnichuk, T N Timofeeva *Zh. Obshch. Khim.*, 1974, **44** 789
93. M D Stadnichuk, T B Kryukova, A A Petrov *Zh. Obshch. Khim.*, 1975, **45** 838
94. T B Kryukova, M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1973, **43** 1063
95. A I Vil'davskaya, K B Rall', A A Petrov *Zh. Obshch. Khim.*, 1971, **41** 1279
96. B M Trost, J M Tour *J. Org. Chem.*, 1989, **54** 484
97. K C Nicolaou, R E Zipkin, N A Petasis *J. Am. Chem. Soc.*, 1982, **104** 5558
98. H J Reich, S K Shah, P M Gold, R E Olson *J. Am. Chem. Soc.*, 1981, **103** 3112
99. P R Hamann, P L Fuehs *J. Org. Chem.*, 1983, **48** 914
100. H Ahlbrecht, W Farnung, H Simon *Chem. Ber.*, 1984, **117** 2622
101. B G Shakhovskoi, M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1964, **34** 2625
102. D W Young *Protective Groups in Organic Chemistry* (Edited by J F W MacOmie) (Translated into Russian), Mir, Moscow, 1976, p. 294
103. A B Holmes, R A Raphael, N K Wellard *Tetrahedron Lett.*, 1976, 1539
104. A B Holmes, C L D Jennings-White, D A Kendric *J. Chem. Soc., Chem. Commun.*, 1983, 415
105. A Kobayashi, Y Shibata, K Yamashit *Agric. Biol. Chem. Jpn.*, 1975, **39** 911
106. M H P J Aerssens, L Brandsma *J. Chem. Soc., Chem. Commun.*, 1984, **735**
107. G E Jones, A B Holmes *Tetrahedron Lett.*, 1982, **23** 3203
108. A B Holmes, C L D Jennings-White, D A Kendrick *J. Chem. Soc., Chem. Commun.*, 1984, 1594
109. K Green, J W Keeping, V Thaller *J. Chem. Res. Synop.*, 1985, 103
110. J Salaun, J Oliver *Nouv. J. Chim.*, 1981, **5** 587
111. J A Miller, G Zweifel *J. Am. Chem. Soc.*, 1983, **105** 1383
112. J A Miller, W Leong, G Zweifel *J. Org. Chem.*, 1988, **53** 1839
113. C E Stracker, W Leong, J A Miller, et al. *Tetrahedron Lett.*, 1989, **30** 6487
114. I M Gverdtsiteli, T P Doksopulo *Dokl. Akad. Nauk SSSR*, 1962, **145** 789
115. I M Gverdtsiteli, T P Doksopulo *Dokl. Akad. Nauk SSSR*, 1963, **150** 1043
116. I M Gverdtsiteli, T P Doksopulo *Soobshch. Akad. Nauk Gruz. SSR*, 1963, **30** 289
117. T Kusumoto, T Hiyama *Chem. Lett.*, 1985, **1405**
118. H X Zhang, G Balavoine *J. Org. Chem.*, 1990, **55** 1857
119. B G Shakhovskoi, M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1965, **35** 1031
120. B G Shakhovskoi *Zh. Obshch. Khim.*, 1969, **39** 524
121. G Zweifel, W Leong *J. Am. Chem. Soc.*, 1987, **109** 6409
122. T Kusumoto, K Nishide, T Hiyama *Bull. Chem. Soc. Jpn.*, 1990, **63** 1947
123. T Kusumoto, K Nishide, T Hiyama *Chem. Lett.*, 1985, 1409
124. T Kusumoto, T Hiyama *Tetrahedron Lett.*, 1987, **28** 1807
125. J Klein, J Y Becker *J. Chem. Soc., Perkin Trans. 2*, 1973, 599
126. W Priester, R West *J. Am. Chem. Soc.*, 1976, **98** 8426
127. T L Chwang, R West *J. Am. Chem. Soc.*, 1973, **95** 3324
128. R L P Jong, L Brandsma *J. Chem. Soc., Chem. Commun.*, 1983, 1056
129. C C Shen, C Ainsworth *Tetrahedron Lett.*, 1979, 93
130. B G Shakhovskoi, A A Petrov *Zh. Obshch. Khim.*, 1967, **37** 1371
131. B G Shakhovskoi, A A Petrov *Khimiya i Prakticheskoe Primenenie Kremniiorganicheskikh Soedinenii: Trudy Soveshchaniya* (The Chemistry and Practical Applications of Organosilicon Compounds: Conference Proceedings) (Edited by D N Andreev), Khimiya, Leningrad, 1968, p. 134
132. L Birkofer, K Richtzenhain *Chem. Ber.*, 1979, **112** 2829
133. B G Shakhovskoi, M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1965, **35** 1714
134. B G Shakhovskoi *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1970, **13** 536
135. N V Komarov, M F Shostakovskii, T D Burnashova *Zh. Obshch. Khim.*, 1968, **38** 1398
136. T J Barton, G P Hassman *J. Am. Chem. Soc.*, 1983, **105** 6316
137. I Kuwajima, K Atsumi, I Azegami *J. Chem. Soc., Chem. Commun.*, 1977, 76
138. K Atsumi, I Kuwajima *Chem. Lett.*, 1978, 387
139. S Gronowitz, T Freid, O Karlson, et al. *Chem. Ser.*, 1981, **18** 192
140. S Akiyama, S Nakatsuji, T Hamamura *Tetrahedron Lett.*, 1979, 2809
141. M D Schiavelli, D M Jung, A K Vaden *J. Org. Chem.*, 1981, **46** 92
142. S N Hanaka, L R Subramanian *Synthesis*, 1982, 85
143. P J Stang *Chem. Res.*, 1982, **15** 348
144. K A Parker, R W Kosley *Tetrahedron Lett.*, 1975, 691
145. N A Buchkova, N V Zotchik, Zh N Motorina, I A Rubstov *Zh. Obshch. Khim.*, 1985, **55** 1111
146. E Geleneser, T Dlouhy, N V Zotchik, I A Rubtsov *The Synthesis of 5-(Trialkylsilyl)pent-2-en-4-ynoic Acids and their Homologues and of 3-Methyl-1-(trimethylsilyl)pent-4-en-1-yn-5-al*, 1978, 13 pp—Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), No. 380-78
147. A Stütz *Angew. Chem., Int. Ed. Engl.*, 1987, **26** 320
148. K A Parker, J J Petraitis, R W Kosley *J. Org. Chem.*, 1982, **47** 389
149. R M Acheson, G C M Lee *J. Chem. Soc., Perkin Trans. 1*, 1987, 2321
150. S Bancel, P Cresson *C. R. Seances Acad. Sci., Ser. C*, 1970, **270** 2161
151. K Nonoshita, H Banno, K Maruoka, H Yamamoto *J. Am. Chem. Soc.*, 1990, **112** 316
152. H Kleijn, H Westmijze, K Kruithof, P Vermeer *Recl. Trav. Chim. Pays-Bas*, 1979, **98** 27
153. T G Back, M V Krishna *J. Org. Chem.*, 1987, **52** 4265
154. V Yu Orlov, S A Lebedev, S V Ponomarev, I F Lutsenko *Zh. Obshch. Khim.*, 1975, **45** 708
155. S J Harris, D R M Walton *Tetrahedron*, 1978, **34** 1037
156. J A Walker, S P Bitler, F Wudl *J. Org. Chem.*, 1984, **49** 4733
157. A Carpita, R Rossi *Tetrahedron Lett.*, 1986, **27** 4351
158. B O Andreini, A Carpita, R Rossi *Tetrahedron Lett.*, 1986, **27** 5533
159. B P Andreini, M Benetti, A Carpita, R Rossi *Tetrahedron*, 1987, **43** 4591
160. B P Andreini, A Carpita, R Rossi *Tetrahedron Lett.*, 1988, **29** 2239
161. M Benetti, A Carpita, R Rossi *Gazz. Chim. Ital.*, 1988, **118** 469
162. E C Stracker, G Zweifel *Tetrahedron Lett.*, 1991, 3329

163. A Alexakis, I Marek, P Mangeney, J F Normant *Tetrahedron*, 1991, **47** 1677
164. K Ruifenberg, H Westmijze, H Keijn, P Vermeer *J. Organomet. Chem.*, 1984, **277** 227
165. K Ruitenberg, P Vermeer *Tetrahedron Lett.*, 1984, **25** 3019
166. H Kleijn, P Vermeer *J. Organomet. Chem.*, 1985, **292** 437
167. H Kleijn, J Meijer, G C Overbeek, P Vermeer *Rec. Trav. Chim. Pays-Bas*, 1982, **101** 91
168. J F Normant *Pure Appl. Chem.*, 1978, **50** 709
169. A Commercon, J F Normant, J Villeras *Tetrahedron*, 1980, **36** 1215
170. J F Normant, A Commercon, J Villeras *Tetrahedron Lett.*, 1975, 1465
171. K Ruitenberg, J Meijer, R J Bullee, P Vermeer *J. Organomet. Chem.*, 1981, **217** 267
172. K S Feldman *Tetrahedron Lett.*, 1982, **23** 3031
173. L Crombie, A J W Hobbs, M A Horsham *Tetrahedron Lett.*, 1987, **28** 4875
174. R W Spencer, T F Tam, G Thomes, et al. *J. Am. Chem. Soc.*, 1986, **108** 5589
175. K Peter, C Vollhardt, L S Winn *Tetrahedron Lett.*, 1985, **26** 709
176. Y Kobayashi, T Shimazaki, F Sato *Tetrahedron Lett.*, 1987, **28** 5849
177. J Reisch, A Bathe *Liebigs Ann. Chem.*, 1988, 69
178. R J Bultin, A B Holmes, E McDonald *Tetrahedron Lett.*, 1988, **29** 2989
179. S A Kende, C A Smith *Tetrahedron Lett.*, 1988, **29** 4217
180. S I Schreiber, L L Kiessling *J. Am. Chem. Soc.*, 1988, **110** 631
181. H Tanaka, K Haraguchi, I Kozumi, et al. *Can. J. Chem.*, 1986, **64** 1560
182. M Isobe, Y Hirose, K Shimokawa, et al. *Tetrahedron Lett.*, 1990, **33** 5499
183. P A Wender, C K Zercher *J. Am. Chem. Soc.*, 1991, **113** 2311
184. G C M Lee, B Tobios, J M Holms, et al. *J. Am. Chem. Soc.*, 1990, **112** 9330
185. P A Wender, J A McKinney, C Mukai *J. Am. Chem. Soc.*, 1990, **112** 5369
186. A S Kende, K Kawamura, R J DeVita *J. Am. Chem. Soc.*, 1990, **112** 4070
187. Y Kobayashi, T Smimozaki, H Taguchi, F Sato *J. Org. Chem.*, 1990, **55** 5324
188. M Kabat, J Kiegiel, N Cohen, et al. *Tetrahedron Lett.*, 1991, **32** 2343
189. K C Nicolaou, J I Ramphal, N A Petasis, C N Serhan *Angew. Chem.*, 1991, **103** 1119
190. C Crevisy, J-M Beau *Tetrahedron Lett.*, 1991, **32** 3171
191. V Ratovelomanana, A Hammond, G Linstrumelle *Tetrahedron Lett.*, 1987, **28** 1649
192. K Nakatani, K Arai, N Hirayama, et al. *Tetrahedron Lett.*, 1990, **31** 2323
193. R Brückner, S W Schenplein, J Suffert *Tetrahedron Lett.*, 1991, **32** 1449
194. J Suffert, R Brückner *Tetrahedron Lett.*, 1991, **32** 1453
195. T Jeffery *Synthesis*, 1987, 70
196. J K Stiell, J H Simpson *J. Am. Chem. Soc.*, 1987, **109** 2138
197. Y Natanaka, K Matsui, T Hiyama *Tetrahedron Lett.*, 1989, **30** 2403
198. J K Stille *Angew. Chem., Int. Ed. Engl.*, 1986, **25** 508
199. W J Scott, J K Stille *J. Am. Chem. Soc.*, 1986, **108** 3033
200. W J Scott, G T Gisp, J K Stille *J. Am. Chem. Soc.*, 1984, **106** 4630
201. C Huynh, G Linsrumelle *Tetrahedron*, 1988, **44** 6337
202. F C Yusupova, G A Gailyunas, G V Nuritdinova, V P Yur'ev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2427
203. V P Yur'ev, G A Gailyunas, F G Yusupova, et al. *J. Organomet. Chem.*, 1979, **169** 19
204. M Ishikawa, J Ohshita, Y Ito, A Minato *J. Chem. Soc., Chem. Commun.*, 1988, 804
205. M Ishikawa, J Ohshita *J. Organomet. Chem.*, 1988, **346** C58
206. J Ohshita, K Furumori, C Matsuguchi, M Ishikawa *J. Org. Chem.*, 1990, **55** 3277
207. M Akita, H Yasuda, A Nakamura *Bull. Chem. Soc. Jpn.*, 1984, **57** 480
208. B M Trost, G Kottirsch *J. Am. Chem. Soc.*, 1990, **112** 2816
209. N Chatani, N Amishiro, S Murai *J. Am. Chem. Soc.*, 1991, **113** 7778
210. Y Sato, Y Kobayashi, M Sugiura, H Shirai *J. Org. Chem.*, 1978, **43** 199
211. W H Okamura, J M Aurrecoechea, R A Gibbs, A W Norman *J. Org. Chem.*, 1989, **54** 4072
212. N N Belyaev, M D Stadnichuk, A A Petrov, A N Belyaev *Zh. Obshch. Khim.*, 1972, **42** 715
213. N N Belyaev, M D Stadnichuk *Doklady IV Vsesoyuznoi Konferentsii po Khimii Atsetilena, Alma-Ata* (Reports at the IVth All-Union Conference on the Chemistry of Acetylene, Alma-Ata), Alma-Ata, 1972, Vol. 2, p. 141
214. K Eiter, F Lieb, H Disselnkötter, H Oediger *Liebigs Ann. Chem.*, 1978, 658
215. E J Corey, G W J Fleet, M Kato *Tetrahedron Lett.*, 1973, 3963
216. M Ahmed, G C Barley, M T W Hearn *J. Chem. Soc., Perkin Trans. 1*, 1974, 1981
217. M Ahmed, G J Broad, E R H Jones, et al. *J. Chem. Res. (S)*, 1982, 199
218. M M Hann, P G Sammes, P D Kennewell, J B Taylor *J. Chem. Soc., Chem. Commun.*, 1980, 234
219. M M Hann, P G Sammes, P D Kennewell, J B Taylor *J. Chem. Soc., Perkin Trans. 1*, 1982, 307
220. N Miles, P G Sammes, P D Kennewell, R Westwood *J. Chem. Soc., Perkin Trans. 1*, 1985, 2299
221. K C Nicolaou, S E Webber *J. Am. Chem. Soc.*, 1984, **106** 5734
222. P E Peterson, R L Bredlove-Leffew *J. Org. Chem.*, 1986, **51** 1948
223. A Fukuzawa, H Sato, M Miyamoto, T Masamune *Tetrahedron Lett.*, 1986, **27** 2901
224. Europ. P. 147.217; *Chem. Abs.*, 1986, **104** 129784d
225. T R Boronoeva, N N Belyaev, M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1974, **44** 1949
226. M D Stadnichuk, N N Belyaev, N I Nesterov *Stroenie i Reaktsionnaya Sposobnost' Kremniiorganicheskikh Soedinenii. Tezisy Dokladov I Vsesoyuznogo Simpoziuma, Irkutsk* (The Structure and Reactivity of Organosilicon Compounds. Abstracts of Reports at the Ist All-Union Symposium, Irkutsk), Irkutsk, 1977, p. 179
227. N I Nesterov, E V Komissarova, N N Belyaev, et al. *Zh. Obshch. Khim.*, 1977, **47** 1425
228. Y Yamakado, M Ishiguro, N Ikada, H Yamamoto *J. Chem. Soc.*, 1981, **103** 5568
229. R Haruta, M Ishiguro, K Furuta, et al. *Chem. Lett.*, 1982, 1093

230. F Kyoji, I Masaharu, H Rynichi, et al. *Bull. Chem. Soc. Jpn.*, 1984, **57** 2768
231. E J Corey, C Ruecker *Tetrahedron Lett.*, 1982, **23** 719
232. E L Overman, A S Thompson *J. Am. Chem. Soc.*, 1988, **110** 2248
233. K Mikami, T Maeda, T Nakai *Tetrahedron Lett.*, 1986, **27** 4189
234. T P Lockart, P B Comit, R G Bergman *J. Am. Chem. Soc.*, 1981, **103** 4082
235. J Oliver, J Salaun *Tetrahedron Lett.*, 1984, **25** 1269
236. J M Palazon, V S Martin *Tetrahedron Lett.*, 1988, **29** 681
237. G Stork, K Zhao *J. Am. Chem. Soc.*, 1990, **112** 5875
238. A I Borisova, N S Vyazankin, A S Medvedeva, I D Kalikhman *Zh. Obshch. Khim.*, 1978, **48** 2800
239. M Taniguchi, K Oshima, K Utimoto *Tetrahedron Lett.*, 1991, **32** 2783
240. P B D de la Mare, R Bolton *Electrophilic Additions to Unsaturated Systems* (Translated into Russian), Mir, Moscow, 1968, 318 pp
241. N N Belyaev, M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1968, **38** 886
242. N N Belyaev, M D Stadnichuk *Zh. Obshch. Khim.*, 1968, **38** 1582
243. T R Boronoeva, N N Belyaev, M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1976, **46** 1551
244. M D Stadnichuk, Doctoral Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1968, 389 pp
245. N N Belyaev, Doctoral Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1985, 336
246. I S Vorob'eva, M D Stadnichuk *Zh. Obshch. Khim.*, 1984, **54** 2731
247. S V Ivanov, M D Stadnichuk *Zh. Obshch. Khim.*, 1990, **60** 1092
248. P E Butler, W R Mueller *Tetrahedron Lett.*, 1966, **50** 2179
249. V A Ryazantsev, M D Stadnichuk *Zh. Obshch. Khim.*, 1979, **49** 930
250. B B Kochetkov, M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1972, **42** 880
251. B B Kochetkov, M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1971, **41** 715
252. K B Rall', A I Vil'davskaya *Zh. Org. Khim.*, 1980, **16** 2054
253. E V Komissarova, N N Belyaev, M D Stadnichuk *Zh. Obshch. Khim.*, 1979, **49** 938
254. N N Belyaev, E V Komissarova, M D Stadnichuk *Zh. Obshch. Khim.*, 1982, **52** 2084
255. Yu A Zhdanov, V I Minkin *Korrelyatsionnyi Analiz v Organicheskoi Khimii* (Correlation Analysis in Organic Chemistry), Izd. Rostov. Univ., Rostov, 1966, pp 85–89
256. B B Kochetkov, Candidate's Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1972, 107
257. M D Stadnichuk, A A Petrov, B B Kochetkov, T B Kryukova *Doklady IV Vsesoyuznoi Konferentsii po Khimii Atsetilena, Alma-Ata* (Reports at the IVth All-Union Conference on the Chemistry of Acetylene, Alma-Ata), Alma-Ata, 1972, Vol. 2, p. 151
258. M D Stadnichuk, V A Ryazantsev, A A Petrov *Zh. Obshch. Khim.*, 1979, **49** 956
259. V A Ryazantsev, M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1980, **50** 1301
260. V A Ryazantsev, M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1980, **50** 694
261. I S Vorob'eva, M D Stadnichuk *Zh. Obshch. Khim.*, 1984, **54** 2064
262. I S Vorob'eva, M D Stadnichuk *Zh. Obshch. Khim.*, 1982, **52** 2803
263. S A Vartanyan, A O Tosunyan *Arm. Khim. Zh.*, 1966, **19** 292
264. A A Petrov, M D Stadnichuk, Yu I Kheruze *Dokl. Akad. Nauk SSSR*, 1961, **139** 1124
265. I G Sulimov, M D Stadnichuk *Zh. Obshch. Khim.*, 1967, **37** 1906
266. I G Sulimov, M D Stadnichuk *Khimiya i Prakticheskoe Primenenie Kremniiorganicheskikh Soedinenii. Trudy Soveshchaniya* (The Chemistry and Practical Applications of Organosilicon Compounds: Conference Proceedings) (Edited by D N Andreev, Khimiya, Leningrad, 1968, p. 57
267. I G Sulimov, M D Stadnichuk *Zh. Obshch. Khim.*, 1967, **37** 2329
268. I S Vorob'eva, M D Stadnichuk *Zh. Obshch. Khim.*, 1983, **53** 2654
269. USSR P. 292 980; *Byull. Izobret.*, 1971, (5) 100
270. USSR P. 318 582; *Byull. Izobret.*, 1971, (32) 59
271. USSR P. 190 877; *Byull. Izobret.*, 1967, (3) 22
272. M S Malinovskii, N G Krivosheeva, A G Yudasina, et al. *Voprosy Khimii i Khim. Tekhnologii*, 1974, (34) 3
273. M S Malinovskii *Epoksidnye Monomery, Epoksidnye Smoly* (Epoxide Monomers, Epoxide Resins) (Edited by M S Salikhov), Baku, 1975, p. 3
274. A A Petrov, V A Kormer, M D Stadnichuk *Zh. Obshch. Khim.*, 1960, **30** 2243
275. M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1962, **32** 2490
276. V A Kormer, A A Petrov *Zh. Obshch. Khim.*, 1964, **34** 1868
277. L M Zubritskii, O E Romanov, Kh V Bal'yan *Zh. Obshch. Khim.*, 1977, 47 1327
278. L N Cherkasov, S I Radchenko, B S Kupin *Zh. Obshch. Khim.*, 1971, **41** 936
279. L N Cherkasov, G I Pis'mennya, S I Radchenko, Kh V Bal'yan *Doklady IV Vsesoyuznoi Konferentsii po Khimii Atsetilena, Alma-Ata* (Reports at the IVth All-Union Conference on the Chemistry of Acetylene, Alma-Ata), Alma-Ata, 1972, Vol. 2, p. 57
280. L N Cherkasov *Kremniiorganicheskie Soedineniya i Materialy na Ikh Osnove: Trudy V Soveshchaniya, Leningrad* (Organosilicon Compounds and Materials Based on Them: Proceedings of the Vth Conference, Leningrad), Nauka, Leningrad, 1984, p. 34
281. J Dunogues, P Bourgeois, J-P Pillot, et al. *J. Organomet. Chem.*, 1975, **87** 169
282. L M Zubritskii, L N Cherkasov, et al. *Zh. Obshch. Khim.*, 1976, **46** 441
283. L M Zubritskii, T N Fomina, Kh V Bal'yan *Zh. Org. Khim.*, 1981, **1** 69
284. L N Cherkasov *Zh. Obshch. Khim.*, 1971, **41** 1561
285. L N Cherkasov, O B Kozlova *Zh. Obshch. Khim.*, 1978, **48** 1664
286. L N Cherkasov, O V Perepelkin *Zh. Obshch. Khim.*, 1976, **46** 2758
287. G A Molander *J. Org. Chem.*, 1983, **48** 5409
288. H Hayami, K Oshima, H Nozaki *Tetrahedron Lett.*, 1984, **25** 4433

289. K Mazuoka, H Yamamoto *Tetrahedron*, 1988, **44** 5001
290. J J Eisch, R J Manfre, D A Komar *J. Organomet. Chem.*, 1978, **159** C13
291. J J Eisch, M W Foxton *J. Org. Chem.*, 1971, **36** 3520
292. A Hassner, J A Soderquist *J. Organomet. Chem.*, 1977, **131** C1
293. J A Soderquist, A Hassner *J. Am. Chem. Soc.*, 1980, **102** 1577
294. G Zweifel, S J Backlund *J. Am. Chem. Soc.*, 1977, **99** 3184
295. A A Petrov, V A Kormer, M D Stadnichuk *Zh. Obshch. Khim.*, 1961, **31** 1135
296. M D Stadnichuk *Zh. Obshch. Khim.*, 1968, **38** 939
297. F Ya Perveev, I I Afonina *Zh. Obshch. Khim.*, 1971, **41** 345
298. N N Belyaev, L I Korchemkina, M D Stadnichuk *Zh. Obshch. Khim.*, 1979, **49** 2630
299. T A Shustrova, N N Belyaev, M D Stadnichuk *Zh. Obshch. Khim.*, 1988, **58** 374
300. O A Kurakin, M D Stadnichuk *Zh. Obshch. Khim.*, 1989, **59** 2581
301. O A Kurakin, M D Stadnichuk *Zh. Obshch. Khim.*, 1988, **58** 367
302. B S Kupin, A A Petrov *Zh. Org. Khim.*, 1965, **1** 244
303. T A Shustrova, N N Belyaev, M D Stadnichuk *Zh. Obshch. Khim.*, 1984, **54** 2781
304. T A Shustrova, N N Belyaev, M D Stadnichuk *Zh. Obshch. Khim.*, 1985, **55** 1777
305. T N Shustrova, Candidate's Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1985, 139 pp
306. K B Rall', A I Vil'davskaya, A A Petrov *Zh. Org. Khim.*, 1978, **14** 1107
307. V V Yakovlev, Candidate's Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1989, 115 pp
308. M F Shostakovskii, N V Komarov, V K Misyanas *Dokl. Akad. Nauk SSSR*, 1967, **173** 843
309. K B Rall', A I Vil'davskaya, A A Petrov *Zh. Obshch. Khim.*, 1972, **42** 1064
310. N N Belyaev, M D Stadnichuk, T R Boroneva *Zh. Obshch. Khim.*, 1976, **46** 1545
311. I G Kolokol'tseva, V N Chistokletov, et al. *Zh. Obshch. Khim.*, 1968, **38** 1820
312. E V Komissarova, N N Belyaev, M D Stadnichuk, et al. *Zh. Obshch. Khim.*, 1978, **48** 705
313. E V Komissarova, Candidate's Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1980, 123 pp
314. K P C Vollhard, L S Yee *J. Am. Chem. Soc.*, 1977, **99** 2010
315. B C Berris, K P C Vollhardt *Tetrahedron*, 1982, **38** 2911
316. Kh V Bal'yan, A A Petrov, Yu I Porfir'eva *Zh. Obshch. Khim.*, 1965, **26** 1926
317. M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1961, **31** 1855
318. M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1962, **32** 3514
319. H Bock, H Seidl *J. Am. Chem. Soc.*, 1986, **90** 5694
320. M D Stadnichuk, A A Petrov *Zh. Obshch. Khim.*, 1963, **33** 2868
321. P J Stang, V Dixit, M D Shiavelli, P Dress *J. Am. Chem. Soc.*, 1987, **109** 1150
322. Y Wakatsuku, H Ymazaki, Y Maruyama, et al. *J. Chem. Soc., Chem. Commun.*, 1991, 261
323. M Asscher, D Vofsi *J. Chem. Soc.*, 1964, 4962
324. USSR P. 536 172; *Byull. Izobret.*, 1976, **43** 62
325. M M Tanaskov, M D Stadnichuk *Zh. Obshch. Khim.*, 1978, **48** 1140
326. V V Korshak, A D Petrov, N G Matveeva, et al. *Zh. Obshch. Khim.*, 1956, **26** 1209
327. M F Shostakovskii, A M Khomutova, et al. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1961, 488
328. Japanese P. 7 308 874; *Chem. Abs.*, 1974, **80** 134034z
329. K Isao, H Nobue *J. Polym. Sci., Part B*, 1971, **9** 275
330. N V Petrukhin, V A Gorbachev, et al. *Vysokomol. Soedin. A*, 1975, **17** 2276
331. Japanese P. 122 668; *Chem. Abs.*, 1987, **107** 242664q
332. Japanese P 11 458; *Chem. Abs.*, 1987, **106** 201784q
333. K C Nicolaou, S E Webber *Synthesis*, 1986, 453
334. K C Nicolaou, S E Webber, J Ramphal, Y Abe *Angew. Chem.*, 1987, **99** 1077
335. M Avignon-Tropis, M Treilhou, J R Pongny *Tetrahedron*, 1991, **47** 7279
336. M Nakagawa *Angew. Chem.*, 1979, **91** 215
337. M Iyoda, S Tanaka, K Nishioka, M Oda *Tetrahedron Lett.*, 1983, **24** 2861
338. Y Onishi, M Iyoda, M Nakagawa *Tetrahedron Lett.*, 1981, **22** 3641
339. A L Costelhano, S Horne, G J Taylor, et al. *Tetrahedron*, 1988, **44** 5451
340. S Akiyama, M Iyoda, M Nakagawa *J. Am. Chem. Soc.*, 1976, **98** 6410
341. Y Aso, M Iyoda, M Nakagawa *Tetrahedron Lett.*, 1984, **22** 1989
342. Y Yoshikawa, M Iyoda, M Nakagawa, et al. *Tetrahedron Lett.*, 1981, **22** 5209
343. K Karabelas, A Hallberg *J. Org. Chem.*, 1988, **53** 4909
344. E Geleneser, E D Lebedeva, N V Zotchik, I A Rubtsov *Synthesis of 8-Hydroxy-3-Methyloct-2-ene-4,6-diyn-1-oic Acid and the Dimethyl Ester of 3,8-Dimethyldeca-2,8-diene-4,6-diyn-1,10-dioic Acid*, Moscow, 1978, 9 pp—Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), No. 3223-78
345. R W Bates, R Fernandez-Moro, S V Ley *Tetrahedron Lett.*, 1991, 2651
346. J Roser, W Erberbch *Synth. Commun.*, 1986, **16** 983

Received 7th April 1992

Translated from *Uspekhi Khimii* 61 2040–2061 (1992) U.D.C. 541.128.13

The partial catalytic oxidation of methane to give oxygen-containing compounds

O V Krylov
Institute of Chemical Physics, Russian Academy of Sciences

ABSTRACT. **The three principal paths of the partial oxidation of methane, to give methanol, formaldehyde, and synthesis gas, have been reviewed. The kinetics and mechanism of the processes have been described. The possible oxidation of methane using different oxidising agents—oxygen and carbon dioxide—has been examined.**

The bibliography contains 139 references.

Contents

I.	Introduction	1118
II.	The oxidation of methane to methanol	1118
III.	The oxidation of methane to formaldehyde	1120
IV.	The oxidation of methane to synthesis gas	1125

I. Introduction

Among the various routes in the partial oxdiation of methane, the recently discovered oxidative condensation of methane to give C_2-hydrocarbons is being most intensively developed. The number of publications on this topic is much greater than the number devoted to other possible routes for the partial oxidation. A number of recent reviews deal with the partial oxidation of CH_4.[1,2]

At the same time, the practical importance of the other directions is apparently much greater than that of oxidative condensation. Among these, the oxidation of methane to methanol occupies a leading position. Methanol is an important component of oxygenate fuels for internal combustion engines. The demand for methanol amounts to millions of tons in this country, and tens of millions of tons worldwide. Thus the search for new economical methods for obtaining methanol, making it possible to replace the traditional method of preparation via synthesis gas, has become one of the most important directions in catalytic studies.

Synthesis gas ($CO + H_2$) is usually obtained by the steam conversion of methane on a nickel catalyst at a high temperature (1000–1200 K)

$$CH_4 + H_2O = CO + 3H_2.$$

In this version, however, the mixture obtained cannot be used directly for the synthesis of methanol, since this requires a different stoichiometric ratio $[CO]:[H_2] = 1:2$. This can be obtained by the direct oxidation of methane using oxygen

$$2CH_4 + O_2 = 2CO + 4H_2.$$

The oxidative transformation of methane to synthesis gas with a ratio $[CO]:[H_2] = 1:1$ is achieved by using CO_2 as the oxidising agent

$$CH_4 + CO_2 = 2CO + 2H_2.$$

This mixture can be used to obtain hydrocarbons by the Fischer–Tropsch synthesis.

The third position of economic importance is occupied by the partial oxidation of methane to formaldehyde. The discovery of selective catalysts for the direct oxidation of methane to formaldehyde would make it possible to replace by a single-stage process the multi-stage methane → synthesis gas → methanol → formaldehyde process.

Reviews of the partial oxidation of methane to oxygen-containing compounds have been published.[3–6] The present review examines publications up to and including 1991 (and early 1992). The liquid-phase homogeneous-catalytic oxidation of methane is not examined.

II. The oxidation of methane to methanol

Homogeneous oxidation. The homogeneous oxidation of methane has been studied in most detail at 673–873 K. It takes place with the intermediate formation of the free radicals CH_3, CH_3O, CH_3O_2, HO_2, HCO, and OH and the molecular species H_2O_2 and CH_3OOH. The kinetics of the formation and disappearance of the free radicals under the conditions of the reaction are often determined by freezing the free radicals in a CO_2 matrix using a trap cooled with liquid nitrogen. The use of freezing in this way combined with ESR *in situ* was first developed in the Erevan Institute of Chemical Physics.[7] A detailed scheme for the oxidation of methane, describing the principal stages of the process, has been published.[8] The reactions

determining the overall rate of the process, and the corresponding rate constants, are given below:

$CH_4 + O_2 = CH_3 + HO_2$, $k_1 = 10^{-10}\exp(-230/RT)$, (1)

$CH_3 + O_2 = CH_3O_2$, $k_2 = 4 \cdot 10^{-13}$, (2)

$CH_3O_2 + M = CH_3 + O_2 + M$, $k_3 = 10^{-14}\exp(-109/RT)$, (3)

$CH_3O + O_2 = CH_2O + HO_2$, $k_4 = 5 \cdot 10^{-14}$, (4)

$OH + CH_4 = CH_3 + H_2O$, $k_5 = 10^{-10}\exp(-35.5/RT)$, (5)

$HO_2 + CH_4 = H_2O_2 + CH_3$, $k_6 = 10^{-12}\exp(-90/RT)$, (6)

$OH + CH_2O = HCO + H_2O$, $k_7 = 1.6 \cdot 10^{-10}\exp(-10.4/RT)$, (7)

$HO_2 + CH_2O = HCO + H_2O_2$, $k_8 = 1.9 \cdot 10^{-11}\exp(-54/RT)$, (8)

$HCO + O_2 = CO + HO_2$, $k_9 = 5.5 \cdot 10^{-11}$, (9)

$H_2O_2 + M = 2OH + M$, $k_{10} = 2.8 \cdot 10^{-7}\exp(-193/RT)$, (10)

$CH_3O_2 + CH_4 = CH_3OOH + CH_3$, $k_{11} = 10^{-12}\exp(-82/RT)$, (11)

$CH_3O_2 + CH_2O = CH_3OOH + HCO$, $k_{12} = 10^{-17}$, (12)

$CH_3OOH = CH_3O + OH$, $k_{13} = 4 \cdot 10^{-15}\exp(-179/RT)$, (13)

$CH_3O + CH_4 = CH_3OH + CH_3$, $k_{14} = 10^{-12.2}\exp(-46/RT)$, (14)

$OH + CO = CO_2 + H$, $k_{15} = 1.6 \cdot 10^{-12.5}\exp(-3.3/RT)$, (15)

$H + CH_2O = H_2 + HCO$, $k_{16} = 1.6 \cdot 10^{-10}\exp(-18/RT)$, (16)

$H + CH_4 = H_2 + CH_3$, $k_{17} = 5 \cdot 10^{-9}\exp(-49.7/RT)$, (17)

$HO_2 + HO_2 = H_2O_2 + O_2$, $k_{18} = 4 \cdot 10^{-12}$, (18)

$H_2O_2 = H_2O + \frac{1}{2}O_2$, $k_{19} = 0.1$, (19)

$OH + H_2O_2 = H_2O + HO_2$, $k_{20} = 1.7 \cdot 10^{-11}\exp(-7.5/RT)$, (20)

$HO_2 + CH_3OH = H_2O_2 + CH_2OH$ $k_{21} = 1.6 \cdot 10^{-12}\exp(-60.3/RT)$, (21)

$CH_3 + CH_3 = C_2H_6$, $k_{22} = 3 \cdot 10^{-11}$. (22)

The rate constants of the unimolecular, bimolecular, and termolecular reactions have the units s^{-1}, cm^3 $molecule^{-1}$ s^{-1}, and cm^6 $molecule^{-2}$ s^{-1} respectively, and the activation energy E_a has the units kJ mol^{-1}. According to this scheme, the chain reaction is initiated by reaction (1), and chain propagation takes place mainly by reactions (2)–(9), (11), (12), and (15)–(17). The main reaction responsible for chain branching is the decomposition of the hydroperoxide CH_3OOH (13), and additional chain branching takes place by the decomposition of H_2O_2 to OH radicals in reaction (10). The principal branching agent is formed by reaction (11) in the initial stages, and by reaction (12) in subsequent stages.

The formation of various products by the oxidation of methane has been examined in a number of studies.[9–15] Reactions (2) and (3) are the forward and back reactions of the equilibrium

$$CH_3 + O_2 \rightleftharpoons CH_3O_2. \quad (23)$$

Equilibrium (23) is displaced to the left at high temperatures and to the right at low temperatures: the heat of the reaction is $Q = -\Delta H \simeq E_a = 109$ kJ mol^{-1}. Thus CH_3 radicals play an important role in the oxidation of methane at higher temperatures. The role of most of the radical reactions increases with increase in temperature. Chain termination takes place by reactions (18) and (22), but mainly by the reactions of the radicals on the walls of the reactor.

Recent studies[9–11] have shown that if later data[16] are used, the value obtained for the equilibrium constant of reaction (23) is 200 times smaller. This leads to a decrease in the previously calculated concentrations of CH_3O_2 and to an increase in the concentration of CH_3 radicals. As pointed out in a number of papers on the oxidative condensation of methane,[1,2] CH_3O_2 radicals lead mainly to extensive oxidation, and CH_3 radicals lead to the oxidative condensation of methane, that is to reaction (22).

The probability of formation of methanol is greatest at high pressures and high ratios of the concentration $[CH_4]:[O_2]$. The main reaction leading to the appearance of CH_3OH is reaction (14). At high pressures (5–10 MPa), the relative role of the different stages changes. The yield of methanol increases significantly, and that of formaldehyde decreases. According to a detailed scheme for the oxidation of methanol,[9–11] a significant contribution to the overall mechanism under these conditions is made not only by reaction (14) but also by the reaction:

$CH_3O + H_2O_2 = CH_3OH + HO_2$, $k_{24} = 2.5 \cdot 10^{-13}\exp(-16.7/RT)$. (24)

The CH_3O radical is formed not only by reaction (13) but also by the reactions

$2CH_3O_2 = 2CH_3O + O_2$, $k_{25} = 1.7 \cdot 10^{-13}$, (25)

$CH_3O_2 + CH_3 = 2CH_3O$, $k_{26} = 4.5 \cdot 10^{-11}$. (26)

CH_3OH is consumed in reaction (21) and also in the reactions

$CH_3OH + CH_3O_2 = CH_3OOH + CH_2OH$, $k_{27} = 5 \cdot 10^{-3}\exp(-60/RT)$, (27)

$CH_3OH + HO_2 = CH_2OH + H_2O_2$, $k_{28} = 1.5 \cdot 10^{-12}\exp(-60/RT)$. (28)

Considering the products of extensive oxidation, CO is formed by reaction (9) and the reaction

$HCO + M = CO + H + M$, $k_{29} = 4 \cdot 10^{-10}\exp(-71/RT)$. (29)

The disappearance of CO and the formation of CO_2 take place by reaction (15) and the reactions

$HO_2 + CO = CO_2 + OH$, $k_{30} = 2.2 \cdot 10^{-10}\exp(-96/RT)$, (30)

$CH_3O + CO = CH_3 + CO_2$, $k_{31} = 2.6 \cdot 10^{-11}\exp(-49.4/RT)$, (31)

$CH_3O_2 + CO = CH_3O + CO_2$, $k_{32} = 1.7 \cdot 10^{-10}\exp(-100/RT)$. (32)

In the high-temperature extensive oxidation of methane the most important reactions are those of the H and O atoms and the OH radical, and not the radical CH_3, CH_3O_2, and CH_3O. The reaction of the radicals with the walls of the reactor is less significant at high pressures than at low pressures.

At 5–10 MPa and 673–873 K the theoretical yield of methanol may reach several percent, calculated for the methane passed. For this purpose, mixtures with very high ratios $[CH_4]:[O_2] = 30-100$ are used. At $[CH_4]:[O_2] = 50$, the yield of CH_3OH in a pilot plant is 1% and the selectivity ~50% for 100% conversion of oxygen.

The selectivity can be increased by finding appropriate conditions for the direct recombination of the radicals

$$CH_3 + OH = CH_3OH. \quad (33)$$

The yield of methanol can also be increased by adding hydrogen to the mixture to give the reactions

$$CH_3OO + H_2 = CH_3OOH + H, \quad k_{34} = 3.6 \cdot 10^{-12}\exp(-93.3/RT), \quad (34)$$

$$CH_3O + H_2 = CH_3OH + H, \quad k_{35} = 3.6 \cdot 10^{-12}\exp(-41.8/RT). \quad (35)$$

The economics of the homogeneous oxidation of methane to methanol have been examined. For example, it has been pointed out[5] that for 100% selectivity of the oxidation of CH_4 to CH_3OH the cost of methanol would be 172 dollars per ton, compared with 248 dollars per ton for the usual method of synthesis. In Russia this process may be even more favourable, since the cost of natural gas is relatively low.

Catalytic oxidation. A catalyst should not be expected to have a marked influence on the rate of the oxidation of methane to methanol at a high pressure. Nevertheless, studies of this topic appear from time to time. For example, catalysts based on the oxides of zinc, cadmium, and nickel have been added to a high-pressure reactor (10 MPa). An increase in selectivity from 50% to 80% was reported.[17,18] The results were not subsequently confirmed, however.

In studies[3,19,20] of the oxidation of CH_4 at a high pressure (3.5–12.5 MPa), 623–723 K, and $[CH_4]:[O_2] = 20:25$, a high selectivity with respect to methanol was achieved—75–80% compared with 40–50% reported by other authors. These experiments were carried out in a stainless steel reactor. This raises the question of the possible influence of the material of the reactor on the oxidation of CH_4 to CH_3OH. Treating a stainless steel reactor with alkali (KOH) decreased the yield of CH_3OH, but did not decrease the yield of CH_3OCH_3, also present in the reaction products; Ni and Cu lowered the yield of methanol considerably. A direct study[20] of heterogeneous and homogeneous additives showed that under these conditions the reactor material has relatively little influence on the reaction rate. The best heterogeneous additive was SnO_2, and the best homogeneous additive was 2,3-dimethylbutane. The results[19,20] showing an increase in selectivity in a stainless steel reactor are not consistent with other studies. For example, other authors[21] obtained a selectivity of only 40% under similar conditions.

The initiating action of a solid catalyst on the oxidation of CH_4 at a high pressure has also been studied.[22] A platinum wire at a temperature of 520 K was introduced at a distance of 10 cm before the reaction zone in a stainless steel reactor lined with quartz, at a pressure of 4.1 MPa, a component ratio $[CH_4]:[O_2]:[N_2] = 30:1:4$, and a reaction temperature of 653–779 K. The reaction temperature was lowered by 60 K. The selectivity with respect to CH_3OH was lowered slightly, but adding 4 mol% H_2 at 673 K produced an almost two-fold increase in the selectivity. The maximum selectivity at this temperature, however, was only 34.6%. In the opinion of the authors cited,[22] the key stage corresponds to reactions (34) and (35). Hydrogen on the surface possibly reacts more effectively than H_2 in the gas phase.

A theoretical analysis and experimental data obtained using M^+ and $(M=O)^+$ ion beams showed that the direct reaction of $(M=O)^+$ with CH_4 to give CH_3OH is possible for M = Fe or Os:

$$FeO^+ + CH_4 \longrightarrow Fe^+ + CH_3OH. \quad (36)$$

The Fe^+ ions obtained can be re-oxidised using N_2O.[23]

Fe=O groups may also be present on the surface of solid catalysts, and their reaction with CH_4 may lead to the direct formation of methanol [reaction (36)] or to the additional generation of CH_3 radicals

$$MO + RH \longrightarrow \dot{M}OH + \dot{R}, \quad (37)$$

which at an increased pressure lead finally to an increase in the yield of methanol.

On the basis of this idea, the firm Sun Oil developed a catalyst for oxidising CH_4 to methanol, consisting of sodium sodalite subjected to partial ion exchange with Fe^{II}.[24] In contrast to the homogeneous process, in this case a significant selectivity in the conversion of CH_4 into CH_3OH was obtained at $[CH_4]:[O_2]$ ratios which were not very high. At 700 K, 5.3 MPa, and $[CH_4]:[O_2] = 3:1$ the selectivity increased from 44% for the homogeneous process to 77% in the presence of Fe–Na-sodalite; the conversion of CH_4 increased from 4.8% to 6.5%. Silicoferrate gave a selectivity of 66% for 5.5% conversion at 688 K.[25] The most promising catalyst is sodium sodalite containing about 13% Fe, the acidity of which had been completely removed by previous reactioin with NaN_3. The authors of a patent[25] state that non-framework cationic iron hydroxo-centres are necessary in the catalyst. Dinuclear $Fe^{II}OFe^{II}$ centres are preferable to $Fe^{III}OFe^{III}$ centres, that is over-oxidation of iron poisons the catalyst.

Data have also been published on the use of acidic catalysts, in particular superacids, for the oxidation of methane to methanol. A selectivity with respect to CH_3OH of 77% (and even 100% with respect to $CH_3OH + CH_2O$) for 3.5% conversion was obtained on the superacid catalyst $Cr^{3+} - Zr^{4+}SO_4/SiO_2$ at a low temperature (523 K). The author cited[26] considers that the reaction involves the intermediate formation of the CH_5^+ ion. The selective formation of CH_3OH from CH_4 on zeolites at increased pressures has been reported: on H-ZSM-5 at 693 K [29] and on Cu-ZSM-5 at 613 K.[28] Oxidation using N_2O gives a higher selectivity than oxidation using O_2. Fe-ZSM-5 zeolite under the same conditions gives only CO and CO_2.[28]

The problem of developing oxidation catalysts for methanol has not been solved. Many studies are not being continued, and published results are not confirmed by subsequent studies. The most promising results have been obtained using Fe-containing catalysts at high pressures and relatively low temperatures. The most probable explanation is additional generation of CH_3 radicals and their subsequent reactions to give CH_3OH.

III. The oxidation of methane to formaldehyde

Homogeneous oxidation. Unlike methanol, formaldehyde is formed with a high probability at low pressures and low concentration ratios $[CH_4]:[O_2]$. It is formed by the decomposition of the hydroperoxide CH_3OOH in reaction (13) and then from the CH_3O radical in reaction (4). The hydroperoxide precursor of formaldehyde is formed mainly by reaction (11), that is from the CH_3O_2 radical.

Calculations[8] carried out for 738 K and initial concentrations $[CH_4] = 3.2 \times 10^{18}$ molecule cm^{-3} and $[O_2] = 10^{18}$ molecule cm^{-3} gave the following maximum values of the concentrations of intermediate products (particle cm^{-3}): $[HO_2] = 4.9 \times 10^{13}$, $[CH_3O_2] = 3.9 \times 10^{12}$, $[CH_3OOH] = 2 \times 10^{14}$, $[CH_3] = 4.7 \times 10^{12}$, $[CH_3OH] = 4 \times 10^{15}$, $[CH_2O] = 2 \times 10^{16}$, $[H_2O_2] = 8 \times 10^{15}$. According to these calculations, which on the whole agree with experimental data, the yield of the desired product of the partial oxidation, that is formaldehyde, is about 1% calculated for the methane reacting, and the yield of methanol is lower by a factor of about ten. The principal oxidation products are CO and CO_2. ~2% ethane is formed. Later calculations[10,11] altered these figures slightly, giving a higher yield of CH_2O and a lower yield of C_2H_6.

Formaldehyde is also formed by the reaction

$$2CH_3O_2 = CH_3OH + CH_2O + O_2, \qquad k_{38} = 7.4 \cdot 10^{-14}, \qquad (38)$$

and is consumed mainly in reactions (7) and (8).

According to a published scheme,[13] in a flow reactor at 773–873 K, the recombination of CH_3 radicals [reaction (22)] with the formation of C_2H_6 predominates at low volume rates, and the reaction

$$CH_3 + O_2 = CH_2O + OH, \qquad (39)$$

predominates at high volume rates.

The decomposition of CH_2O under homogeneous flow conditions has been studied.[14,21] At 873 K for 20% conversion of methane, about 60% CH_2O decomposes in the empty reactor. According to experimental data,[14] the maximum yield of CH_2O (3.46%) was obtained for a mixture with $[CH_4]:[air] = 1:5$ at 923 K and 5 MPa (6.7% conversion, selectivity 51.6%). Under these conditions, filling the reactor with SiO_2 and other oxides lowers the yield of formaldehyde.

Catalysts of the oxidation of methane to formaldehyde. Dowden and co-workers[29] were among the first to study the oxidative conversion of methane into formaldehyde. According to their theoretical ideas, a catalyst for the production of formaldehyde should have the functions of dehydrogenation and the introduction of an oxygen atom. Oxides of Fe^{3+} and Cr^{3+} are best for the first function, and oxides of V^{5+}, Mo^{6+}, Ti^{4+}, and Zn^{2+} are best for the second. Of the catalysts studied,[29] the oxides of Cr^{3+} and Mn^{3+} had the highest activity; Fe^{3+} phosphate had medium activity, but the highest selectivity.

A large number of oxide catalysts were subsequently studied. An appreciable activity in the formation of formaldehyde was shown by pure SiO_2 (finely divided quartz, or silica gel).[30–32] The low selectivity of Al_2O_3[30,31] was attributed to the high rate of the successive conversion of formaldehyde to oxides of carbon both by oxidation and by the decomposition of CH_2O to $CO + H_2$. The yield of CH_2O on silica gel at 879 K was 2% (selectivity 34%, 6.1% conversion). Modifying the silca gel with B_2O_3 increased the yield to 3.5%. On an aluminosilicate modified by H_3PO_4 the yield of CH_2O was 2.9% (selectivity 48%, 6% conversion), and on an aluminosilicate modified by H_3BO_3 the yield was 2.5% (selectivity 3.5%, 7% conversion).

HCl increases both the total conversion of methane on SiO_2 and the yield of formaldehyde. According to Mel'tser and co-workers,[33] HCl poisons the centres responsible for the extensive oxidation of CH_2O to CO_2. Covering the SiO_2 with hydrogen peroxide also increases the yield of CH_2O.[34]

A large number of oxides, phosphates, and silicates have been studied as catalysts of the oxidation of methane to formaldehyde.[35–37] In the opinion of the authors cited, a high selectivity and a high yield can be obtained on catalysts with a high acidity. High yields of CH_2O were obtained, for example, at 873 K on tin phosphate $Sn_2P_2O_7$ (9.0%, selectivity 96%), on SiP_2O_7 (5.1%, selectivity 82.8%), and on an aluminosilicate treated with H_3PO_4. It was also shown that the best of the transition metal phosphates are those most difficult to reduce. It is considered[35] that on the acidic OH groups the following reaction takes place:

$$CH_4 + -OH_s \longrightarrow -OCH_3 + H_2O \xrightarrow{O_2} \begin{matrix} -O \\ \diagdown \\ \quad CH_2 \\ \diagup \\ -O \end{matrix} \longrightarrow$$

$$\longrightarrow CH_2O + O_s(-OH_s).$$

Under recirculating conditions with freezing of the products, the yield of formaldehyde reached 14–16%, and even 18% in some experiments.

Aluminosilicates containing 10–11% Al_2O_3 and modified by added oxides of iron, zirconium, vanadium, cerium, bismuth, and chromium have also been studied;[38–40] the yield of CH_2O was ~2%. The maximum yield (2.6%) was obtained on an aluminosilicate containing added 2% cerium phosphate and 0.05% P_2O_5 at 1023 K. Adding 0.2–0.5% dimethyl ether $(CH_3)_2O$ to the content zone made it possible to lower the reaction temperature by 100 K and to raise the yield of CH_2O to 5–5.6%.[40] It is possible, however, that a significant contribution to the yield of formaldehyde is made by the decomposition of dimethyl ether itself. The use of circulation of the reaction mixture with the removal of both CO and CO_2 from the mixture made it possible to increase the yield of CH_2O to 12.5% and the selectivity to 65% on one of the most active catalysts, $Mo-P-Al-SiO_2$.[39]

Almost all workers who have studied the oxidation of methane to formaldehyde have used SiO_2 or aluminosilicates as carriers. MgO and Al_2O_3 were more active than SiO_2, but gave only CO and CO_2.

Various oxides deposited on SiO_2 to concentrations of 9.2% have been studied on catalysts.[42] The highest yields of CH_2O at 923 K and $[CH_4]:[O_2] = 1$ were obtained on Ga_2O_3 (3.6%), Bi_2O_3, Al_2O_3, and ZrO_2, and the highest selectivity on P_2O_5, WO_3, B_2O_3 (>60%), Sb_2O_3, Nb_2O_5, Al_2O_3, and MgO (>30%). Here also, the acidic oxides are more active.

The largest number of studies has been carried out for the MoO_3/SiO_2 system.[42–50] On this catalyst, CH_4 is oxidised to CH_2O at 823–923 K. 85% selectivity was achieved for ~3% conversion, and 30% selectivity for 7% conversion. Formaldehyde is not formed on pure MoO_3 without SiO_2. The selectivity was increased by adding oxides of chromium[44] and copper,[46] but adding iron, chromium, cobalt, and sodium[47] lowered the selectivity of CH_2O formation compared with Mo/SiO_2, although some of them increased the degree of conversion. The catalyst $CoMoO/SiO_2$ at 873 K gave a selectivity of 50.3% for the oxidation of CH_4 to CH_3OH, and of 16.9% for the oxidation to CH_2O.[44] A system consisting of the deposited complex $MoCl_5/R_4Sn/SiO_2$ has also been studied[50] as starting material for the synthesis of a catalyst. The process was based on the ease of the replacement of the M=O group in the ligand by the carbene complex $M=CH_2$, which it is assumed could be converted directly into CH_2O. A selectivity of 80% was obtained for a low degree of conversion.[50]

A significant increase in the yield of oxygen-containing products on MoO_3/SiO_2 was achieved using N_2O instead of O_2 as oxidising

agent.[46,51–58] At 823 K the degree of conversion of CH_4 on a 1.7% MoO_3/SiO_2 catalyst increased from 0.5% to 6.0%, and the selectivity reached 55% for CH_2O and 38% for CH_3OH.[54] The highest yield of CH_2O and CH_3OH was obtained by adding water vapour to the original mixture; at P_{H_2O} = 20 kPa the total selectivity with respect to CH_3OH + CH_2O reaches 99% for 26% conversion. Other authors[56,57] also reported a high selectivity of the oxidation of CH_4 to CH_2O using N_2O, but with a much lower degree of conversion. The activation energy of this reaction is ~170 kJ mol^{-1}.[58]

At a concentration of 1–5% Mo in SiO_2, molybdosilicic acid is formed on the surface and takes part in the oxidation of methane to formaldehyde.[56] Appreciable selectivity in the oxidation of CH_4 by N_2O (up to 80% for 2% conversion) was observed[59–65] on heteropolyacids $HPMo_{12}O_{40}$ and their salts, deposited on SiO_2. A correlation between the acidity of the heteropolyacid and the yield of CH_2O has been reported.[66] A very high yield of CH_2 (12–16%) was obtained.[66] Breakdown of the Keggin structure at a temperature above 873 K leads to the loss of activity and selectivity. The activity of $H_3PMo_{12}O_{40}/SiO_2$ increased in the presence of chlorine-containing additives such as CH_2Cl_2 or CCl_4; at 799 K the degree of conversion was 12%, and the selectivity 32%.[65]

A mixed catalyst containing oxides of molybdenum, iron, bismuth, nickel, and magnesium deposited on SiO_2 showed a selectivity of 86.5% in the oxidation of CH_4 to CH_2O for 8.9% conversion at 923 K.[67]

V_2O_5/SiO_2 gave results similar to those for MoO_3/SiO_2.[49] In the oxidation of CH_4 to formaldehyde using N_2O, a 2% V_2O_5/SiO_2 catalyst gave appreciable activity at temperatures 80–100 K lower than those for MoO_3/SiO_2.[53,57] The activation energy was 88 kJ mol^{-1}. The possibility of increasing the selectivity on membrane V_2O_5/SiO_2 catalysts has been reported.[68] For 1% conversion, the selectivity with respect to CH_2O increased from 5% to 20%.

Unusual effects in both of the reactions CH_4 + O_2 and CH_4 + N_2O were detected in a study of the influence of mechanochemical activation on the catalytic properties of the systems MoO_x/SiO_2, VO_x/SiO_2, and WO_x/SiO_2.[69–72] After mechanical mixtures of Mo + SiO_2, MoO_3 + SiO_2, V + SiO_2, and V_2O_5 + SiO_2 has been ground in a ball mill or subjected to high pressure with shear in a Bridgman cell, practically no extensive oxidation was observed. The selectivity with respect to formaldehyde increased to 100% for 3% conversion at 873 K. At the same time, MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts impregnated before grinding showed no change in selectivity even after grinding; a change was observed only after the mechanical grinding of a mixture of the two oxides. Electron microscopy and electron diffraction showed that under the conditions of the mechanical treatment of a mixture of the two oxides, encapsulation takes place, that is the particles of the active phases MoO_3 or V_2O_5 are covered with silica gel. This encapsulation is confirmed by a study of the Mössbauer spectra of mixtures of Fe and SiO_2 powders subjected to mechanical grinding. Encapsulated iron, covered with silica gel, remains in the metallic state under the conditions of CH_4 oxidation, whereas ordinary iron powder is oxidised to Fe_2O_3 under these conditions.

The encapsulation of the oxides of molybdenum or vanadium in SiO_2 capsules alters the fractions of the active centres involved in the partial and extensive oxidation of methane. The centres of CO_2 formation are blocked, but the CH_2O formation centres remain. The enveloping of M_xO_y by silica gel also apparently hinders the supply of electrons to the molecule being oxidised. The oxidation of CH_4 to CH_2O requires only half the number of electrons required to oxidise CH_4 to CO_2.

Active phases have also been deposited on SnO_2. On Bi_2O_3/SnO_2, methane is oxidised by oxygen with a selectivity with respect to CH_2O of ~80%. In the reaction of CH_4 with N_2O on the same catalyst, the selectivity with respect to CH_2O reaches 98.2% for 2.6% conversion.[73] Formaldehyde is also formed on an MoO_3 monolayer deposited on SnO_2.[74]

Fe-containing catalysts (like Mo-containing catalysts) have often been used to convert methane into formaldehyde.

Fe–Nb–B–O is a selective catalyst.[73] At a fairly high temperature (1023–1073 K), 70–80% selectivity was obtained for 2.7–14.3% conversion and a yield of CH_2O of 2–3.8%. The activation energy of the process is 250 kJ mol^{-1}. X-Ray photoelectron spectroscopy (XPS) detected the phases $FeNbO_4$, $FeNb_{11}O_{29}$, Fe–Nb–B–O (oxidation state of iron > 3+), and B_2O_3 on the surface. Oxidation using N_2O on the same catalyst gave the same selectivity and the same activation energy, but the activity was halved. A published study[76] of the activity of various oxides in the oxidation of methane to formaldehyde to some extent represents a continuation of other work.[75]

A high selectivity has been obtained on $MoO_3.Fe_2O_3$.[77] The same authors reported[78] a very high yield of CH_2O (22.5%) and a selectivity of 83.6% on this catalyst, but no subsequent work has been published. On $Fe_3(PO_4)_2$ promoted using $La_3(PO_4)_2$, a selectivity with respect to CH_2O or 30% was observed for 3.7% conversion at 953 K.[79] Water vapour lowered the selectivity of the transformation of CH_4 into CH_2O, as a result of the formation of HCOOH. At the same time, on pure Fe_2O_3, only extensive oxidation was observed. Adding 1% CuO and 1% Fe_2O_3 to ZnO gave the catalyst $Cu_{0.01}Fe_{0.01}Zn_{0.98}O$, which showed a selectivity of 43% for 0.02% conversion at 823 K, and a selectivity of 10% for 2.5% conversion at 1023 K.[80] XPS indicated the presence of Cu^+ and Fe^{3+} on the surface of this catalyst. Its activity and selectivity were much higher than on pure ZnO. The authors cited[80] attribute its behaviour in the oxidation of CH_4 to CH_2O to the necessity of a combination of redox properties (Fe^{2+}/Fe^{3+} and Cu^+/Cu^{2+}) and Lewis acidity (Fe^{3+}).

The results of a number of studies of iron-containing catalysts have been analysed.[14] It was concluded that the highest yields of CH_2O on these catalysts are no higher than those obtained under the same conditions in an empty reactor.

Data have also been published on metallic catalysts of the oxidation of methane to formaldehyde. According to Wang and co-workers,[81] palladium promoted with CH_2Cl_2 can bring about the selective oxidation of methane to formaldehyde. It has been shown,[14] however, that at 723–873 K only extensive oxidation is observed on Pd modified by chlorine. An increase in the selectivity of the action of anatase was observed after it was modified with CH_2Cl_2; a yield of CH_2O of 2.8% was obtained at 848 K.

The selective oxidation of methane by another oxidising agent (CO_2) was carried out on brass gauze with a specific surface of 24.3 m^2 g^{-1} which had been oxidised and reduced several times. When CH_4 + CO_2 pulses are introduced into a stream of nitrogen at 653–733 K, the only oxidation product is formaldehyde. If however methane is added to CO_2 as carrier gas, only methanol is obtained, in yields of 1.23–4.36% at 873 K.[82]

It is difficult to identify general regularities in the selection of catalysts of the oxidation of methanol to formaldehyde. Nevertheless, in the work of most authors, three groups of catalyst are clearly distinguished: 1, Mo- or V-containing deposited oxide catalysts; 2, Fe-containing oxide catalysts; 3, acidic catasyts. Despite the relationship between selectivity and acidity noted by

various workers, oxide systems deposited on SiO_2 were more active and selective than oxides deposited on Al_2O_3 or aluminosilicates.

In almost all cases the oxidation of methane to formaldehyde was carried out at temperatures 100–200 K lower than the oxidation condensation of methane, that is at 723–973 K. As in the oxidative condensation of methane, various limiting yields apparently exist; their values (3–4%) are appreciably lower than those in the oxidative condensation of methane. The individual cases where higher yields were obtained[35,40,66,77] require further study.

Mechanism of the catalytic oxidation of methane to formaldehyde. Two mechanisms of the oxidation of methane to formaldehyde are distinguished: 1, a heterogeneous–homogeneous mechanism, in which the selectivity is controlled mainly by gaseous reactions; 2, a heterogeneous mechanism, in which the selectivity is controlled by processes on the surface. The existence of limiting yields tends to support the heterogeneous–homogeneous mechanism. On the other hand, data on the chemical features of the selection of catalysts tend to support the heterogeneous mechanism. The mechanism of the oxidation of methane to formaldehyde is examined in a large number of publications.

The detection of free radicals under the conditions of the oxidation of methane to formaldehyde provides the principal evidence for the heterogeneous–homogeneous mechanism. One of the first studies proving the formation of CH_3O_2 radicals in this reaction involved freezing out the radicals in a CO_2 matrix.[30] According to the scheme given by the authors cited, however, an increase in the yield of free radicals facilitates non-selective extensive oxidation and leads to a decrease in the yield of CH_2O.

Adding C_2H_6 to a $CH_4 + O_2$ mixture increased the selectivity of the oxidation of CH_4 at 833–913 K to CH_2O on SiO_2 and decreased the yield of CO. This was attributed[83] to an increase in the formation of methyl radicals from C_2H_6. Under the given conditions, CH_3 radicals are converted into CH_3O_2 and CH_3O. A correlation has been noted[33] between the yield of CH_3O_2 radicals and the yield of CH_2O under the conditions of the oxidation of methane on SiO_2. With increase in temperature, the yield of CH_2O and the concentration of RO_2 pass through a maximum at 903 K. HCl increases the total degree of conversion, but decreases the yield of radicals, although the yield of CH_2O increases. According to the authors cited,[33] HCl poisons the centres for the extensive oxidation of CH_2O to CO_2. Depositing H_2O_2 on SiO_2 also increases the yield of CH_2O and free radicals.[34]

According to Otsuka and co-workers,[75] on an Fe–Nb–NB–O catalyst, methyl radicals are formed in the primary reaction of methane with the surface oxygen O_s, and formaldehyde is formed by the secondary reaction of CH_3 with O_s;

$$\begin{aligned} &CH_4 + O_s \longrightarrow CH_3 + OH_s, \\ &CH_3 + O_s \longrightarrow CH_2O + \tfrac{1}{2} H_2, \\ &2OH_s \longrightarrow O_s + H_2O. \end{aligned} \qquad (40)$$

It is considered[84] that the selectivity of action of catalysts of the oxidative condensation of methane can be displaced from C_2-hydrocarbons to CH_2O by changing the conditions of the process. Increase in the flow rate of a mixture with $[CH_4]:[O_2]:[Ar] = 6:1:6$ over an MgO catalyst from 1000 h^{-1} to 48 000 h^{-1} increased sharply the selectivity of the oxidation of CH_4 to CH_2O. For 9% conversion of O_2, a selectivity with respect to CH_2O of 65% was observed, but at 11% conversion of O_2 the selectivity decreased to almost zero, with a simultaneous increase in the selectivity of the transformation to CO to 65% and the appearance of ethane. With increase in the conversion the selectivity with respect to C_2H_4 and CO_2 increases. Following the scheme given by Gesser and co-workers,[19] Hargreaves and co-workers[84] examined the competition between two main reactions: the recombination of CH_3 radicals [reaction (22)] and their oxidation to CH_2O [reaction (39)]. The first reaction is kinetically of second order with respect to CH_3, and its probability is higher at low flow rates, whereas the second is of first order with respect to CH_3, and its probability is greater at high flow rates. At low pressures in the gas phase, CH_3 radicals are converted into CH_3OH.

Thus according to Hargreaves and co-workers,[84] the same catasts increase the rates of both the oxidative condensation of methane and the oxidation of CH_4 to formaldehyde and methanol. The part played by the catalyst involves the generation of CH_3 radicals, and the selectivity is determined by secondary gas-phase reactions.

The same conclusion, namely that CH_2O can be obtained at high volume rates of a $CH_4 + O_2$ mixture, was reached by other workers.[85] Under these conditions, a selectivity of 28% was obtained for the oxidation of methanol to CH_2O on silica gel at 873 K, for 12% conversion. It has been shown[76] that ethane and formaldehyde have as precursor the same intermediate product, apparently the CH_3 radical, and that the direction of the reaction is determined by the external parameters, mainly temperature and pressure.

The nature of the primary centres O_s in the catalyst, activating methane, is also important. Isotopic exchange experiments[75] showed that the oxygen of the catalyst O_s is firmly bound and does not exchange with $^{18}O_2$ under the catalysis conditions. It is lattice oxygen, and not oxygen from the gas phase, that is mainly introduced into the reaction products CH_2O, CO, and CO_2.

Additional data on the nature of the centres O_s are obtained by studying the catalysts by ESR. MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts show ready reduction of the $\equiv Mo^{VI}=O$ and $\equiv V^{V}=O$ groups to the radical centres $Mo^{VI}O^-$ and $V^{V}O^-$ respectively and then to $Mo^{V}O^-$ (or $Mo^{V}OH^-$) or $V^{IV}O^-$ (or $V^{IV}OH^-$). The centres O^- detected by ESR are readily formed by the reaction of these catalysts with N_2O

$$Mo^{V} + N_2O \longrightarrow Mo^{VI}O^- + N_2. \qquad (41)$$

A mechanism has been proposed[51,52] for the subsequent reaction of CH_4 with these centres:

$$\begin{aligned} &Mo^{VI}O^- + CH_4 \longrightarrow Mo^{VI}OH^- + CH_3, \\ &Mo^{VI}O^{2-} + CH_3 \longrightarrow Mo^{V}OCH_3. \end{aligned} \qquad (42)$$

Decomposition of the surface methoxyl groups gives formaldehyde

$$Mo^{V}OCH_3^- + Mo^{VI}O^{2-} \longrightarrow Mo^{V}OH^- + CH_2O, \qquad (43)$$

and their reaction with water gives methanol

$$Mo^{V}OCH_3^- + H_2O \longrightarrow Mo^{V}OH^- + CH_3OH. \qquad (44)$$

Non-selective oxidation takes place by the reaction

$$8Mo^{VI} + 4O^{2-} + CH_4 \longrightarrow 8Mo^{V} + 2H_2O + CO_2, \qquad (45)$$

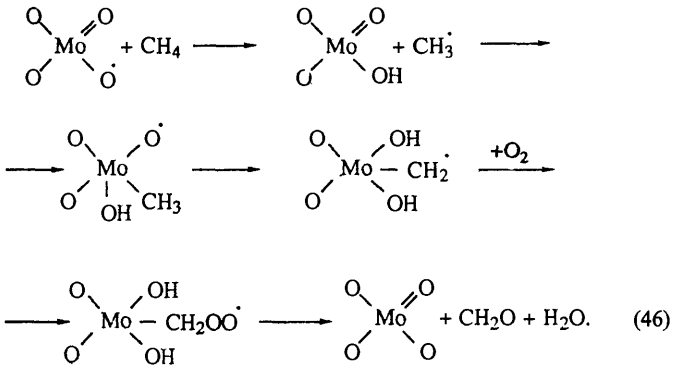
that is one-electron transfer from the centres O^- gives CH_2O, and two-electron transfer from the centres O^{2-} gives CO_2. According to this scheme there are no homogeneous stages, apart from the generation of free radicals and their reaction on the surface.

Methoxyl groups have been detected from their infrared spectra on Mo/SiO_2 and V/SiO_2 catalysts.[51,52,86,87] It has also been pointed out that on other catalysts, OCH_3 groups may be intermediate

products in the extensive oxidation of methane.[88] In contrast to the case of methane, in the oxidation of CH_3OH the activity and selectivity were lower when N_2O was used as oxidising agent than when O_2 was used.[89] O^- evidently does not take part in the oxidation of metanol.

V_2O_5/SiO_2 is one of the few catalysts in which the formation and disappearance of stabilised O^- on reduction and oxidation have been conclusively established by ESR.[90] O^- is formed by the reaction of N_2O with $V^{4+}O/SiO_2$. The reaction of O_2 with this catalyst gives O^- and O_2^-.[91]

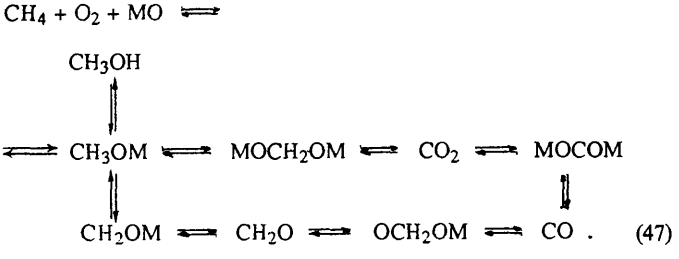
The mechanochemical grinding of $MoO_3 + SiO_2$ gives high concentrations of Mo^{5+} radical centres. The following mechanism was proposed for the oxidation of CH_4 on this catalyst:[72]



(46)

Pure SiO_2 without molybdenum or vanadium shows a fairly high selectivity with respect to CH_2O (up to 38%), but a low activity at 873 K.[92] Heating SiO_2 to 1273 K increases both the yield of CH_2O and the selectivity (to 53%). The high-temperature dehydroxylation of SiO_2 apparently leads to the formation of radical and biradical centres on the surface.

Purely heterogeneous schemes for the oxidation of methane to formaldehyde have also been published. For example, the oxidation of CH_4 on deposited MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts has been modelled[50] using the rate constants, selected from the literature, of the surface stages of the parallel–consecutive scheme (only the principal steps are given):



(47)

On the whole, the scheme provides a satisfactory description of the experimental data. Here, the explanation for the limiting yields of formaldehyde is that it is an intermediate product in the oxidation to CO. The oxidation of CH_4 to CH_3OH takes place in parallel, and CO_2 is formed by two paths: directly from methane via surface transformations, and with the intermediate formation of CO in the gas phase.

Nevertheless, there are more data in support of the heterogeneous–homogeneous mechanism. The following conclusions have been established.

1. The active centre are stabilised radical centres on the surface of the oxides, probably O^-.

2. The reaction of methane with them gives CH_3 radicals, which escape into the gas phase.

3. At a temperature below 879–929 K they react with oxygen, forming CH_3O_2, CH_3O, and CH_3OOH, which finally give formaldehyde.

4. At high temperatures, long contact times, and high pressures, transformations of the radicals give other products: CO, CO_2, C_2H_6, C_2H_4, decreasing the selectivity with respect to formaldehyde.

The mechanism of the formation of CH_2O on acidic catalysts is less clear. In this case also, possibly, latent homolytic stages should be sought.

Experimental modelling of the oxidation of methane to formaldehyde. Controlled conditions can be used to establish the part played by various parameters in catalysis. Such conditions can be created photochemically and mechanochemically.

The influence of γ-irradiation on a V/SiO_2 catalyst in a $CH_4 + O_2$ mixture has been studied.[93] Subsequent thermal desorption led to the formation of up to 15% formaldehyde. In the opinion of the authors cited,[93] the most probable source of CH_2O is surface methoxyl groups formed by the reaction

$$CH_3 + O^- \longrightarrow CH_3O^-,$$

although methoxyl groups were not detected on the surface. The formation of CH_2O was also observed on ultraviolet irradiation of 5% MoO_3/SiO_2 in a mixture with $[CH_4]:[O_2] = 3:1$ at 473 K.[94] CO and CO_2 are formed at a higher temperature.

When TiO_2 [95] and MoO_3 [96] are irradiated in $CH_4 + O_2$ mixtures, small quantities of methanol are formed.

The molybdenyl bond in MoO_3 can be activated both photochemically and by thermal excitation[97–99] by the reaction

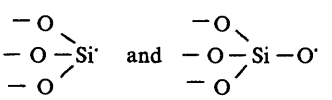
$$Mo^{VI}O^{2-} \rightleftharpoons [Mo^{V}O^{-}]^*.$$

The $Mo^{V}O^-$ pairs were not detected by ESR, because of their short lifetime, but were detected by photoluminescence. The reaction of the O^- in this pair with CH_4 can give CH_3 radicals.[100]

The phototransformations of $CH_4 + O_2$ on various oxides have been studied.[101] Two competing processes were observed: the formation of hydrocarbons and oxygen-containing products. Excitation by light in the band gap leads mainly to the formation of oxygen-containing products, and excitation of the impurity levels to the formation of hydrocarbons. The dissociative photo-adsorption of CH_4 leads to the formation of excited surface OH groups. The surface is gradually poisoned, but can be regenerated by high-temperature treatment in oxygen.

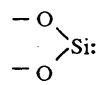
The study of the oxidation of methane by ESR *in situ* is made difficult by the very low concentration of active centres. In addition, they are situated on the surface of the oxide catalyst. This makes it impossible to study them in the presence of such gases as O_2 or H_2O. High concentrations of free-radical centres can be obtained by mechanical treatment, for example by grinding the oxides in a ball mill.

The mechanical grinding of SiO_2 gives very high concentrations of defects:[102–107] $10^{12}-10^{13}$ cm^{-2}, that is up to 1% of the number of surface atoms. Free-radical defects are formed by the homolytic splitting of siloxane bonds

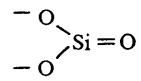


Grinding in oxygen also leads to the formation of $\equiv Si-O-O^{\cdot}$ and

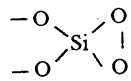
$\equiv Si-O-O-O^{\cdot}$ centres. The silicon atom is joined to three lattice oxygen atoms. A second type of defect is diamagnetic; the Si atom is joined to two O atoms of the lattice. In this set, silicone groups



silanone groups



and siladioxirane groups



have been identified. The reactions and transformations of these groups in contact with methane and oxygen have been studied.

The radical centres $\equiv Si-O^{\cdot}$ react with methane to give CH_3 radicals

$$\equiv Si-O^{\cdot} + CH_4 \longrightarrow \equiv Si-OH + CH_3. \quad (48)$$

The reaction takes place rapidly even at 78 K without significant activation energy. The CH_3 radicals are subsequently captured by diamagnetic centres; the structure of the new formations has been determined by ESR.

$$= Si: + CH_3^{\cdot} \longrightarrow = \dot{S}i-CH_3,$$

$$=Si= O + CH_3^{\cdot} \longrightarrow =Si\begin{matrix}O^{\cdot}\\ \diagdown\\ CH_3\end{matrix} \longrightarrow =Si\begin{matrix}OH\\ \diagdown\\ CH_2^{\cdot}\end{matrix},$$

$$=Si\begin{matrix}O\\ \diagup\\ \diagdown\\ O\end{matrix} + CH_3^{\cdot} \longrightarrow =Si\begin{matrix}O^{\cdot}\\ \diagdown\\ OCH_3\end{matrix} \longrightarrow =Si\begin{matrix}OH\\ \diagdown\\ OCH_2^{\cdot}\end{matrix} \quad (49)$$

Despite the high concentration of radical centres $=Si-O^{\cdot}$, practically no reaction between them and CH_3 is observed. The reaction of oxygen with the centres formed by reaction (49) gives formaldehyde

$$\equiv Si-CH_2^{\cdot} + O_2 \longrightarrow \equiv Si-CH_2OO^{\cdot} \longrightarrow \equiv Si-O^{\cdot} + CH_2O,$$

$$\equiv Si-OCH_2^{\cdot} + O_2 \longrightarrow \equiv Si-OCH_2OO^{\cdot} \longrightarrow \equiv Si-O-O^{\cdot} + CH_2O. \quad (50)$$

To complete the catalytic cycle, it is necessary to add to reactions (48)–(50) another stage, namely the dehydration of the $\equiv Si-OH$ group. This is apparently the most difficult stage.

Another possible route for the formation of CH_2O is by the thermal decomposition of the methoxyl groups, which on SiO_2 takes place at 973 K [108,109]

$$\equiv Si-O-CH_3 \longrightarrow \equiv Si-H + CH_2O. \quad (51)$$

The formation of methoxyl groups was noted in the reaction of SiO_2 with methane.[108]

Thus the mechanochemical modelling of the oxidation of CH_4 on SiO_2 shows a similarity in the homogeneous and heterogeneous radical processes. The reaction of the molecules with the radical centres of the surface takes place readily; the regeneration of the active centres is difficult.

Formaldehyde can also be obtained by the reaction of free radicals, for example CH_3O_2, with the surface. The following reaction is probable on mechanochemically treated (MoO_3 + SiO_2)-catalysts

$$CH_3O_2 + Mo^{V}OH^{-} \longrightarrow CH_2O + H_2O + Mo^{V}O^{-} (\rightleftharpoons Mo^{VI}O^{2-}).$$

This reaction explains the experimentally observed formation of CH_2O at 823–879 K,[72] when the rate of the initial formation of CH_3 radicals is fairly high, but equilibrium (23) is displaced towards CH_3O_2.

IV. The oxidation of methane to synthesis gas

The oxidation of methane by oxygen. The oxidation of methane to synthesis gas is a weakly exothermic reaction

$$CH_4 + {}^1/_2O_2 = CO + 2H_2, \ \Delta H = -44 \text{ kJ mol}^{-1}. \quad (52)$$

Reaction (52) is thermodynamically allowed ($\Delta G < 0$) over a wide temperature range, and in principle can take place with a selectivity of 100%. This process is carried out non-catalytically, for example in the synthesis gas generators of Shell and Texaco in the range 1400–1700 K.[110,11]

On catalysts, reaction (52) is usually complicated by the extensive oxidation of methane

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad (53)$$

and by the endothermic steam conversion of methane and reaction of CH_4 with CO_2

$$CH_4 + H_2O = CO + 3H_2, \ \Delta H = 207 \text{ kJ mol}^{-1}, \quad (54)$$

$$CH_4 + CO_2 = 2CO + 2H_2, \ \Delta H = 246 \text{ kJ mol}^{-1}. \quad (55)$$

Reaction (54) is displaced towards synthesis gas above 580 K, and reaction (55) above 910 K. Conversion of water gas also takes place

$$CO + H_2O = CO_2 + H_2, \ \Delta H = -35 \text{ kJ mol}^{-1}. \quad (56)$$

The value of ΔG for reaction (56) at 1100 K is negative (−25 kJ mol^{-1} at 300 K); above 1100 K the equilibrium is displaced to the left.

Deposited nickel catalysts of the steam conversion of methane are most frequently used. In a flow reactor with a nickel catalyst deposited on a refractory material, different reactions were observed in different layers of the catalyst at 1002–1173 K.[112] The exothermic extensive reaction (53) took place in the first layer, and the endothermic reactions (54) and (55) in subsequent layers. This gave a CH_4 + CO + CO_2 + H_2 mixture, corresponding to thermodynamic predictions. Different reactions taking place in different layers have been observed in other studies.[110,113,114] Stoichiometric synthesis gas was obtained in CH_4 + O_2 mixtures with an oxygen deficit on nickel deposited on mullite.[113]

The activity and selectivity of nickel catalysts deposited on various carriers: Al_2O_3, $SiO_2-Al_2O_3$, $ZrO_2-Al_2O_3$, and HY zeolite, were studied.[110] 5% Ni on a carrier in all cases gave a selectivity with respect to CO_2 + H_2 > 90% and >92.5% conversion of CH_4; for Ni/Al_2O_3 and Ni/SiO_2-ZrO_2, a selectivity and conversion of about 96% were obtained. For 1% Ni, however, appreciable activity and selectivity were obtained only on the non-acidic carriers Al_2O_3 and SiO_2-ZrO_2. It was shown[110] that nickel cations on acidic carriers are not completely reduced to metal. Non-reduced nickel gives

practically no H_2 in the reaction products. All the catalysts were active and selective at high Ni concentrations (> 5%).

The oxidation of methane to synthesis gas on 25% Ni/Al_2O_3 at 723–1173 K was studied.[114] Above 973 K the selectivity with respect to CO + H_2 reaches 95% with complete conversion of CH_4. XPS and electron diffraction studies of the catalyst showed that in the first layer of the catalyst in the reaction mixture the spinel $NiAl_2O_4$, moderately active in extensive oxidation, is formed. In the second layer, a mixture of phases NiO + Al_2O_3, which is an active catalyst of extensive oxidation, is formed. In the third layer, reactions (54)–(56) take place as far as complete thermodynamic equilibrium. Thus it was confirmed that the oxidation of CH_4 to synthesis gas takes place by the sequence of reactions (53)–(56). This combination of reactions helps to overcome the highly endothermic character of the steam conversion of methane, that is reaction (54).

A combination of the steam and oxygen conversion of methane [reactions (54) and (52)] is carried out in industry. Steam conversion is carried out in the first reactor at 973 K and $[H_2O]:[CH_4] = 2$, and oxygen conversion in the second reactor at a low CH_4 concentration and 1223 K. This gives stoichiometric synthesis gas with a lower consumption of natural gas and energy.[115]

A study of the selective oxidation of methane to CO + H_2 on palladium catalysis deposited on oxides showed[116] that the catalysts 1% Pd(γ-Al_2O_3, Y_2O_3, La_2O_3, TiO_2, ZrO_2, HfO_2, CeO_2) give synthesis gas with a selectivity greater than 90%; for Pd/SiO_2 the selectivity at 1023 K was 63.7%. The degree of conversion of CH_4 at 1023 K was 35–66%. The highest selectivity (99.5%) was obtained on Pd/γ-Al_2O_3 for 58% conversion. The selectivity is lowered by the formation of CO_2, which in the opinion of the authors cited[116] takes place in the gas phase, while CO is formed on the surface.

The oxidation of methane at 673–973 K by noble-metal catalysts deposited on γ-Al_2O_3 has been studied.[117] In a reducing medium (a gas mixture with $[CH_4]:[CO]:[O_2] = 2:1:3$) a CO + H_2 mixture was obtained, and in an oxidising medium ($[CH_4]:[CO]:[O_2] = 2:1:10$) only extensive oxidation took place. The order of activity in the oxidation of CH_4 to synthesis gas is Rh > Pd $\simeq$ Pt. Adding CeO_2 to the catalyst suppresses completely its ability to give CO. CO in the gas phase has little influence on the yield of products.

Rh/SiO_2 was the most active and selective of the noble metals deposited on SiO_2.[118] On Rh, Ru, Pd, and Ni deposited on SiO_2, the yield of synthesis gas exceeded 90%. At the same time, extensive oxidation of CH_4 took place on Fe and Co/SiO_2. Oxidised metallic catalysts have a low activity.

Synthesis gas can be obtained by oxidising methane on catalysts containing lanthanides and noble metals, even at a low temperature (777 K).[119–121] On $Ln_2M_2O_7$ catalysts, where Ln = La, Eu, Gd, Yb, and M = Ru, Ir, a yield of CO + H_2 of 92–94% was obtained with a selectivity of up to 99% at a high volume rate of 4×10^4 h^{-1}. The highest selectivity (98–99%) was observed for $Y_2Ru_2O_7$. The catalysts Ru, Pd, Ir, Ni/Al_2O_3 were also active. X-Ray data showed that under the synthesis conditions the oxide catalyst decomposes to the metal

$$2Eu_2Ir_2O_7 \longrightarrow 2Eu_2O_3 + 4Ir + 4O_2.$$

Iridium particles with dimensions of 3 nm are formed. Reaction (56) decreases the selectivity slightly. The yield of CO + H_2 decreases with increase in pressure.

Thus the highest activity and selectivity in the oxidative conversion of methane into synthesis gas are shown by the metals of the platinum group and nickel, which activate hydrogen (and correspondingly the recombination of H atoms). This ability is lost when the metals are oxidised. After the removal of the first H atom, CH_4 is apparently transformed rapidly into $CH_{2\,ads}$, CH_{ads}, C_{ads}, and then CO. The process is undoubtedly highly selective, but its practical realisation requires the special production of oxygen, and this makes the large-scale production of synthesis gas by reaction (52) less favourable than steam conversion (54).

The combination of the oxidative conversion of CH_4 into synthesis gas with other reactions is also of interest. A combination of three reactors without intermediate separation has been used[122] for the selective oxidation of methane to propanal C_2H_5CHO. The oxidative condensation of methane to ethane on $K/BaCO_3$ and the transformation of CH_4 + O_2 into synthesis gas on 1% Rh/Al_2O_3 at a high temperature (1139–1153 K) are carried out in two parallel reactors. The hydroformylation of ethane on a homogeneous Rh catalyst is carried out in a third reactor at a low temperature (993 K). A selectivity with respect to C_2H_5CHO of 27% is achieved for 49% conversion.

The oxidation of methane using CO_2. The direct reaction of methane with CO_2 on metallic catalysts has been studied by many workers, beginning with the work of Fischer and Tropsch.[123] In addition to reaction (55), reactions (56) and (57) also take place. The formation of ethane [reaction (58)] is also possible:[124]

$$CH_4 + 2CO_2 = C + 2CO + 2H_2O, \quad (57)$$

$$CH_4 + 3CO_2 = 4CO + 2H_2O, \quad (58)$$

$$2CH_4 + CO_2 = C_2H_6 + CO + H_2O. \quad (59)$$

All four reactions (55) and (57)–(59) are endothermic and take place at high temperatures (900–1200 K). At 1073 K, $\Delta G < 0$ for reactions (55)–(58), and $\Delta G > 0$ for reaction (59).

Reaction (55) often takes place as a side reaction in the steam conversion of methane. A study of its kinetics on an Ni catalyst at 1070–1173 K showed[125] that the reaction rate is described by the same equation as the steam conversion

$$r = \frac{k_1 p_{CH_4}}{1 + k_2 p_{H_2O}/p_{H_2} + k_3 p_{CO}}, \quad (60)$$

where k_1, k_2, k_3 are constants, and p_{CH_4}, p_{H_2O}, p_{H_2}, and p_{CO} the partial pressures of methane, water, hydrogen, and carbon monoxide respectively. The explanation given[124] is that CH_4 reacts first not with CO_2 but with H_2O, and the hydrogen formed reacts rapidly with CO_2 by a reaction which is the reverse of reaction (56), with the regeneration of H_2O.

In accordance with Eqn. (57), the reaction of CH_4 with CO_2 gives carbon, which poisons the nickel catalyst. It is obtained both from methane by its dissociation to C + $2H_2$ and from CO by the Boudouard reaction. Various methods are used for the industrial preparation of synthesis gas from CH_4 + CO_2. The first of Haldor Topsoe uses a CH_4 + CO_2 + H_2O mixture to decrease the poisoning of the catalyst and blocking of the tubes by carbon.[126,127] It has also developed the SPARG process (1173 K, 0.9 MPa), in which sulphur vapour is added to the reacting gases. Sulphur passivates nickel and prevents the formation of carbon.

Ni/SiO_2 was much more active than the oxides CaO and Fe_2O_3. The temperature of 50% conversion was 910 K on Ni/SiO_2, and 1200–1300 K on the oxides.[128] The oxides are covered by carbon more rapidly than nickel. At 1073 K the degree of conversion of a CH_4 + CO_2 mixture into synthesis gas was 83.1% on Ni/Al_2O_3,

74.2% on Co/Al_2O_3, and only 3.4% on Fe/Al_2O_3. The reaction rate was approximately 1.5 times lower on Ni/SiO_2 than on Ni/Al_2O_3.[129]

Metals of the platinum group are also active in the carbon dioxide conversion of methane.[130–133] The reaction takes place at an appreciable rate even at 773 K. A study of the reaction by the transverse pulse method showed that CO is formed when the CO_2 pulse is introduced. C_2H_6 and C_2H_4 are formed from the first CH_4 pulses, followed by rapid deactivation at 773 K and by slow deactivation at 823 K. Rh/Al_2O_3 and Pd/Al_2O_3 are poisoned more slowly than the others, and Ru/Al_2O_3 more rapidly. The order of specific activities in the $CO_2 + CH_4$ reaction is Rh > Pd > Ru > Pt > Ir/Al_2O_3, which corresponds to the order of the activities in the dissociation $CO_2 \rightarrow CO + O_{ads}$.[131] According to much of the data,[130,131,133] Rh/Al_2O_3 is the most active. Acidic carriers were found to be more favourable, since they facilitate the dispersion of the deposited metals.

The reversible reaction $CO_2 + CH_4 \rightleftarrows 2H_2 + 2CO$, that is the production of synthesis gas at high temperatures and methanation at low temperatures, is convenient for the creation of cells using solar energy;[132] the endothermic reaction takes place on heating by the sun, and the exothermic reaction takes place to remove the energy. The 1% Ru/Eu_2O_3 catalyst with a ruthenium particle size of 3 nm and the hexagonal ruthenium structure was found to be best for this purpose.

All the deposited noble metals studied were shown to be highly active.[134,135] Another important feature is that in almost all cases the product is a gas mixture with $[CO]:[H_2] = 1$, that is practically no side reactions take place. For a mixture with $[CH_4]:[CO_2] = 1$ at 1050 K, the yields of synthesis gas CO + H_2 were 1% on Al_2O_3, 85% on 1% Ni/Al_2O_3, 73% on 1% Pd/Al_2O_3, 89% on 1% Ru/Al_2O_3, 87% on 1% Rh/Al_2O_3, and 89% on 1% Ir/Al_2O_3. Coking was most rapid for the catalyst Ni/Al_2O_3 and Pd/Al_2O_3. The most stable to coking was Ir/Al_2O_3, which remained active for 260 h. On Ru/Al_2O_3 the yields of H_2 was greater than that of CO. In a $13CH_4 + 6O_2 + CO_2$ mixture the yield on Ni/Al_2O_3 can be increased by 91%, and the reaction becomes thermally neutral. For a $4CH_4 + O_2 + 9CO_2$ mixture the gas obtained contained exactly 50% CO and 50% H_2, and no carbon was formed on the surface.

New types of catalyst, stable to carbon formation, have been studied.[136–139] The effect of various additives on Ni/SiO_2 catalysts was studied. Of the oxides of nickel, iron, copper, chromium, and manganese, the oxides of manganese were found to be most effective. In their presence the extent of carbon formation decreased, and the degree of transformation of CO_2 increased with increase in the proportion of manganese in the nickel catalyst.

Subsequent study showed that reaction (55) can be carried out without nickel. A 5% Ca–12% Mn–O/Al_2O_3 catalyst was most effective under stationary conditions. In its presence at 1140 K at a volume rate of 900 h^{-1} with an equimolar mixture of CO and H_2, the conversion of CH_4 was 83.1%, the conversion of CO_2 62.7%, and the selectivity with respect to H_2 76.5%. At 1200 K at the start of work with a fresh catalyst, extensive oxidation of methane takes place involving the oxygen of the catalyst, and there is no transformation of CO_2. As the reaction and reduction of the catalyst take place, CO_2 is activated. The concentration of CO and H_2 increase continuously. With a catalyst operating under stationary conditions at 1200 K, the conversion of CO_2 and CH_4 is complete, and the selectivity is 99.7% for CO, and 84.6% for H_2. The activity is preserved for a long time, and practically no formation of carbon by reaction (57) takes place.

A study of the phase composition of an operating Ca–MnO/SiO_2 catalyst showed[137,138] that during the reaction the more highly oxidised phases Mn_2O_3 and Mn_3O_4 are reduced, and only the reduced phase MnO is detected in the catalyst. After the production of a stable catalyst composition, the formation of carbide and metallic manganese phases was not observed.

A study of the reaction under alternating conditions (the reaction of alternately CH_4 and CO_2 with the catalyst) showed that on the fresh catalyst, C_2H_4 and C_2H_6 are formed from methane, possibly with the participation of carbonate phases, since oxidative dimerisation takes place.[139] After reduction and phase transformation from the oxidised phases to MnO, the formation of C_2H_6 and C_2H_4 decreases and CO appears. The rates of formation of hydrogen under stationary catalysis conditions (3×10^{-3} mol g^{-1} h^{-1}) and in the reductive reaction of CH_4 with the catalyst (1.7×10^{-3} mol g^{-1} h^{-1}) are comparable. The rate of the reaction of CO_2 with the reduced catalyst (re-oxidation of the catalyst), however, is greater than the rate of reduction.

Mamedov[136] concluded that the conversion of methane to synthesis gas using CO_2 on a manganese catalyst does not take place by a redox mechanism. During the catalysis, the stationary phase MnO is not reduced and is not oxidised, but prevents carbon formation. Electron microscopy detected coke deposits as thin layers on the reduced MnO centres. CO_2 reacts with MnO and forms an intermediate carbonate complex on the surface, methane dissociates, and the carbon fragment reacts with oxygen.

$$CH_4 + MnO \rightleftarrows MnO \ldots C + 2H_2,$$
$$CO_2 + MnO \rightleftarrows MnCO_3,$$
$$MnCO_3 + MnO \ldots C \longrightarrow 2MnO + 2CO,$$
$$MnCO_3 + H_2 \longrightarrow MnO + CO + H_2O,$$
$$MnO \ldots C + H_2O \longrightarrow MnO + CO + H_2.$$

When redox additives are introduced into MnO, the reaction becomes an alternating redox reaction. Only reaction (58) is observed on a K–Cr–Mn–O/SiO_2 catalyst.

References

1. Y Amenomiya, V I Birss, M Goledzinowski, et al. *Catal. Rev.*, 1990, **32** 163
2. O V Krylov *Usp. Khim.*, 1992, **61**(8) 1550 [English translation in *Russ. Chem. Rev.*, 1992(8)]
3. H D Gesser, N R Hunter, C B Prakash *Chem. Rev.*, 1985, **85** 235
4. J H Lunsford *Methane Conversion*, Elsevier, Amsterdam, 1988, p. 359
5. M J Brown, N D Parkyns *Catal. Today*, 1991, **8** 305
6. J L Mackie *Catal. Rev.*, 1991, **31** 169
7. A B Nalbandyan, A A Mantashyan *Elementarnye Protsessy v Medlennykh Gazofaznykh Raktsiyakh* (Elementary Processes in Slow Gas-Phase Reactions), Erevan, 1975, pp 120–124
8. I A Vardanyan, A B Nalbandyan *Int. J. Chem. Kinet.*, 1980, **17** 801
9. V I Vedeneev, M Ya Gol'denberg, N I Gorban', M A Teitel'boim *Kinet. Katal.*, 1988, **29** 7
10. V I Vedeneev, M Ya Gol'denberg, N I Gorban', M A Teitel'boim *Kinet. Katal.*, 1988, **29** 1291
11. V I Vedeneev, M Ya Gol'denberg, N I Gorban', et al. *Kinet. Katal.*, 1988, **29** 1297
12. A A Borisov, E V Dragalov, V M Zamanskii, et al. *Kinet. Katal.*, 1985, **26** 35

13. H Zanthoff, M A Baerns *Ind. Eng. Chem. Res.*, 1990, **29** 2
14. T R Baldwin, R Buch, G D Squire, S C Tsang *Appl. Catalysis*, 1991, **74** 137
15. Z S Andrianova, A N Ivanova, P E Matkovskii, G G Startseva *Kinet. Katal.*, 1992
16. M L Poutsma *Free Radicals*, Wiley, New York, 1972
17. V E Leonov, L M Kalinichenko, Yu S Shublyakova, in collected papers *Kataliz i Katalizatory* (Catalysis and Catalysts), No. 15, Naukova Dumka, Kiev, 1977, p. 6
18. Yu L Vysotskii, L E Semikhina, Yu A Shuster, in collected paper *Kataliz i Katalizatory* (Catalysis and Catalysts), No. 17, Naukova Dumka, Kiev, 1979, p. 82
19. H D Gesser, N R Hunter, L A Morton *Proc. Symp. on Methane Activation: Intern. Chem. Congress on Pacific Basis Soc.*, Honolulu, 1989, p. 23
20. N R Hunter, H D Gesser, L A Morton, P S Yarlagadda *Appl. Catalysis*, 1990, **57** 45
21. R Burch, G D Squire, S C Tsang *J. Chem. Soc., Faraday Trans. 1*, 1989, **85** 3561
22. K Omata, N Fukuoka, K Fujimoto *Catalysis Lett.*, 1991, **12** 227
23. H Schwarz *Angew. Chem.*, 1991, **30**(7) 820
24. V A Durante, D W Walker, W H Seitzer, J E Lyons *Proc. Symp. on Methane Activation: Intern. Chem. Congress on Pacific Basic Soc.*, Honolulu, 1989, p. 20
25. US P. 4 918 249; *Chem. Ind.*, 1990, **68**(2) 34
26. Huang Xiao-Kong *Chem. Eng. News*, 1990, **68**(4) 21
27. P S Yarlagadda, N R Hunter, *Fuel Sci. Technol.*, 1987, **5** 169
28. J R Anderson, P Tsai *J. Chem. Soc., Chem. Commun.*, 1987, (19) 143
29. D A Dowden, C R Schnell, G T Walker *Principles of the Prediction of Catalytic Action, Proceedings of the Fourth International Congress on Cataysis* (Translated into Russian), Vol. 2, Nauka, Moscow, 1970, p. 198
30. L Ya Margolis, L A Nersesyan, A B Nalbandyan *Trudy Vsesoyuznoi Konferentsii po Mekhanizmu Kataliticheskikh Reaktsii* (Proceedings of the All-Union Conference on the Mechanism of Catalytic Reactions), Mocow, 1974
31. L A Nersesyan, I A Vardanyan, L Ya Margolis, A B Nalbandyan *Dokl. Akad. Nauk SSSR*, 1973, **220**(3) 605
32. S Kasztelan, J B Moffat *J. Chem. Soc., Chem. Commun.*, 1987, (21) 1669
33. L Z Mel'tser, T A Garibyan, R R Grigoryan, et al. *React. Kinet. Catal. Lett.*, 1989, **38** 229
34. V T Minasyan, G L Grigoryan, A B Nalbandyan *Arm. Khim. Zh.*, 1981, **34** 623
35. V I Gomonai, in collected papers *Kataliz i Katalizatory* (Catalysis and Catalysts), Vol. 26, Naukova Dumka, Kiev, 1989, p. 52
36. V I Gomonai, D I Mel'nik, K Yu Sekeresh *Trudy 4 Vsesoyuznoi Konferentsii po Mekhanizmu Kataliticheskikh Reaktsii* (Proceedings of the Fourth All-Union Conference on the Mechanism of Catalytic Reactions), Vol. 2, Moscow, 1986, p. 72
37. V A Borko, V I Gomonai, K Yu Sekeresh *React. Kinet. Catal. Lett.*, 1980, **14** 439
38. A Ya Averbukh, N Yu Pavlova *Geterogennye Kataliticheskie Protsessy* (Heterogeneous Catalytic Processes), Leningrad, 1979, p. 94
39. I A Zuev, A V Vilenskii, I P Mukhlenov *Zh. Prikl. Khim.*, 1988, **68** 2607
40. Yu A Ivanov, A Ya Averbukh, I P Mukhlenov, L I Masienko *I Konferentsiya po Okislitel'nomu Katalizu. Tezisy Dokladov* (Summaries of Papers Presented at the First Conference on Oxidative Catalysis), Vol. 2, Baku, 1978, p. 576
41. G N Kastanas, G A Tsigdinos, J W Schwank *Appl. Catalysis*, 1986, **44** 33
42. N D Spencer *J. Catal.*, 1988, **109** 309
43. T Tatsui, Y Aimoto, H Tominaga *Proc. Symp. on Methane Activation: Intern. Chem. Congress on Pacific Basin Soc.*, Honolulu, 1989, p. 149
44. Q Zhu, M Zhong, J Xiao, X Zhao *Proc. Symp. on Methane Activation: Intern. Chem. Congress on Pacific Basin Soc.*, Honolulu, 1989, pp. 113, 117
45. R Pitchai, K Klier *Catal. Rev.*, 1986, **28** 14
46. E M Coda, M Kennedy, J B Mc Monagle, B K Hodnett *Catal. Today*, 1990, **6** 559
47. M Kennedy, A Sexton, B Kartheuser, et al. *Catal. Today*, 1992, **13** 447
48. Y Barbaux, A E Elamrani, J P Bonnelle *Catal. Today*, 1987, **1** 144
49. N D Spencer, C J Pereira *J. Catal.*, 1989, **116** 309
50. M D Amiridis, J E Rekcesce, J A Dumesik, et al. *AlChE J.*, 1991, **37** 87
51. R S Liu, M Iwamoto, J H Lunsford *J. Chem. Soc., Chem. Commun.*, 1981, (1) 78
52. H F Liu, R S Liu, K Y Liew *J. Am. Chem. Soc.*, 1984, **106** 4117
53. K J Zhen, M M Khan, C H Mak, G A Somorjai *J. Catal.*, 1985, **94** 501
54. H Iwamoto, S Kagawa, J H Lunsford *Shokubai (Catalyst)*, 1987, **23** 278
55. K I Aika, G A Somorjai *J. Catal.*, 1985, **91** 269
56. Y Barbaux, A R Elamrani, E Payen, et al. *Appl. Catalysis*, 1988, **44** 117
57. E M Coda, B K Hodnett *New Developments in Selective Oxidation: Proc. I Intern. Congress*, Elsevier, Amsterdam, 1989, p. 459
58. M M Khan, G A Somorjai *J. Catal.*, 1985, **91** 263
59. S Kasztelan, J B Moffat *J. Catal.*, 1987, **106** 512
60. S Kasztelan, J B Moffat *J. Catal.*, 1987, **109** 206
61. S Kasztelan, E Payen, J B Moffat *J. Catal.*, 1988, **112** 320
62. S Kasztelan, J B Moffat *J. Catal.*, 1989, **116** 82
63. S Kasztelan, E Payen, J B Moffat *J. Catal.*, 1990, **125** 45
64. S Kasztelan, J B Moffat *Proc. 9th Intern. Congress on Catalysis*, Chem. Inst. Canada, Calgary, 1988, Vol. 2, p. 883
65. S Ahmed, S Kasztelan, J B Moffat *Faraday Disc.*, 1989, **87** 23
66. G A Savel'eva, S A Tungatarova, P M Shagisbeev, et al. *Proc. 7th Intern. Symp. on Heterogeneous Catalysis*, Sofia, 1991, p. 715
67. Japanese P. 62 217 336; *Appl. Catal.*, 1986, **26** 410
68. C R F Lund *Catal. Lett.*, 1992, **12** 395
69. O V Krylov *Disc. Faraday Soc.*, 1989, **87** 50
70. G A Vorob'eva, V A Zhorin, D P Shashkin, et al. *Kinet. Katal.*, 1987, **28** 1017
71. A F Firsova, G A Vorob'eva, A A Bobyshev, et al. *Kinet. Katal.*, 1991, **32** 395
72. O V Krylov, A A Firsova, A A Bobyshev, et al. *Catal. Today*, 1992, **13** 301
73. F Solymosi, I Tombacz, G Kutsan *J. Chem. Soc., Chem. Commun.*, 1985, (20) 1455
74. M Niwa, H Yamada, Y Murakami *J. Catal.*, 1992, **134** 331

75. K Otsuka, T Komatsu, K Jinno, et al. *Proc. 9th Intern. Congress on Catalysis*, Chem. Inst., Calgary, 1988, Vol.2, p. 915
76. M Yu Sinev, K Otsuka *Chem. Lett..*, 1992
77. G N Kastanas, C Tsigdinos *Proc. 11th Meet. Catalysis*, Dearborn, 1987, Abstract PFO-31
78. G N Kastanas, C Tsigdinos *Proc. Spring AIChE Meet.*, Houston, 1989, p. 52d
79. K J Zhen, C W Teng, Y L Bi *React Kinet. Catal. Lett.*, 1987, **34** 295
80. Z Sojka, R G Herman, K Klier *J. Chem. Soc., Chem. Commun.*, 1991, (3) 185
81. Y N Wang, G W Simmons, J A Marcos, K. Klier *Proc. Symp. on Methane Activation: Intern. Chem. Congress on Pacific Basin Soc.*, Honolulu, 1989, p. 81
82. S Mohanty, K Gadgil, M K Sarkar *Proc. IX Intern. Symp. on Alcohol Fuels (ISAF, Firenza, 1991)*, Ecofuel., Milano, 1991, p. 113
83. G N Kastanas, G A Tsigdinos, J W Schwank *J. Chem. Soc., Chem. Commun.*, 1988, (19) 1298
84. J S J Hargreaves, G J Hutchings, R W Joyner *Nature (London)*, 1990, **348** 3428
85. I A Guliev, A Kh Mamedov, V S Aliev *Azerb. Khim. Zh.*, 1978, (1) 35
86. T I Jang, J H Lunsford *J. Catal.*, 1986, **103** 35
87. F S Feil, J H Van Ommen, J R H Ross *Langmuir*, 1987, **3** 688
88. R A Shafranovskii, G N Zhizhin, M Yu Sinev, et al. *Kinet. Katal.*, 1990, **30** 202
89. H Schwarz *Angew. Chem.*, 1991, **30** 820
90. M Che, A J Tench *Adv. Catal.*, 1982, **31** 7
91. A M Volodin, V A Bol'shov *Kinet. Katal.*, 1992, **33**
92. A Parmaliana, F Frusteri, D Miceli, et al. *Appl. Catalysis*, 1991, **78** L7
93. S L Kaliaguine, B N Shelimov, V B Kazanskii *J. Catal.*, 1978, **55** 384
94. T Suzuki, K Wada, M Shima, Y Watanabe *J. Chem. Soc., Chem. Commmun.*, 1990, (15) 1059
95. G N Kuz'min, M V Knat'ko, S V Kurganov *React. Kinet. Catal. Lett.*, 1983, **23** 313
96. M D Ward, J F Brazdil, S O Mehandru, A B Anderson *J. Phys. Chem.*, 1987, **91** 6515
97. E S Yang, J H Lunsford *J. Catal.*, 1980, **63** 505
98. V B Kazanskii *Kinet. Katal.*, 1983, **24** 1388
99. C Louis, M Che, M Anpo *Research Chem. Intermediates*, 1991, **15** 81
100. N A Lipatkina, V A Shvets, V B Kazanskii *Kinet. Katal.*, 1978, **19** 979
101. O V Kotova, Candidate's Thesis, Leningrad State University, Leningrad, 1986
102. V A Radtsig *Kinet. Katal.*, 1979, **20** 488
103. A A Bobyshev, V A Radtsig *Kinet. Katal.*, 1981, **22** 1540
104. A A Bobyshev, V A Radtsig *Kinet. Katal.*, 1988, **29** 638
105. A A Bobyshev, V A Radtsig *Khim. Fiz.*, 1988, **7** 950
106. A A Bobyshev, V A Radtsig *Kinet. Katal.*, 1990, **31** 925
107. A A Bobyshev, V A Radtsig, I A Senchenya *Kinet. Katal.*, 1990, **31** 932
108. M J D Low, E McNellis, H Mark *J. Catal.*, 1986, **160** 328
109. V V Brei, V M Gun'ko, V D Khavryuchenko, A A Chuiko *Kinet. Katal.*, 1990, **31** 1164
110. W J M Vermeiren, F Bloomsma, P A Jacobs *Catal. Today*, **1992, 13** 427
111. J Eilers, S A Posthuma, S T Sie *Catal. Lett.*, 1990, **7** 253
112. M Prettre, C Eichner, M Perrin *Trans. Faraday Soc.*, 1946, **43** 355
113. K Huszar, G Racz, G Szekely *Acta Chem. Hung.*, 1971, **70** 287
114. D Dissanayake, M P Rosynek, K C C Kharas, J H Lunsford *J. Catal.*, 1991, **132** 117
115. I Dybkyjaer, J B Hansen *Econ. Eng. Rev.*, 1985, **17** 13
116. A K Bhattacharya, J A Breach, S Chaud, et al. *Appl. Catalysis*, 1992, **A80** L1
117. S H Oh, P J Mitchell, R M Siewart *J. Catal.*, 1991, **132** 287
118. J Nakamura, S Umeda, K Kubashiro, et al. *Shokubai (Catalyst)*, 1991, **33** 99
119. A T Ashcroft, A K Cheetham, J S Foord, et al. *Nature (London)*, 1990, **344** 319
120. P D F Vernon, M L H Green, A K Cheetham, A T Ashcroft *Catal. Lett.*, 1990, **6** 181
121. R H Jones, A T Ashcroft, D Waller, et al. *Catal. Lett.*, 1991, **8** 169
122. M L H Green, S C Tsung, P D F Vernon, A P E York *Catal. Lett.*, 1992, **13** 341
123. F Fischer, H Tropsch *Brennstoff Chem.*, 1928, **9** 39
124. K Aika, T Nishiyama *Proc. 9th Intern. Congress on Catalysis*, Chem. Inst. Canada, Calgary, 1988, Vol. 2, 907
125. I M Bodrov, L O Apel'baum *Kinet. Katal.*, 1967, **8** 379
126. J R Rostrup-Nielsen *Methane Conversion: Proc. Symp. Prod. Fuels and Chemicals from Natural Gas, Auckland, 1987*, Elsevier, Amsterdam, 1988, p. 73
127. J Topp-Jorgensen *Methane Conversion: Proc. Symp. Prod. Fuels and Chemicals from Natural Gas, Auckland*, 1987, Elsevier, Amsterdam, 1988, p. 293
128. T Sodesawa, A Dobashi, F Nozaki *React. Kinet. Catal. Lett.*, 1979, **12** 107
129. O Tokunaga, S Ogasawara *React. Kinet. Catal. Lett.*, 1989, **39** 69
130. Y Sakai, H Saito, T Sodesawa, F Nozaki *React. Kinet. Catal. Lett.*, 1984, **24** 253
131. F Solymosi, G Kutsan, A Erdöhelyi *Catal. Lett.*, 1991, **11** 149
132. J S H Q Perera, J W Couves, G Sanker, J M Thomas *Catal. Lett.*, 1991, **11** 219
133. M Masai, H Kado, A Miyake, et al. *Methane Conversion: Proc. Symp. Prod. Fuels and Chemicals from Natural Gas, Auckland, 1987*, Elsevier, Amsterdam, 1988, p. 67
134. A T Ashcroft, A K Cheetham, M L H Green, F D F Vernon *Nature (London), 1991*, **352** 225
135. P D F Vernon, M L H Green, A K Cheetham, A T Ashcroft *Catal. Today*, 1992, **13** 417
136. A Kh Mamedov, Doctoral Thesis, Institute for Theoretical Problems in Chemical Technology, Azerbaidzhan Academy of Sciences, Baku, 1991
137. A Kh Mamedov, S V Mirzabekova, Sh A Nuriev, et al. *Neftekhimiya*, 1990, **30** 30
138. A Kh Mamedov, P A Shiryaev, D P Shashkin, O V Krylov *New Developments in Selective Oxidation: Proc. I World Congress*, Elsevier, Amsterdam, 1989, p. 477
139. A Kh Mamedov, S R Mirzabekova, V S Aliev, O V Krylov *Kinet. Katal.*, 1992, **33** 591

Received 13th July 1992

Translated from Uspekhi Khimii 61 2062–2077 (1992) U.D.C. 541.128;542.97.13;66.094.32

Hydroxylation of aromatic compounds with nitrous oxide. New possibilities of oxidative catalysis on zeolites

A S Kharitonov, V I Sobolev, G I Panov
Boreskov Institute of Catalysis, Siberian Division of the Russian Academy of Sciences

ABSTRACT. Studies on the use of zeolites in partial oxidation reactions are surveyed. Attention is concentrated on recent investigations of the gas-phase oxidative hydroxylation of aromatic compounds with nitrous oxide. Best results were achieved in the study of the simplest reaction of this type — the oxidation of benzene to phenol: in the presence of iron-containing ZSM-5 zeolites, the reaction proceeds with nearly 100% selectivity and a degree of conversion of benzene of 25–30%.

Further development of this method for the introduction of hydroxy-groups may lead to new possibilities for the creation of effective technologies in the field of organic synthesis.

The bibliography includes 87 references.

Contents

I.	Introduction	1130
II.	Hydroxylation of benzene in the presence of traditional catalysts	1131
III.	The search for new systems. Zeolites	1132
IV.	The nature of the catalytic activity of zeolites	1133
V.	Specific features of nitrous oxide as an oxidant. The mechanism of the hydroxylation of benzene	1135
VI.	Hydroxylation of benzene derivatives	1136
VII.	Conclusion	1137

I. Introduction

Oxidation processes constitute one of the commonest classes of chemical reactions. This applies both to natural proceses, where oxygen effects a continuous turnover of chemical reactions, and in the field of technical catalysis carried out by man. The endeavour by investigators to create economically more effective and ecologically clean technologies has stimulated the search for new catalysts exhibiting a high selectivity.

Zeolites were not regarded for a long time as promising catalysts for oxidation reactions despite their wide scale and successful use in many other fields of catalysis. Considerable changes occurred in this respect during the last decade. They are associated with the creation at the beginning of the 1980s of titanosilicate zeolites having a structure of the ZSM-type and the discovery of their unique properties in oxidation reactions involving H_2O_2. The titanosilicate zeolites proved to be effective catalysts of a wide range of reactions occurring in the liquid phase, such as the oxidation of alcohols, epoxidation of alkenes, hydroxylation of aromatic compounds, and the conversion of cyclohexanone into an oxime.[1–5] The range of these reactions is being expanded and communications concerning the selective oxidation of lower paraffins to secondary and tertiary alcohols in the presence of titanosilicates have appeared.[6–8] Some of these reactions can be achieved also in the presence of other zeolites of the pentasil type.[9–11]

Whereas in the reviews of recent years these advances in liquid-phase oxidation have been assessed as one of the most important achievements in the field of organic synthesis,[12–15] the results obtained in the gas-phase oxidative catalysis on zeolites appear much more modest. The transfer of reactions to the gas phase has many technological advantages. However, the consequent increase in temperature precludes the use in this instance of hydrogen peroxide because of its vigorous uncontrolled decomposition. On the other hand, the employment of molecular oxygen, which is a traditional oxidant for heterogeneous-catalytic gas-phase reactions, has not so far led to major successes.

The partial oxidation of hydrocarbons is achieved as a rule in the presence of transition metal oxides.[16,17] Their activity is due to the more or less facile electron transfer and their capacity for the reversibility of their oxidation state on interaction with oxygen and the substance oxidised. Zeolites themselves cannot serve as active oxidation catalysts, but the possibility of their use as carriers is nevertheless of great interest. The regular structure, high surface area, and high adsorption potential create preconditions for the attainment of a wide variety of states of the deposited component. Indeed, numerous studies have shown that, after its introduction into a zeolite, a metal can have different states:[18] it can exist in the form of isolated ions in the tetrahedral positions within the zeolite lattice, as isolated cations serving as the counterions, as small clusters and associated species within the porous system, and as part of the composition of the highly disperse oxide phase distributed on the outer surface of the zeolite. Such a wide variety of forms is hardly possible in other systems and it would appear that it should lead to extensive prospects for the acceleration of various oxidation reactions.

However, studies carried out mainly in the 1970s and examined extremely fully in a monograph[19] have not on the whole justified these expectations. In many instances, the authors were able to demonstrate fairly effective reaction parameters on zeolites (for example, the epoxidation of ethylene on Ag/CaX [20] and the oxidative ammonolysis of toluene on Cu/ZSM-5 [21]), but such parameters do not attain the level ensured by the best traditional systems.

One of the causes of this is that the transition metals introduced into a zeolite matrix (particularly in the form of isolated ions) lose their activity. The decrease in the atomic catalytic activity can reach several orders of magnitude compared with massive oxides.[19] O_2 isotope exchange data have shown[22–24] that this is associated primarily with the loss of ability to activate molecular oxygen. To some extent, this result is natural bearing in mind that O_2 is

activated via its dissociative adsorption on the catalyst surface[25,26] involving the transfer of four or at least two electrons, which can be hardly readily achieved on small clusters let alone isolated metal cations.

A change in the structure of the zeolite lattice and also in the coordination environment can affect significantly the oxidative catalytic properties of cations introduced into the zeolite.[27–31] The oxidation of hydrocarbons on zeolites is frequently complicated by a number of side reactions occurring on the acid surface centres and deactivating the catalyst as a consequence of the deposition of coke.

During the last decade, the interest in gas-phase oxidation on zeolites has been maintained at an extremely low level. Analysis of the literature shows that only isolated reports concerning this aspect of research have appeared at major international conferences on zeolites and also at congresses on catalysis (Table 1). It is remarkable that not a single study devoted to gas-phase oxidation on zeolites was presented at the Symposia on "Heterogeneous Catalysis and Fine Organic Synthesis"[12] and "New Advances in Selective Oxidation".[33,34]

Table 1. Studies on gas-phase oxidation in the presence of zeolites presented at International Congresses, Conferences, and Symposia.

Location (year) of Congresses, Conferences, and Symposia	Number of studies	Refs.
Congresses on catalysis		
Tokyo (1980)	0	[32]
Berlin (1984)	2	[26]
Calgary (1988)	2	[24]
Conferences on zeolites		
Lyons (1980)	1	[35]
Reno (1983)	2	[21]
Prague (1984)	0	[36]
Portoroz (1984)	0	[37]
Tokyo (1986)	2	[2]
Wurzburg (1988)	0	[13]
Amsterdam (1989)	2	[14]
Symposia on selective oxidation		
Louvian (1986)	0	[33]
Rimini (1989)	2	[4]
Louvain (1991)	0	[34]

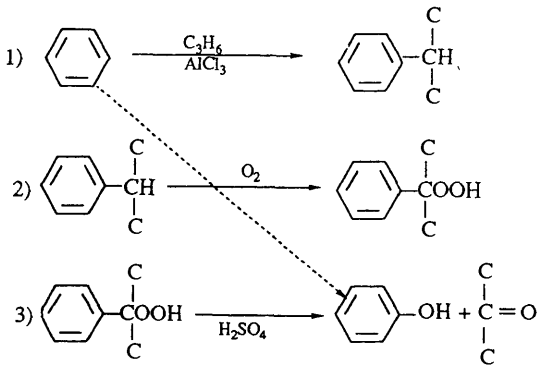
During the 1980s, a new trend arose in the field of oxidative heterogeneous catalysis. Namely it involved the use as the oxidant of not only free (molecular) oxygen but also of bound oxygen in the form of various oxygen-containing molecules.[38–45] To a large extent, this trend arose in the search for methods whereby the catalytic activation of methane and other lower paraffins could be achieved. The greatest interest among the non-traditional oxidants attaches to molecular nitrous oxide. The replacement of molecular oxygen by N_2O, including systems on zeolites,[39,40,45] frequently makes it possible to increase significantly the selectivity of the oxidation reactions.

The effective properties of nitrous oxide as a source of oxygen was manifested particularly strikingly in the study of the oxidative hydroxylation of an aromatic ring, which is a complex and difficult reaction. Studies on these lines were carried out mainly during the last 4–5 years. Although at the present stage it is difficult to reach a final assessment, nevertheless such investigations have yielded, in our view, extremely promising results and they become a basis for the creation of new ecologically clean technologies for organic synthesis and zeolites. The rest of the present review is in fact devoted to a consideration of these studies.

II. Hydroxylation of benzene in the presence of traditional catalysts

The introduction of a hydroxy-group into an aromatic ring is a difficult problem in the synthesis of organic intermediates: phenols naphthols, hydroxyamines, hydroxyacids, etc. Industrial hydroxylation procedures as a rule involve indirect multistage processes which frequently require the application of corrosive chemicals.[46,47] The simplest reaction of this type, the oxidation of benzene to phenol, is carried out via the so called cumene process comprising three stages (see the Scheme below): (1) alkylation of benzene with propene leading to the formation of isopropylbenzene (cumene); (2) oxidation of cumene to a hydroperoxide: (3) decomposition of cumenyl hydroperoxide to phenol and acetone. The first and third stages are carried out catalytically in the liquid phase using acid catalysts, which usually consist of $AlCl_3$ (stage 1) and H_2SO_4 (stage 3). Naturally this involves problems of the corrosion of the apparatus and negative environmental consequences. Furthermore, the cumene method suffers from a further disadvantage, namely the formation of each mole of phenol is accompanied by the formation of one mole of the accompanying product—acetone, which cannot always find an equivalent market for its sale because of the much smaller requirement for this product.[48] Therefore efforts have been made in numerous laboratories to seek new ways of synthesising phenol.

Scheme



The most radical procedure for the solution of this problem—the introduction of a hydroxy-group via the direct single-stage oxidation of benzene with oxygen, indicated by a dashed arrow in the Scheme, has attracted much attention by investigators. However, numerous attempts, undertaken on these lines in the course of several decades, did not lead to success. The interaction with oxygen is accompanied by the decomposition of the benzene ring and the formation of either maleic anhydride (in the presence of specially selected

catalysts) or extensive oxidation products. In the oxidation of alkylbenzenes, for example, toluene, the process involves primarily the substituent and leads to the formation of benzaldehyde or benzoic acid.[16]

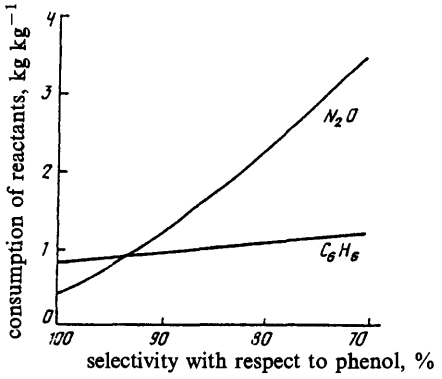


Figure 1. Consumption of benzene and nitrous oxide in the synthesis of phenol as a function of the selectivity of the oxidation of benzene to phenol.

A new reaction was discovered in 1982 — the oxidation of benzene with nitrous oxide:[49,50]

$$C_6H_6 + N_2O = C_6H_5OH + N_2. \quad (1)$$

It made it possible to achieve a fundamentally new level of selectivity with respect to phenol. Best results were obtained in the presence of deposited vanadium, molybdenum, and tungsten oxides. At 550 °C and after the addition of 30% of H_2O to the reaction mixture, the selectivity with respect to phenol on deposited catalysts reached 71% for a benzene conversion of 10%. These results aroused lively responses,[51,52] in which the environmental safety of the new process was emphasised and extremely optimistic assessments of its practical prospects were made. Plans for pilot tests in a reactor with a fluidised catalyst bed were reported. However, the process was not realised in practice.

The parameters of the vanadium catalyst proved to be inadequate and it was not possible to find better catalysts, primarily as regards their selectivity. Selectivity is the most important parameter in partial oxidation processes. On the other hand, in processes involving N_2O, this parameter assumes a particularly great importance since, in contrast to molecular oxygen, nitrous oxide is a fairly expensive oxidant, whose cost is comparable to that of benzene. Whereas the conversion of one benzene molecule into phenol via reaction (1) requires one nitrous oxide molecule, the extensive oxidation to CO_2 and H_2O via the reaction

$$C_6H_6 + 15N_2O = 6CO_2 + 3H_2O + 15N_2, \quad (2)$$

requires 15 N_2O molecules. Fig. 1 shows that the decrease in selectivity leads not only to an increase in the consumption of benzene but, and this is particularly important, also to an increase in the consumption of nitrous oxide. For 70% selectivity, the consumption of N_2O exceeds almost by an order of magnitude the theoretical consumption corresponding to 100% selectivity. Taking this into account, one can hardly speak of the practical realisation of the process if selectivity at a level of 85–90% has not been achieved.

III. The search for new systems. Zeolites

The results of Iwamoto and co-workers[49,50] stimulated the search for new more effective catalytic systems. The reaction proved to have very stringent requirements. A large number of compounds of different chemical nature, some of which are listed in Table 2, were tested. Much attention was devoted to attempts at the improvement of vanadium catalysts, which made it possible to increase appreciably their stability.[53] However, the characteristics of vanadium catalysts could not be fundamentally improved in relation to the early investigation,[50] despite the use of different methods of preparation, the introduction of modifying additives, and the employment of various oxidants (O_2, N_2O, NO, SO_2). All the other compounds presented in Table 2 proved to be either inactive or the reaction proceeded in the direction of extensive oxidation in their presence, which is particularly characteristic of platinum group metals. Only a few catalysts yielded small amounts of phenol.

Table 2. Catalytic systems tested in the oxidation of benzene to phenol.

Systems based on V_2O_5	Systems with oxides	Systems with metals	Zeolites
		Catalysts	
V_2O_5	Al_2O_3, SiO_2	Ru/Al_2O_3,	A, X, Y
V_2O_5/SiO_2,	TiO_2, Fe_2O_3	Ag/Al_2O_3,	erionite
V_2O_5/TiO_2,	NiO, ZnO,	Ag/C,	clinoptilolite,
V-Mo-O/SiO_2,	Fe_2O_3·MoO_3,	Pd/SiO_2,	mordenite,
V-W-O/SiO_2,	NiO·Cr_2O_3,	Pd/C,	$AlPO_4$-5,
V-Cu-O/SiO_2,	Fe-Bi-Mo-P-O,	Pt/Al-Si-O	ZMS-5
V-Ti-O/SiO_2,	ZnO/SiO_2,		ZSM-11
V-Fe-O/SiO_2,	In_2O_3/SiO_2,		ZSM-5 zeolites
V-Na-O/SiO_2,	Bi_2O_3/SiO_2,		containing
V-Mg-O/SiO_2	CdO/SiO_2,		V, Cr,
	BaO/SiO_2,		Mn, Co, Ni,
	Fe_2O_3/SiO_2,		Ti, Zn, Se,
	ZnO/C		Pd, Pt
		Oxidants	
O_2, N_2O	N_2O, O_2	N_2O, O_2	N_2O_2, O_2
NO, SO_2			

The results obtained in the presence of zeolites were extremely unexpected. Table 3 presents the results of tests on certain zeolites under conditions close to those in experiments with vanadium catalysts. Evidently an appreciable amount of phenol was detected in the reaction products in a number of instances. Particularly promising results were obtained for zeolites of the type of pentasil ZSM-5 and $AlPO_4$-5. Three groups of investigators concluded independently in 1988 that ZSM-5 zeolites are extremely promising catalysts for the oxidation of benzene to phenol with nitrous oxide: Suzuki et al.[54] (Tokyo Technological Institute), Hubelman et al.[55]

(The Rhone-Poulenc Company), and Kharitonov et al.[56] (Institute of Catalysis, Novosibirsk). The zeolite catalysts made it possible to reduce the reaction temperature to 300–400 °C, to abandon the introduction of water vapour into the reaction mixture, and, what is most important, to ensure a high selectivity with respect to phenol. Although the maximum yield of phenol in these investigations was low (8–16%), it became clear that a system had been found which can serve as a basis for the creation of new effective catalysts. Further studies made it possible to improve greatly the parameters of the zeolite catalysts and to extend the range of reactions.[57–62]

Table 3. Catalytic properties of zeolites in the oxidation of benzene to phenol.

Type of zeolite	$SiO_2 : Al_2O_3$ molar ratio	Specific surface, $m^2 g^{-1}$	X, %	S, %
A	2.1	580	0.5	0
X	3.1	690	2.5	10
Y	4.8	890	6	5
Erionite	4.8	460	2.5	0
Clinoptilolite	10	80	16	0
Mordenite	14.9	620	12	0
ZSM-5	260	530	7.9	100
$AlPO_4$-5	–	300	4.5	100
Al_2O_3	–	200	11	0
SiO_2	–	190	0	–

Note. Composition of the reaction mixture (mol%); C_6H_6—5; N_2O—20; He—76; T = 500 °C; contact time 2 s; X = degree of conversion of benzene; S = selectivity with respect to phenol.

IV. The nature of the catalytic activity of zeolites

1. The role of iron

It appears unlikely that a reaction as involved and as stringent in its requirements as the oxidation of benzene to phenol could be achieved as a result of the influence of the aluminosilicate skeleton of the zeolite. According to Minachev and Kharlamov,[63] certain oxidation-reduction reactions can occur on alkali and alkaline earth metal cations forming part of the zeolite. However, in this instance all investigators emphasise the importance of the conversion of the ZSM-5 zeolite into the H-form. Indeed, as can be seen from Fig. 2, with increase in the sodium content with activity of the zeolite falls appreciably. Under these conditions, the selectivity of the reaction is unaffected and remains 100% in all cases.

It appears more natural to postulate that the activity may be associated with the presence in the zeolite of admixtures of transition metals to which no importance was attached in the first investigations. This may concern primarily iron, which is the commonest impurity introduced in the synthesis of zeolites. The influence of iron has been studied in detail.[64] For this purpose, a series of zeolite specimens with the ZSM-5 structure were synthesised. They had approximately the same $SiO_2 : Al_2O_3$ = 100 molar ratio but different iron contents, varying from 0.004 to 0.72 wt.% Fe_2O_3. The specimens of this iron-aluminosilicate series were designated by Fe(Al)-*N*, where *N* is a number indicating the content of iron expressed in wt.% Fe_2O_3.

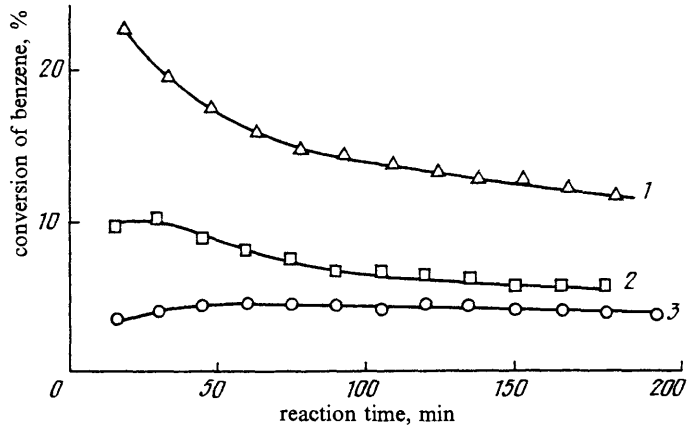


Figure 2. Dependence of the degree of conversion of benzene in the oxidation with nitrous oxide on the sodium content in the Fe(Al)-0.08 specimen (SiO_2/Al_2O_3 = 100; Fe_2O_3 = 0.08 wt.%). Na_2O content (wt.%): *1*, 0.06; *2*, 0.8; *3*, 1.1. Composition of the reaction mixture (mol%): C_6H_5—5, N_2O—20; He—75; T = 350 °C; contact time 2 s.

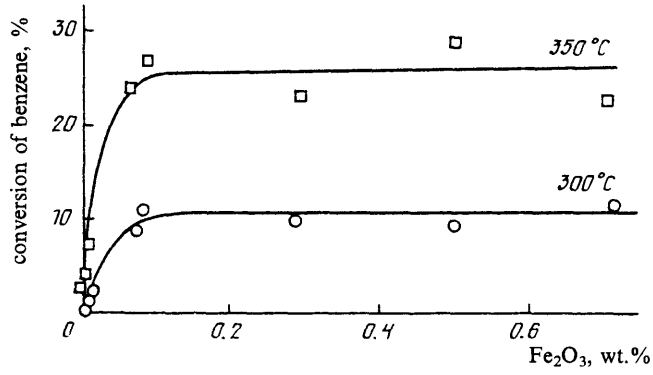


Figure 3. Dependence of the degree of conversion of benzene on the iron concentration in the Fe–Al–Si ZSM-5 zeolite specimens. The reaction conditions were the same as in Fig. 2.

Fig. 3 illustrates the dependence of the degree of conversion of benzene on the iron content in the Fe–Al–Si system plotted on the basis of the data of Panov et al.[64] Indeed, the Fe(Al)–0.004 and Fe(Al)–0.007 specimens, synthesised taking all possible precautions and virtually free of iron (0.004 and 0.007 wt.% Fe_2O_3 respectively), proved to be relatively inactive. With increase in the iron content to

0.1 wt.%, the degree of conversion of benzene increases appreciably but subsequently changes little. The Fe–Al–Si specimens containing 0.07–0.7 wt.% Fe_2O_3 exhibit such a high activity that they ensure a degree of conversion of benzene (X) at a level of 10% already at 300 °C with a selectivity with respect to phenol of 100%. At 350 °C, the degree of conversion reaches 25% for a selectivity of 95% and above on the best specimens. For higher values of X, the reaction selectivity falls owing to the further oxidation of phenol. Under these conditions, benzoquinone, catechol, hydroquinone, dibenzofuran, and cresol appear among the reaction products. The overall selectivity with respect to these substances can reach several per cent.[64]

The question of the catalytic properties of other metals is of considerable interest. Tests on specimens of the ZSM-5 zeolite containing V, Cr, Mn, Co, Ni, Cu, Ti, Zn, Sc, Pd, and Pt, which were introduced either during the synthesis of the zeolite[64] or by ion exchange,[54] showed that they are all inactive in the oxidation of benzene to phenol. It may be that iron is one of the few or even the only element capable of promoting this reaction with a high degree of efficiency. This question merits further careful study. One may note an analogy in the mechanism of the action of iron in the Fe-ZSM-5 composition and in cytochrome P-450 as well as certain artificial systems simulating its operation. These are systems which are also capable of effecting with a high degree of selectivity the oxidative hydroxylation of hydrocarbons, including the oxidation of benzene to phenol.[65]

2. The influence of aluminium

The iron introduced into the Al–Si matrix plays a decisive role in the catalytic properties of the ZSM-5 zeolite. The Fe–Al–Si specimens with the optimum iron content are greatly superior in their effectiveness to all other known catalysts, including ZSM-5 zeolites without specially added iron.[54–58] However, iron-containing zeolites with the same structure can be synthesised also in the absence of aluminium on a purely silicate base. Comparison of these two systems was of great interest from the standpoint of the influence of the chemical composition of the zeolite matrix on the catalytic properties of the added iron.

For this purpose, a study has been made[66] of a series of ZSM-5 zeolite specimens with an Fe–Si composition and a low content of the aluminium admixture (0.01–0.03 wt.% Al_2O_3) but with extensive variation of the iron content: from 0.003 to 4.8 wt.% Fe_2O_3. The formula Fe–N was used to designate these specimens. Fig. 4 shows that the influence of iron in this system is just as marked as in the Fe–Al–Si system. Thus, whereas in the presence of the Fe–0.003 specimen the oxidation of benzene with nitrous oxide occurs at a barely appreciable rate only at 500 °C, in the presence of specimens containing more than 2 wt.% Fe_2O_3 the degree of conversion of benzene reaches 25% already at 350 °C.

Although the relations illustrated in Figs. 3 and 4 are similar, attention should be drawn to the appreciable difference in the abscissa scales corresponding to the iron content. In order to represent the picture as a whole, the data concerning the influence of iron in the Fe–Si and Fe–Al–Si systems are presented in Fig.5 using logarithmic coordinates. Evidently, the relations in these two systems are appreciably displaced relative to one another in respect of the iron content. Thus, in order to attain the same degree of conversion in the case of the Fe–Si system, it is necessary to introduce 10–30 times more iron than in the Fe–Al–Si system. Conversely, for the same iron concentration, the activity of specimens containing aluminium is in many instances an order of magnitude or more higher than the activity of specimens without aluminium. Such a marked influence of aluminium suggests that the active centres for the reaction include not only Fe atoms but also Al atoms.

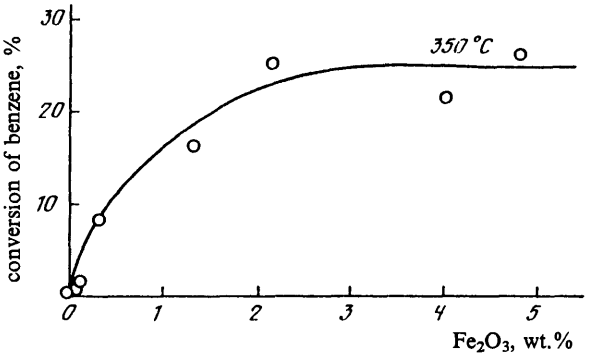


Figure 4. Dependence of the degree of conversion of benzene on the iron concentration in the Fe–Si ZSM-5 zeolite specimens. The reaction conditions were the same as in Fig. 2.

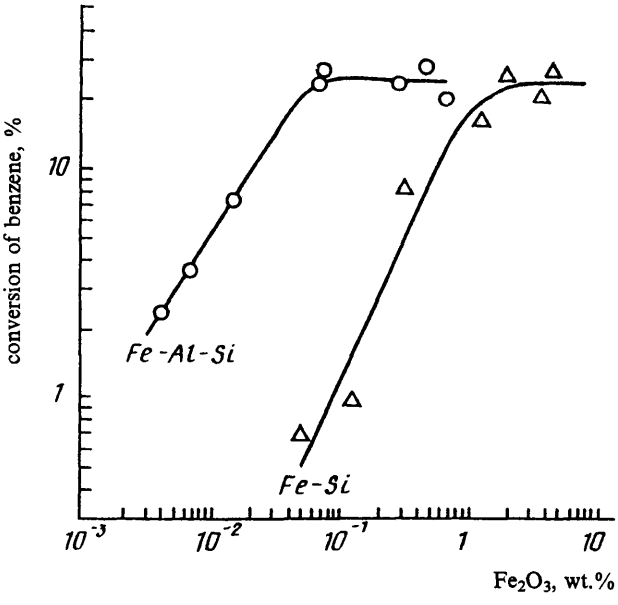


Figure 5. Dependence of the degree of conversion of benzene on the iron concentration in the Fe–Si and Fe–Al–Si ZSM-5 zeolite specimens at 350 °C. The reaction conditions were the same as Fig. 2.

This hypothesis was examined in a study[24] involving the analysis of the influence of iron on the catalytic activity of Fe-ZSM-5 specimens in the N_2O decomposition reaction. Direct comparison of

the concentration of the active centres (which can be reliably measured in these systems) with the concentration of the impurity Al atoms did not confirm this hypothesis. According to the above data,[24,66] the presence of aluminium does not affect the composition and catalytic properties of the iron-containing active centres but leads to their higher concentration as a consequence of the favourable effect of aluminium on the distribution of iron in the zeolite matrix.

V. Specific features of nitrous oxide as an oxidant. The mechanism of the hydroxylation of benzene

Iron oxide is known to exhibit a moderate activity in extensive oxidation reactions but it does not promote partial oxidation reactions.[16] The activity of the iron-containing zeolites in the oxidation of benzene to phenol therefore appears to be an extremely unexpected property of iron, manifested in the presence of nitrous oxide.

Table 4. The influence of the nature of the oxidant on the oxidation of benzene to phenol on Fe-ZSM-5 and Fe_2O_3 specimens.

Catalyst	N_2O oxidant		O_2 oxidant	
	X, %	*S*, %	*X*, %	*S*, %
Fe - 2.15	25.6	96.0	3.3	0.0
Fe(Al) - 0.08	27.0	99.0	0.0	-
Fe_2O_3	5.5	0.0	24.5	0.0

Note. Composition of the reaction mixture (mol%); C_6H_6 — 5; N_2O — 20; He — 75; T = 500 °C; contact time 2 s.

The specific features of nitrous oxide as an oxidant constitute one of the most interesting aspects of the study of the mechanism of the hydroxylation of benzene. These specific features are clearly seen on examining Table 4, which presents data for the oxidation of benzene on two typical Fe-ZSM-5 specimens with the Fe—Si and Fe—Al—Si compositions. Evidently, the replacement of nitrous oxide by molecular oxygen entails a sharp decrease in the rate of reaction. Whereas the degree of conversion of benzene on both specimens at 350 °C in the presence of N_2O is 25—27%, in the presence of O_2 and the ferrosilicate Fe—2.1 specimen it diminishes to 3% and on the ferroaluminosilicate Fe(Al)—0.08 specimen it diminishes to an infinitesimal value. [In the presence of O_2, the activity of the Fe(Al)—0.608 specimen is so low that the benzene oxidation reaction proceeds at a measurable rate only at 550 °C.] The fact that the reaction pathway changes completely under these conditions merits special attention. Instead of the formation of phenol with a selectivity of 96—99%, only total oxidation products are formed in the presence of O_2.

Such a marked influence of the nature of the oxidant justifies the hypothesis that this is associated with significant changes in the state of the surface oxygen. This stimulated a series of studies on the mechanism of the nitrous oxide decompositon reaction in the presence of the ZSM-5 zeolites,[23,24,67,68] because this particular reaction supplies oxygen to the catalyst surface. Such investigations established that the introduction of iron into the zeolite results in the formation of active centres (called α-centres), on which the decomposition of N_2O is accompanied by the formation of a new form of surface oxygen (the α-form), whose properties have been studied in detail.[23,24,67—70] The main features of this form of oxygen are that (1) it exists on iron-containing active centres of ZSM-5 but not on Fe_2O_3 and many other iron-containing specimens investigated, (2) the energy of the bond between this form of oxygen and the surface is anomalously low and close to the bond energy in the O_2 molecule, (3) is it thermally stable up to 300 °C, above which it undergoes irreversible desorption, (4) it is formed on decomposition of N_2O but not on adsorption of O_2, and (5) it is highly reactive—it participates in O_2 isotope exchange at room temperature and oxidises CO and CH_4.

α-Oxygen has been compared with the thoroughly investigated surface oxygen radical-ions O^- and O_2^-.[71] The reactivity of the α-form is close to that of the O^- radical-ion,[72—74] but it exhibits a number of significant differences which preclude the identification of these two forms of oxygen. According to Haber's classification,[26] the α-form should be regarded as an electrophilic state of surface oxygen. According to Sheveleva et al.,[66] the ability to form the α-form of surface oxygen actually accounts for the specific behaviour of N_2O as a benzene oxidant. The mechanism of formation of phenol with participation of the α-form (O) can be represented by the following stages:

(1) $N_2O + ( ) \rightarrow N_2 + (O)$,
(2) $C_6H_6 + (O) \rightarrow (C_6H_5OH)$,
(3) $(C_6H_5OH) \rightleftarrows C_6H_5OH + ( )$.

The formation of phenol is not observed in the presence of catalysts which do not contain α-oxygen. This is indicated both by the results, already mentioned, which were obtained in the presence of ZSM-5 zeolites containing different transition metals (other than iron) and the results of tests on oxide and metallic systems presented in Table 2. This is likewise confirmed by numerous unsuccessful attempts, undertaken by ourselves jointly with Krivoruchko and Skripchenko, to synthesise active catalysts by introducing iron into various non-zeolite matrices (Al_2O_3, SiO_2, TiO_2, MgO, and ZnO). Neither the existence of the α-form nor the formation of phenol were observed in any of these instances.

It has been shown[24] that the rate of decomposition of N_2O is determined by the concentration of the active centres which fix the α-form of surface oxygen, and is described by a single relation, involving direct proportionality, which is valid for all the specimens of the Fe—Si and Fe—Al—Si systems. If the mechanism of the oxidation of benzene represented by stages (1)—(3) is valid, then the above single relation should also hold for this reaction. Indeed, if the degree of conversion of benzene is represented by its dependence not on the concentration of iron (as was done in Fig. 5) but on the concentration of the active centres c_α, then we obtained a single relation for all the test specimens, which is illustrated in Fig. 6. In contrast to the decomposition of N_2O, this relation reaches a plateau at a high concentration of α-centres, which can be explained by the inhibiting effect of the reaction product—phenol.[66] Starting with a certain value of c_α, this inhibition becomes so significant that it virtually compensates for the further increase in the number of active centres.

A quantum-chemical model of the active centres, which makes it possible to account for the characteristics of α-oxygen on Fe-ZSM-5, has been described.[75]

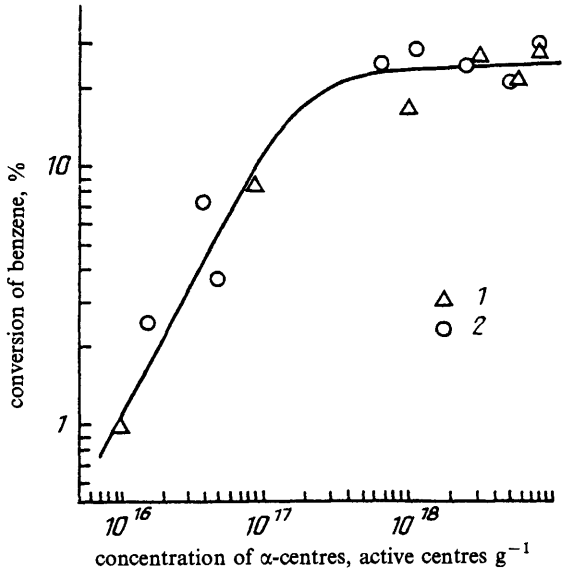


Figure 6. Dependence of the degree of conversion of benzene on the concentration of active centres on the Fe–Si and Fe–Al–Si ZSM-5 specimens at 350 °C. The reaction conditions were the same as in Fig. 2; *1*, Fe–Si; *2*, Fe–Al–Si.

Table 5. Prices of certain chemical products (USA, October, 1989).

Product	Price, U.S. dollars/tonne	Product	Price, U.S. dollars/tonne
Benzene	467	Catechol	4300
Nitrous oxide	507	Resorcinol	10000
Phenol	1091	Hydroquinone	4300

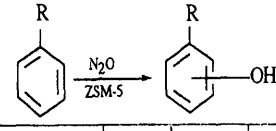
VI. Hydroxylation of benzene derivatives

The data published in the literature on the oxidation of benzene with nitrous oxide permit the conclusion that the best zeolite catalysts afford a yield of phenol up to 25–30% for a selectivity of 95–100%.[64,66] It must be admitted that, compared with numerous classical gas-phase oxidation processes, these results appear extremely modest. Thus in the oxidation of acrolein to acrylic acid[76] or of methanol to formaldehyde[77] in the presence of oxide catalysts, the yield of products reaches 95–98%. However, bearing in mind that this reaction is an alternative to the cumene process where the degree of convesion of the reactant in each of the three stages does not exceed 20–30%, the above parameters do not appear quite so bad.

According to the existing prices (Table 5), the expenditure on the raw material in the synthesis of phenol in terms of the above parameters should be 60–75% of the cost of the phenol, which can apparently ensure the competitiveness of the new process. This expenditure can be diminished somewhat by employing, instead of nitrous oxide of medical grade, a product with a lower degree of purification.

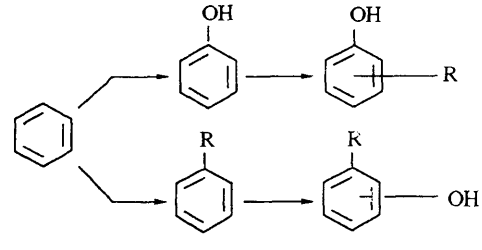
The question whether the given hydroxylation method is applicable to the preparation of more complex products which are more difficult to synthesise is important from the practical point of view. As can be seen in relation to dihydric phenols (Table 5), the cost of substituted phenols is much higher than that of phenol, so that the expenditure on nitrous oxide would no longer be significant in this case.

Table 6. Oxidative hydroxylation of benzene derivatives.



Initial compound	T, °C	X, %	S, %	Proportions of isomers, %			Refs.
				o	m	p	
Cl	330	6.7	100	58	$m \simeq p$		[54]
F	350	9.2	90.4	26.7	20.0	53.3	[55]
	400	11.0	90.4	31.1	22.7	46.2	
	450	15.2	85.3	24.4	23.7	51.9	
CH_3	350	48.1	22	$o \simeq m \simeq p$			[60]
OH	325	8.0	98	17	–	83	[60]
	350	11.5	92	18	–	82	

Two fundamentally different ways of synthesising benzene derivatives containing two substituents in the aromatic ring are possible:



These procedures differ in the sequence in which the functional groups are introduced. In view of the inadequate effectiveness of the existing hydroxylation methods, the first procedure is used nowadays in the vast majority of instances, i.e. phenol is synthesised initially and then the appropriate second group introduced with the aid of alkylation, halogenation, nitration, etc. processes.[46,47] In many cases, the processes in the second stage proceed non-selectively, require a large number of distillations, and afford a low yield of the product. For this reason, the search for effective aromatic ring hydroxylation methods, which would not involve the functional groups already introduced, is of considerable interest.

The hydroxylation of benzene derivatives with the aid of N_2O has so far been little investigated, although the possibility of such reactions in principle is not open to doubt. Table 6 presents the results of the oxidative hydroxylation of halobenzenes, toluene, and phenol. It is of interest to note that hydroxylation with the aid of nitrous oxide proceeds also when the aromatic ring contains deactivating substituents such as fluorine and chlorine, which (so far as we are aware) cannot be achieved in liquid-phase hydroxylation with the aid of peroxides.

In the oxidation of halobenzenes and toluene, hydroxylation takes place with formation of all three geometrical isomers, whereas in the oxidation of phenol, only the *o*- and *p*-isomers, i.e. catechols and hydroquinone (benzoquinone), are formed. The differences in the proportions of isomers may be associated both with the different nature of the substance oxidised and with the different chemical composition of the catalysts, the details of which are not reported in the patents.

VII. Conclusion

The earlier attempts in 1960–1970 to employ zeolites in oxidative catalysis did not yield positive results. This is because the transition metals introduced into the zeolite lose their ability to activate molecular oxygen. Although it has been possible in a number of instances to achieve effective parameters of the metal-containing zeolites, nevertheless they did not reach the level ensured by the best catalyst of the traditional type.

Studies carried out in the last decade led to a qualitative change in the situation. This was mainly promoted by two factors: the synthesis of high-silica zeolites of the type of pentasil and their metal-silicate analogues and the use of bound oxygen in the form of various oxygen-containing compounds.

The most effective among the oxygen-containing compounds proved to be H_2O_2 and N_2O. The results of the liquid-phase oxidation with hydrogen peroxide on titanosilicate zeolites are well known. They led to the development of a series of new methods for carrying out the reactions. In the present review, we attempted to draw attention to recent successes in the reactions involving gas-phase oxidation with nitrous oxide. The best parameters in this respect were achieved in the oxidation of benzene to phenol in the presence of iron-containing ZSM-5 zeolites. The uniqueness of this catalytic system is due to the existence of a specific form of surface oxygen formed on decomposition of the N_2O molecules.

Hydroxylation with the aid of nitrous oxide is particularly promising for the synthesis of complex compounds containing several functional groups in the aromatic ring. Studies on these lines are in an initial stage. The few, unfavourable data on the oxidation of benzene derivatives show that in this instance the reactions do not proceed quite so smoothly as in the oxidation of benzene itself and entail a reduced selectivity with respect to useful products. A faster deactivation of the catalysts is to be expected, although the existing patents to not report this.

Gas-phase reactions are known to have a series of important technological advantages over the liquid-phase version. However, analysis of the existing experimental data shows[78–80] that, when complex syntheses are carried out, these advantages may be lost as a consequence of the complications associated with the inadequate thermal stability of the reacting molecules and the difficulty of their desorption from the catalyst surface. Naturally, these complications must be taken into account in assessing the prospects of gas-phase oxidative hydroxylation. Nevertheless, the possibility of using an oxidant as readily available, safe, and cheap, as N_2O, which has considerable advantages over the oxidants used in the liquid phase, may significantly tip the scales in favour of this procedure. Furthermore, attention should be drawn to yet another important feature, namely the fact that the presence of deactivating substituents in the aromatic ring is not an obstacle to the introduction of a hydroxy-group with the aid of N_2O.

The importance of the search for new ways of hydroxylating aromatic compounds is so great that even the level of parameters already achieved is of practical interest. These parameters will undoubtedly be improved by a wide variety of methods for the modification of zeolites which permit a detailed adjustment of the most important characteristics of zeolites such as the chemical compositions of their internal and external surfaces, acidity, pore structure, steric selectivity, etc.[18,19,81–85] Hitherto, these procedures have not been used to optimise the catalysts of the oxidation with nitrous oxide.

An important step would also be to extend studies of this type to other classes of zeolites and zeolite-like materials, the number of which constantly grows by virtue of the advances in the adoption of new methods of their synthesis.[18,86,87] It may be hoped that further research will permit an appreciable increase in the effectiveness of this new method for the hydroxylation of aromatic compounds and probably its extension to other classes of organic substances.

References

1. US P. 4 410 501
2. G Perego, G Bellussi, C Corno, et al. *New Developments in Zeolite Science and Technology: Proceedings of the 7th International Conference on Zeolites*, Tokyo, Elsevier, Kodansha, 1986, p. 129
3. B Notary *Innovation in Zeolite Materials Science: Proceedings of International Symposium, Nieuwpoort, 1987*, Elsevier, Amsterdam, 1988, p. 413
4. U Romano, A Esposito, F Maspero, et al. *New Developments in Selective Oxidation: Proceedings of International Symposium, Rimini, 1989*, Prepr. Univ., Bologna, 1989, Paper B1
5. P Roffia, G Leofanti, A Casana, et al. *New Developments in Selective Oxidation: Proceedings of International Symposium, Rimini, 1989*, Prepr. Univ., Bologna, 1989, Paper 42
6. M G Clerici *Appl. Catal.*, 1991, **68** 249
7. D R C Huybrecht, L Bruyker, P A Jacobs *Nature (London)*, 1990, **345** 240
8. T Tatsumi, M Nakamura, S Nagishi, H Tominaga *J. Chem. Soc., Chem. Commun.*, 1990, 476
9. US P. 4 578 521

10. A Thangaraj, R Kumar, P Ratnasamy *Appl. Catal.*, 1990, **57** L1
11. J S Reddy, S Sivasanker *Catal. Lett.*, 1991, **11** 241
12. H Bekkum, H W Kouwenhoven *Heterogeneous Catalysis and Fine Chemicals: Proceedings of International Symposium*, Elsevier, Poitiers, 1988, p. 45
13. R F Parton, J M Jacobs, D R Huybrecht, P A Jacobs *Zeolites as Catalysts, Sorbents and Detergents Builders: Proceedings of International Symposium*, Wurzburg, Elsevier, 1988, p. 163
14. W F Hoelderich *Zeolites: Facts, Figures, Future: Proceedings of the 8th International Zeolite Conference*, Amsterdam, Elsevier, 1989, p. 69
15. Ya I Isakov, Kh M Minachev *Neftekhimiya*, 1990, (30) 291
16. G I Golodets *Geterogenno-Kataliticheskoe Okislenie Organicheskikh Veshchestv* (Heterogeneous-Catalytic Oxidation of Organic Substances), Naukova Dumka, Kiev, 1978, 375 pp
17. O V Krylov, V F Kiselev *Adsorbtsiya i Kataliz na Perekhodnykh Metallakh i Ikh Oksidakh* (Adsorption and Catalysis on Transition Metals and Their Oxides), Khimiya, Moscow, 1981, 286 pp
18. P Ratnasamy, R Cumar *Catalysis Today*, 1991, **9** 328
19. K G Ione *Polifunktsional'nyi Kataliz na Tseolitakh* (Polyfunctional Catalysis on Zeolites), Nauka, Novosibirsk, 1982, 230 pp
20. N Giordano, S Montelacini, C Zen *Proceedings of the 3rd International Conference on Molecular Sieves*, Zurich, 1973, p. 449
21. J C Oudejans, F J Gaag, H Van Bekkum *Proceedings of the 6th International Zeolite Conference, Reno, 1983*, Butterworths, 1984, p. 536
22. D B Tagiyev, Kh M Minachev *New Developments in Zeolite Science and Technology: Proceedings of the 7th International Conference on Zeolites, Tokyo*, Elsevier, Kodansha, 1986, p. 981
23. G I Panov, V I Sobolev, A S Kharitonov *J. Mol. Catal.*, 1990, **61** 85
24. V I Sobolev, G I Panov, A S Kharitonov, V N Romannikov, A M Volodin, K G Ione *J. Catal.*, 1992, **138** 312
25. G K Boreskov *Catalytic Science and Technology*, Springer-Verlag, Berlin, 1982, Vol. 3, p. 39
26. J Haber *Proceedings of the 8th International Congress on Catalysis, Berlin*, Verlag Chemie, 1984, Vol. 1, p. 85
27. K G Ione, P N Kuznetsov, V N Romannikov, N V Klyueva *Primenenie Tseolitov v Katalize* (Applications of Zeolites in Catalysis), Nauka, Novosibirsk, 1977, p. 103
28. Z Tvaruzkova, G Centi, P Jiru, F Trifiro *Appl. Catal.*, 1985, **19** 307
29. R F Howe, H Minming *Proceedings of the 9th International Congress on Catalysis, Ottawa*, 1988, Vol. 4, p. 1585
30. A Miyamoto, Y Iwamoto, H Matsuda, I Inui *Catal. Lett.*, 1991, **11** 1233
31. A V Kucherov, T N Kucherova, A A Slinkin *Catal. Lett.*, 1991, **10** 289
32. *New Horizons in Catalysis: Proceedings of the 7th International Congress on Catalysis, Tokyo*, 1980, 1537 pp
33. *New Developments in Selective Oxidation: Proceedings of the European Workshop Meeting, Louvain-La-Neuve*, 1986; *Catal. Today*, 1987, **1**(1/3) 365
34. *New Developments in Selective Oxidation: Preprint from the 3rd European Workshop Meeting, Louvain-La-Neuve*, 1991, 780 pp
35. *Catalysis By Zeolites: Proceedings of International Symposium, Lyons*, 1980, 351 pp
36. *Structure and Reactivity of Modified Zeolites: Proceedings of International Conferences, Prague*, 1984, 376 pp
37. *Zeolite: Synthesis, Structure, Technology and Application: Proceedings of International Symposium, Portoroz-Portorose*, 1984; Stud. Surf. Sci. Catal., 1985, **24** 690
38. A E Lisovskii, Z A Talibova, A E Portyanskii, A M Musaev, T G Alkhazov *Neftekhimiya*, 1983, **35** 622
39. S S Shepelev, K G Ione *React. Kinet. Catal. Lett.*, 1983, **23** 319
40. S N Vereshchagin, N N Shishkina, A G Anshits *New Developments in Selective Oxidation: Proceedings of International Symposium, Rimini, 1989*, Prepr. Univ. Bologna, 1989, Paper F. 2
41. A Kh Mamedov, P A Shiryaev, D P Shashkin, O V Krylov *New Developments in Selective Oxidation: Proceedings of International Symposium, Rimini, 1989*, Prepr. Univ. Bologna, 1989, Paper F. 1
42. Z G Osipova, S B Ushkov, V D Sokolowskii, A V Kalinkin *New Developments in Selective Oxidation: Proceedings of International Symposium, Rimini, 1989*, Prepr. Univ. Bologna, 1989, Paper H. 4
43. L W Zatorskii, G Centi, J L Nieto, et al. *Catal. Lett.*, 1991, **11** 1243
44. G J Hutchings, M S Scurell, J R Woodhouse *Chem. Soc. Rev.*, 1989, **18** 251
45. J R Anderson, P Tsai *J. Chem. Soc., Chem. Commun.*, 1987, **19** 1435
46. J M Tedder, A Nechvatel, A Jubb *Basic Organic Chemistry* (Translated into Russian), Mir, Moscow, 1977, 701 pp
47. L S Efros, M V Gorelik *Khimiya i Tekhnologiya Promezhutochnykh Produktov* (The Chemistry and Technology of Intermediates), Leningrad, 1980, 475 pp
48. Ph M Kohn, L Bolton, R Cottrell *Chem. Eng.*, 1979, **86** 62
49. Japanese P. 58–146522
50. M Iwamoto, K Matsukami, S Kagawa *J. Phys. Chem.*, 1983, **87** 903
51. *Chem. Econ. Eng. Rev.*, 1982, **14** 47
52. *Process Econ. Intern.*, 1983, **4** 48
53. A S Kharitonov, A I Yartsev, E A Paukshtis, et al. *React. Kinet. Catal. Lett.*, 1988, **37** 7
54. E Suzuki, K Makashiro, Y Ono *Chem. Soc. Jpn. Chem. Commun.*, 1988, 953
55. French P. 2 630 735
56. USSR P. Appl. 4 446 646, 22.06.88; Granted from 26.07.89
57. Europen P. 341 165
58. French P. 2 648 810
59. USSR P. Appl. 4 673 039, 22.02.89; Granted from 25.12.89
60. USSR P. Appl. 4 746 635, 11.08.89; Granted from 29.07.91
61. US P. 5 001 280
62. US P. 5 055 623
63. Kh M Minachev, V V Kharlamov *Okislitel'no-Vosstanovitel'nyi Kataliz na Tseolitakh* (Oxidation-Reduction Catalysis on Zeolites), Nauka, Moscow, 1990, 147 pp
64. G I Panov, G A Sheveleva, A S Kharitonov, et al. *Appl. Catal.*, 1992, **82** 31
65. N Kitajima, M Ito, H Fukui, Y Moro-oka *J. Chem Soc., Chem. Commun.*, 1991, 102
66. G A Sheveleva, G I Panov, A S Kharitonov, et al. *Sibirskii Khim. Zh.*, 1992, (5) 93

67. G I Panov, V I Sobolev, A S Khartinov *Catalytic Science and Technology*, Kodansha, Tokyo, 1991, Vol. 1, p. 171
68. A S Kharitonov, V I Sobolev, G I Panov *Kinet. Katal.*, 1989, **30** 1512
69. V I Sobolev, O N Kovalenko, A S Kharitonov, et al. *Mendeleev Commun.*, 1991, **1** 29
70. V I Sobolev, A S Kharitonov, G I Panov *Dokl. Akad. Nauk SSSR*, 1989, **301** 1419
71. V I Sobolev, Candidate's Thesis in Chemical Sciences, Novosibirsk, 1991
72. N I Lobatkina, V A Shvets, V B Kazanskii *Kinet. Katal.*, 1978, **19** 979
73. K N Spiridonov, O V Krylov *Problemy Kinetiki i Kataliza*, 1975, **16** 7
74. K Aika, J H Lunsford *J. Phys. Chem.*, 1977, **81** 1393
75. M Y Filatov, A G Pelmenshchikov, G M Zhidomirov *Proceedings of the 10th International Congress on Catalysis*, Budapest, 1992, p. 31
76. T V Andrushkevich, G Ya Popova *Usp. Khim.*, 1991, **60**(9) 1999 [English translation in *Russ. Chem. Rev.*, 1991(9)]
77. B I Popov, N G Skomorokhova *React. Kinet. Catal. Lett.*, 1981, **18** 101
78. I Pasquone *Catalysis Today*, 1987, **1** 297
79. R A Sheldon *Catalysis Today*, 1987, **1** 351
80. G Perot, M Guisnet *J. Mol. Catal.*, 1990, **61** 173
81. N Topsoe, F Joensen, E D Deruane *J. Catal.*, 1988, **110** 404
82. L Rongsheng, Z Wuyang, W Quon *Appl. Catal.*, 1991, **71** 185
83. A V Kucherov, A A Slinkin *Kinet. Katal.*, 1987, **28** 1198
84. Y F Chu, C F Keweshan, E F Vansant *Appl. Catal.*, 1990, **57** 749
85. E S Shpiro, G V Antoshin, O P Tkachenko, et al. *Appl. Catal.*, 1985, **19** 31
86. D E W Vaughan *Catal. Lett.*, 1991, **11** 95
87. S Schubert, H M Ziethen, A X Trautwein, et al. *Appl. Catal.*, 1990, **57** 735

Received 18th June 1992

Translated from *Uspekhi Khimii* **61** 2078–2104 (1992) U.D.C. 541.127

The kinetics of gas-phase processes in systems containing carbon and sulphur

V S Arutyunov
Institute of Chemical Physics, Russian Academy of Sciences, Moscow

ABSTRACT. Data on the kinetics of the processes in gas-phase systems containing carbon and sulphur, which are of considerable importance in the combustion of sulphur-containing fuels, the reduction of industrial sulphur-containing gases, the industrial preparation of sulphur, etc., have been reviewed.

The bibliography contains 87 references.

Contents

I. Introduction 1140
II. The role of sulphur compounds and their transformation in the combustion and oxidation of hydrocarbons 1140
III. The gas-phase reduction of sulphur dioxide by hydrocarbons 1143
IV. The formation of carbon disulphide and carbonyl sulphide in gas-phase processes 1148
V. The kinetics and mechanism of the processes in the C–S–O system 1148
VI. The combined oxidation, photolysis, and radiolysis of carbon- and sulphur-containing compounds 1150
VII. The reaction of carbon- and sulphur-containing molecules in atmospheric processes 1152

I. Introduction

The kinetics of gas-phase reactions involving even basic sulphur-containing molecules have not been well studied. The principal results have been obtained in studies of the transformation of sulphur-containing compounds in the atmosphere,[1,2] their role in combustion and high-temperature corrosion,[3,4] and a number of model reactions (the oxidation of hydrogen sulphide,[5] carbon disulphide,[6] and various others). There has recently been a steady increase in the practical importance of gas-phase processes involving both sulphur-containing and carbon-containing compounds. These include the purification and processing of sulphur-containing natural gases,[7,8] the reduction of concentrated industrial sulphur-containing gases by hydrocarbons,[9,10] the production of gaseous sulphur[9,11] and carbon disulphide,[12] etc. The need to develop new industrial processes and to optimise existing ones arouses a natural interest in the kinetics and mechanism of these reactions. Unfortunately, there have been very few studies of the kinetics of gas-phase reactions involving compounds of sulphur and carbon, except for several model reactions (the oxidation of CS_2 and COS). There are very few published data on the rate constants of elementary reactions involving carbon- and sulphur-containing species.[13] Difficulties arise when attempts are made to extend generally accepted ideas about the decisive role of radical processes in complex gas-phase reactions, so clearly demonstrated in the description of the oxidation of hydrocarbons, to the kinetics of processes involving sulphur-containing molecules.

The present review attempts to summarise available data on the kinetics of gas-phase processes in systems containing compounds of sulphur and carbon.

II. The role of sulphur compounds and their transformation in the combustion and oxidation of hydrocarbons

The concentration of sulphur in different types of hydrocarbon fuel varies over a very wide range, in some cases amounting to several tens percent. The interest in the chemistry of combustion processes involving sulphur compounds is related to three basic problems: 1, the direct influence of sulphur compounds on combustion processes; 2, atmospheric pollution by sulphur-containing combustion products, principally SO_2;[3] and 3, high-temperature corrosion involving sulphur compounds, where a fundamental role is played by SO_3 molecules.[4,14]

A practically exhaustive review of work on combustion in sulphur-containing systems carried out up to 1972 has been published.[15] The presence of sulphur even in quantities less than 1%, particularly in rich mixtures, has a significant influence on all the characteristics of a process, namely temperature, rate of flame propagation, carbon formation, and the formation of NO_x. These effects are a direct manifestation of the chemistry of sulphur, primarily its influence on the concentration of radicals in the flame. The chemistry of sulphur compounds in hydrogen flames has been studied in most detail. Since the same processes predominate in hydrocarbon flames, it is appropriate to examine them briefly in this section.

Both experiments and numerical modelling show that even in rich flames, SO_2 is the predominant sulphur-containing compound, irrespective of the compound in which sulphur is introduced into the flame, although for rich mixtures the formation of H_2S, S_2, and other reduced compounds of sulphur is much more favourable from the thermodynamic viewpoint.[16] On the other hand, even in very lean mixtures it is rarely possible to detect sulphur trioxide SO_3 in quantities greater than several percent of the SO_2 concentration, and this also shows poor agreement with the result expected for thermodynamic equilibrium.[15] Elemental sulphur S_2 is the sulphur-containing species of second importance in flames, but its

concentration also does not reach the equilibrium values. The increase in the SO_2 concentration in rich flames leads to a predominant increase in the formation of S_2 from H_2S.[16]

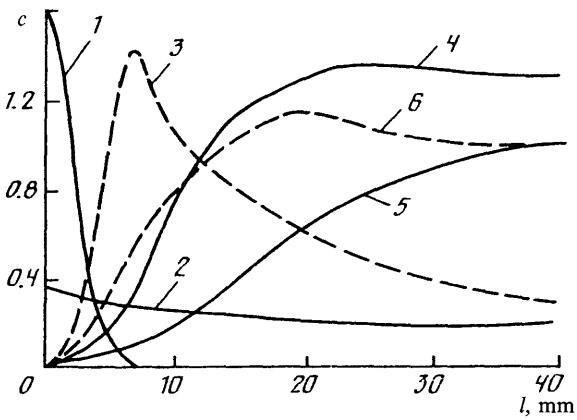
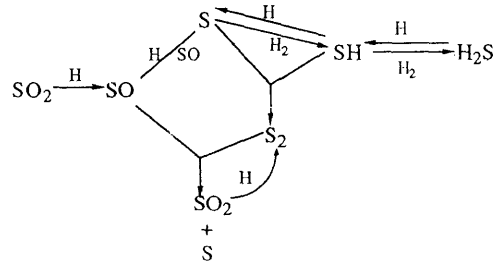


Figure 1. Experimental concentration profiles (c is the mole fraction) of the products in a laminar hydrogen flame $H_2/O_2/Ar$ containing 3% SO_2 (φ = 2.0, [Ar] = 37%, p = 150 torr);[16] *1*, 12.8[O_2]; *2*, 10[SO_2]; *3*, 400[SO]; *4*, 300[S_2]; *5*, 300[H_2S]; *6*, 4000[SH]; l is the distance along the flame.

An important feature of sulphur-containing flames is their two-stage character. Even after the principal combustion processes are complete, sulphur compounds continue to undergo continuous processes of rearrangement, associated with a change in temperature and the concentration of radicals. A detailed experimental and theoretical study of sulphur-containing hydrogen flames[16] has shown that the principal intermediate product, from which all reduced compounds of sulphur are formed, is SO, which is rapidly formed in the main reaction zone in the presence of high concentrations of radicals, but its concentration decreases sharply when the main combustion process is complete (Fig. 1). Reduced compounds of sulphur (S_2, SH, H_2S) begin to be formed after the maximum concentration of SO has been passed, and the S_2 and H_2S concentration profiles are approximately the same. An important role in the chemistry of sulphur compounds in flames is played by diffusion processes. Practically all reduced compounds of sulphur formed in the later stages of the process diffuse back into the zone of lower temperatures and higher concentrations of radicals, where they undergo exothermic reactions to give more highly oxidised compounds. An important conclusion from the work cited,[16] confirmed by mathematical modelling, is that all the reduced compounds of sulphur are produced by the intermediate formation of S atoms, as shown in the diagram for the transformations of sulphur-containing compounds in a laminar hydrogen flame in the zone corresponding to the completion of the main oxidation processes



The most significant influence of sulphur on the processes in flames is related to its catalytic action in radical recombination processes. According to the proposed mechanism[17]

$$H + SO_2 + M \longrightarrow HSO_2 + M,$$
$$H + HSO_2 \longrightarrow H_2 + SO_2,$$
$$OH + HSO_2 \longrightarrow H_2O + SO_2,$$

the presence of sulphur has a significant influence on the concentration of radicals driving the chain process. Thus according to calculations,[16] the presence of up to 3% sulphur lowers the maximum concentration of H atoms by a factor of two, and their concentration in the post-combustion zone by a factor of more than ten. This naturally leads to the experimentally observed decrease in the rate of propagation of the flame and to the increase in the temperature in relatively cold rich flames by almost 100 K.[16,18]

Although the principal active sulphur-containing species S, SO, and SH have been identified experimentally in flames, attempts to record the presence in flames of the radicals HSO_2 and HSO_3, which according to existing ideas are responsible for the catalytic recombination of radicals, have as yet been unsuccessful, despite the fact that, according to calculations, HSO_2 is formed very rapidly in the flame, and the estimated $H-SO_2$ bond energy exceeds 48.5 kcal mol^{-1} and possibly reaches 63 kcal mol^{-1}.[19] Nevertheless, the real existence of these radicals can hardly be doubted. Their exclusion from the kinetic schemes gives values for the concentrations of reduced compounds of sulphur which are 10–100 times lower than the values actually observed. In addition to indications of the formation of these radicals in solid matrices, there are experimental indications of the existence in the gas phase of HSO_3 radicals with a lifetime of about 1 μs.[20] The catalytic influence of SO_2, which lowers the concentration of radicals in the flame, brings about a significant shift in the distribution of sulphur-containing species towards the formation of more highly reduced compounds of sulphur.[16]

There are experimental indications[21] of the possible existence under certain conditions of the opposite effect of promotion of slow oxidation processes by the reaction

$$HO_2 + SO_2 \longrightarrow SO_3 + OH,$$

but this requires more detailed study.

The formation and decomposition of sulphur trioxide are the most important processes in the zone after sulphur-containing flames. As already noted, even in a large excess of oxygen SO_3 is rarely formed in quantities greater than several percent of the SO_2 concentration. Nevertheless, the presence of even these small quantities of SO_3 is of considerable importance for the kinetics and

more particularly the technology of combustion processes. The principal channel for the formation of SO_3 is the reaction

$$O + SO_2 + M \longrightarrow SO_3 + M,$$

so that, for example, the quantity of SO_3 formed in the oxidation of carbon monoxide, where the concentrations of oxygen atoms are high, is much greater than in hydrogen and hydrocarbon flames. For the same reason, the addition to the flame of substances which react rapidly with oxygen atoms leads to a significant decrease in the SO_3 concentration.[15] These questions are closely related to the problems of corrosion by sulphur.

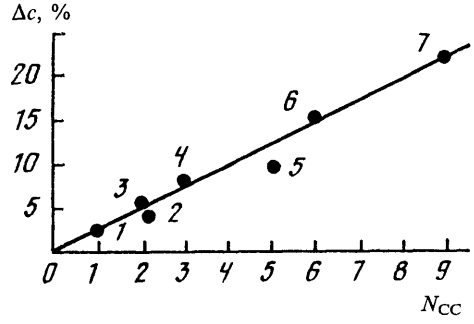


Figure 2. Influence of sulphur dioxide on the ignition limits of hydrocarbons; Δc, % is the required increase in the concentration of hydrocarbons for the addition of 20 torr SO_2 to its mixture with 200 torr oxygen (T = 700 °C);[15] N_{CC} is the number of C–C bonds in the hydrocarbon; *1*, ethane; *2*, acetone; *3*, ethylene; *4*, acetylene; *5*, n-hexane; *6*, cyclohexane; *7*, benzene.

The above processes involving sulphur-containing molecules predominate to the same extent in both hydrogen and hydrocarbon flames, and have been briefly examined here in order to give a more complete picture of the role of sulphur in oxidation processes. A specific feature of sulphur-containing hydrocarbon flames is the formation of CS_2, COS, and organosulphur compounds, and this has been much less extensively studied. Very little is known about the influence of SO_2 on the kinetics of the slow oxidation of hydrocarbons. It has been shown[22] that even at 200–250 °C the addition of SO_2 to a reaction mixture containing methane, n-hexane, methanol, or dimethyl ether leads to the formation of SO_3. In other studies of the slow oxidation of organic compounds,[23] however, only the presence or formation of oxides of nitrogen in the mixture led to appreciable consumption of SO_2, and from this it was suggested that at temperatures below 700 °C the rate of the reaction of SO_2 with oxygen-containing radicals (apart from O atoms) is negligible. The inhibiting influence of SO_2 is also revealed by the need to increase the partial pressure of the organic compounds in order to return the mixture to the ignition region.[23] In the ignition process, SO_2 apparently competes with the fuel for the chance to react with free radicals. A good correlation is observed between the quantity of added hydrocarbon required to compensate the influence of a given quantity of SO_2 and the number of C–C bonds in the molecule (Fig. 2). Since the rapid oxidative decomposition of the organic molecule must be preceded by the rupture of C–C bonds, the observed correlation suggests that SO_2 in some way is able to prevent this rupture.

The kinetics of the formation of sulphur-containing products have been studied[3] for different oxidation conditions and different hydrocarbons and sulphur-containing molecules. Flames of propane, methane, acetylene, and also hydrogen and its mixtures with carbon monoxide in the temperature range 1580–1800 K were studied. The sulphur-containing additives used were 0.23 mol% thiophen C_4H_4S and H_2S or 0.23–0.4 mol% SO_2. The relative deviation of the composition of the mixture from the stoichiometric fuel : oxidant ratio varied in the range φ = 0.6–1.7.

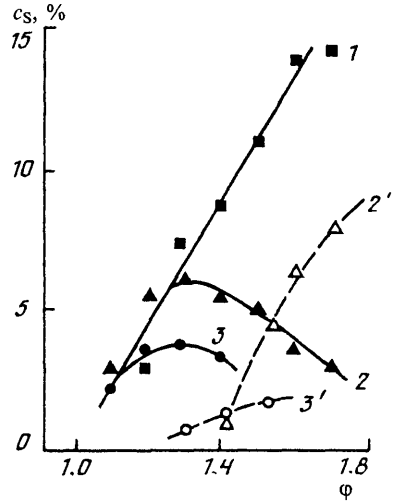


Figure 3. Concentration of sulphur (c_S) as hydrogen sulphide (*1–3*) and cabron disulphide (*2',3'*) in hydrogen and hydrocarbon flames for different values of φ (T = 1802 K, p = 0.92 atm);[3] *1*, H_2; *2,2'*, C_2H_2; *3,3'*, C_3H_8.

In the combustion of hydrocarbons with the addition of H_2S or SO_2, the following stable sulphur-containing products were detected: SO_2, SO_3, H_2S, COS, and CS_2. When C_4H_4S was used as the sulphur-containing additive, it was also detected in the combustion products. Other organosulphur molecules, including thiols, were not detected. For non-hydrocarbon flames, in addition to SO_x, only H_2S was detected. As already noted, SO_2 is always the predominant product. In lean mixtures, not more than 2–3% of the total sulphur is present as SO_3, and in rich mixtures the total concentration of sulphur in all other compounds (H_2S + COS + $2CS_2$ + C_4H_4S) does not exceed 20% (the sulphur concentration balance was determined for a propane flame at 1700 K). The type of compound containing the added sulphur had no significant influence on the yield of H_2S, CS_2, and COS. In contrast to the linear increase in the yield of H_2S in a hydrogen flame with increase in φ, in hydrocarbon flames this increase takes place only up to a certain value of φ, which corresponds to the start of the appearance of CS_2 and COS (Fig. 3). The start of the decrease in the H_2S concentration also coincides with the appearance of appreciable

quantities of unburned carbon, indicating the preferential formation of CS_2 and COS with increase in the quantity of unburned hydrocarbon in the gases. As shown below (section III), CS_2 in fact becomes the principal primary sulphur-containing product when there is a large deficit of oxygen in the system.

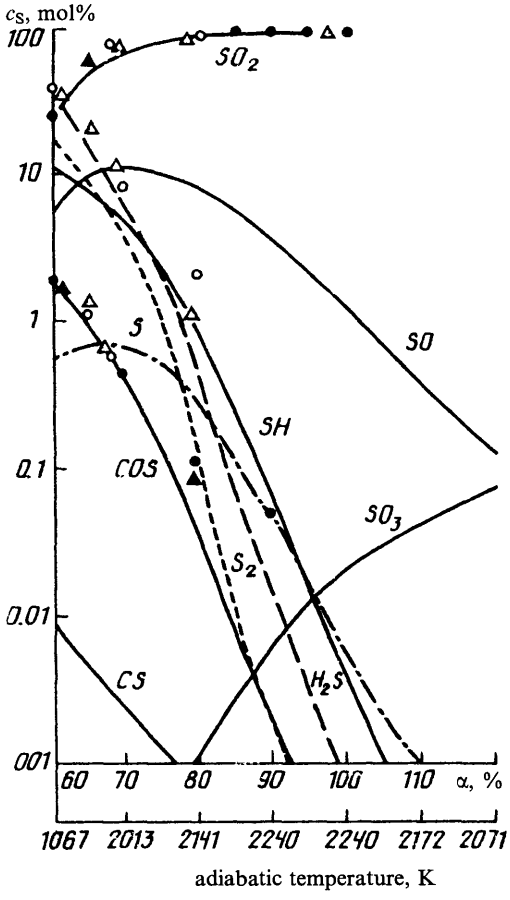


Figure 4. Equilibrium distribution of sulphur-containing components in a propane–air flame at an initial SO_2 concentration of 1%; the points correspond to the experimental data;[15,24] α is the fuel : air ratio (as a percentage of the stoichiometric ratio).

Increase in temperature naturally increases the part played by labile compounds of sulphur, so that in flames at 1500–2000 °C the equilibrium concentrations of these labile species may reach appreciable values. At these high temperatures, the attainment of the thermodynamically equilibrium composition of these products in the flames may be expected, but when the gases are cooled this equilibrium may be quenched before cooling is complete. Thermodynamic calculations of the composition of the products from hydrocarbon flames containing sulphur have been carried out.[24] The results are given in Fig. 4 as a function of the fuel : air ratio (as a fraction of the stoichiometric ratio $\varphi = 1$). Even with an air deficit of 20%, 90% of the sulphur is present as SO_2, and almost all the rest is present as SO. It is only at an air deficit of 40% that appreciable quantities of H_2S, S_2, and SH are present in addition to SO_2. With a 20% excess of air, however, less than 0.1% of the sulphur was present as SO_3. An interesting feature is that the calculation of the compositions of sulphur-containing hydrogen flames gives similar results.[4]

There have been practically no studies of the kinetics of the combined oxidation of hydrocarbons and sulphur-containing compounds at comparable concentrations. The practical interest in this topic is related primarily to the processing of natural gas with a high concentration (greater than 10%) of sulphur dioxide and the reduction of concentrated sulphur-containing gases by hydrocarbons. The marked difference in the reactivities of hydrogen sulphide and organosulphur compounds compared with that of alkanes, in particular methane, suggests that the processes involved in the oxidation of these compounds may be largely independent; this will be examined in more detail in section VI. Some data on the influence of high SO_2 concentrations on the combustion of mixtures of natural gas with air and oxygen have been published.[25] The tip of the peninsula of the range of flame propagation in a natural gas–air–carbon dioxide mixture corresponds to a concentration of 25% CO_2 in the mixture, whereas for sulphur dioxide this value is lowered to 16% SO_2. Since in the range 1100–1800 °C CO_2 and SO_2 have almost identical thermodynamic properties, the increased flame-extinguishing action of SO_2 compared with CO_2 is apparently related to the chemical inhibiting action of SO_2 on the chain process of methane combustion. For mixtures of natural gas and oxygen, the difference between the influences of CO_2 and SO_2 is even less marked, apparently because of the greater intensity of combustion of the oxygen flames.[25]

We carried out experiments to determine the range of stable combustion of methane–air mixtures containing up to 20% of added sulphur dioxide. The results agree well with published data.[25] Although sulphur dioxide shows a slightly stronger inhibiting action than carbon dioxide, the difference is not so dramatic as might have been expected from the results of studies using low concentrations of sulphur dioxide. With increase in the concentration of sulphur dioxide, the chemistry of the processes taking place evidently changes, and the role of sulphur dioxide is not limited to its participation in the catalytic recombination of radicals, particularly in the combustion of rich mixtures, where it may become the supplier of the additional oxygen required for oxidation. The results indicate that the stable combustion of methane–air mixtures containing up to 20% sulphur dioxide is possible in principle.

Unfortunately, up to the present it has apparently not even been possible to construct more or less adequate kinetic models of the transformation of sulphur-containing compounds in the combustion of hydrocarbons, and all attempts undertaken in this direction have been largely speculative in character.

III. The gas-phase reduction of sulphur dioxide by hydrocarbons

The largest group of kinetic studies of systems containing carbon and sulphur has been carried out on the reduction of industrial sulphur-containing gases by various hydrocarbons. Solid, liquid, and gaseous hydrocarbons have been used,[9] but the use of gaseous hydrocarbons (natural gas) appears to be most fully developed.

The high-temperature homogeneous reduction of concentrated sulphur-containing gases by natural gas has passed industrial tests at

the Noril'sk mining and metallurgical combine for processing waste gases from metallurgical processes with a sulphur dioxide concentration of up to 20%. The concentrated sulphur-containing waste gases are purified, and commercial sulphur is produced.[10] At the high-temperature reduction stage, the yield of sulphur is 55–60%. The total yield of sulphur with allowance for subsequent catalytic completion of reduction by the Klaus method is 80–85%. The process was first patented in 1933,[26] and tested industrially in the nineteen-forties,[27,28] but not even the most general ideas about its mechanism have been published.

Available data on the thermodynamics of the reduction of sulphur dioxide by methane show that the reaction can take place almost to completion at temperatures of 1250–1350 °C. Data on the composition of the equilibrium gaseous mixtures, found with allowance for side reactions, have been published.[29] They show that the equilibrium yield of sulphur increases with increase in temperature and with increase in the molar ratio $SO_2:CH_4$, reaching 100% at $SO_2/CH_4 = 2$ and $T > 1300$ °C. In addition, the equilibrium yield of sulphur increases with decrease in pressure.

Some of the first studies of the kinetics of the heterogeneous–homogeneous reduction of sulphur dioxide by methane were carried out by Yushkevich and co-workers,[30] Zawadzki and co-workers,[31] and Walker.[32] Yushkevich studied the kinetics of the two-stage reduction of sulphur dioxide by methanol at 700–1000 °C on bauxite with subsequent conversion of the gaseous sulphur compounds at 370 °C on the same catalyst. At a sulphur dioxide concentration of 14.7%, a ratio $SO_2/CH_4 = 2$, and a flow rate of 350 h^{-1}, the yield of sulphur was 85% at 900 °C, 82% at 800 °C, and 13% at 700 °C. According to these studies, the reaction is heterogeneous–catalytic up to a temperature of 1000 °C, and the products at thermodynamic equilibrium should be sulphur or carbon disulphide.[32] At low ratios $N = SO_2/CH_4$, that is in an excess of methane, reduction to hydrogen sulphide takes place.

Zawadzki[31] studied the process in quartz reactors at a ratio N = 2.2–3.4 and temperature of 820–1135 °C, and found that on quartz the reaction takes place only at $T > 800$ °C; up to 1050 °C the reaction is apparently heterogeneous, and above 1050 °C it takes place in the gas phase. In addition to elemental sulphur, large quantities of COS and CS_2 are formed. The formation of large quantities of COS is not consistent with thermodynamic considerations, so that the authors cited suggested that on quartz the reaction is retarded at an intermediate stage, and that carbonyl sulphide is unstable and can decompose in two directions:

$$COS \longrightarrow CO + S,$$
$$2COS \longrightarrow CS_2 + CO_2.$$

Berkman and Kushnir[33] made a detailed study of the methane process in a quartz flow reactor, and they consider that the conclusion that large quantities of COS are formed is based on unreliable methods of analysis, and that carbon disulphide is the principal and primary product of the non-equilibrium reduction of sulphur dioxide by methane. The influence of the reagent ratio $N = SO_2/CH_4$ on the composition of the products at 800 °C was also studied. The results show that the principal reduction product in all cases is carbon disulphide and that its yield is almost independent of the reagent ratio and corresponds to approximately two thirds of the reduced sulphur. The sum $H_2S + S$ is therefore also almost constant, and over a wide range of $N > 0.4$ the principal product is sulphur, and hydrogen sulphide becomes the predominant product only at very high methane concentrations ($N < 0.4$). The methane oxidation products CO and CO_2 are present in the approximate ratio 2:1.

Increase in temperature increases the extent of the reduction (at a constant rate of supply of the gases $V = 22$ ml min^{-1}) and decreases the yield of carbon disulphide.[33] The decrease in the yield of carbon disulphide at low values of N (excess of the reducing agent) leads to an increase in the yield of hydrogen sulphide for a constant yield of sulphur. At high values of N the decrease in the yield of carbon disulphide is accompanied by an increase in the yield of sulphur, and there is practically no hydrogen sulphide. The methane oxidation products are CO and CO_2; at $N < 1$, as a result of a deficit of the oxidising agent SO_2, increase in temperature leads to a marked increase in the yield of CO, whereas at $N > 2$ the yield of carbon dioxide increases. The rate (extent) of the reduction at 800 °C also depends on the type of quartz (non-transparent quartz is approximately two times more active) and on the time for which it has been used.[33] The catalytic activity gradually decreases by a factor of almost four, and neither heating in a stream of oxygen nor treatment with hot acids increases the established catalytic activity of the quartz. The relative distribution of the sulphur-containing products of the reduction of sulphur dioxide by methane, however, is not influenced by the difference in the catalytic activities of different types of quartz, or by change in the contact time, or by the decrease in the activity with time, which influence only the extent (that is the rate) of the reduction.

The methane reduction of sulphur dioxide at concentrations of 10–100% and at higher temperatures up to 1250 °C has been studied.[29] The process was carried out in quartz flow reactors with an internal diameter of 4–23 mm and a length of 38–100 mm at a constant flow rate of the mixture of 2.4 litre h^{-1}. The separation of carbon was observed in the reaction zone at 900 °C and sometimes at 1100 °C, but not at 1250 °C. Experiments were also carried out on the reduction by domestic gas, shown by chromatographic analysis to contain about 14% ethane, 80% propane, and some methane and nitrogen. The results of the experiments at 1100 °C and 1250 °C were approximately the same as those for the reduction by methane.

It has been concluded[29,32] that the rate of the reduction of sulphur dioxide by methane is controlled by the rate of its thermal decomposition. Describing the rate of the thermal decomposition of methane by the first-order equation:

$$-\frac{d[CH_4]}{dt} = K[CH_4] = A\exp(-E/RT)\,[CH_4]$$

and taking for the rate constant the value $k = 7.08 \times 10^{13} \exp(-87250/RT)$ s^{-1}, the authors cited[29] calculated the kinetics of the thermal decomposition of methane and compared them with the experimentally observed kinetics of the transformation of sulphur dioxide. Satisfactory agreement between the calculated and experimental curves was obtained.

The conclusion[34,35] that sulphur dioxide reacts with methane only after oxygen is used up is interesting. These results were obtained in a study of the kinetics of the reaction and the yield of products in the $SO_2–CH_4–O_2$ system under flow conditions in the presence of a catalyst ($T = 732–831$ °C).

Some data of interest for an understanding of the mechanism of the process were also obtained in practical work on the extraction of sulphur from rich metallurgical gases. In particular, the technological parameters of the high-temperature process depend markedly on the initial concentration of oxygen in the gases being

processed,[36] the presence in the gases of water vapour (up to 5–7% in real gases), and other factors. Increase in the oxygen concentration leads to a decrease in the degree of conversion; in addition, oxygen brings about additional heating of the reaction mixture by the heat of the reaction.[9] Published studies[36] showed that the extent of the reduction of sulphur dioxide by methane depends on the flow rate of supply of the reagents.

A detailed study of the kinetics of the reduction of sulphur dioxide by methane in the temperature range 1000–1360 K has been carried out.[37,38] The process was carried out under static conditions in quartz reactors with a diameter of 21–46 mm. The kinetics of the process were followed from the infrared and ultraviolet spectra of the reagents and products.

The following equations of first-order reactions were obtained for the maximum rate of consumption of the reagents:

$$-\frac{d[CH_4]}{dt} = 6.5\cdot10^{10}\exp(-72000/RT)\,[CH_4]\ cm^{-3}\ s^{-1}$$

$$-\frac{d[SO_2]}{dt} = 2.7\cdot10^{9}\exp(-64000/RT)\,[SO_2]\ cm^{-3}\ s^{-1}.$$

These results indicate that the rate of consumption of methane in this system and the rate of the thermal decomposition of pure methane practically coincide.[39] In any case, in the temperature range 1100–1500 K the rates of these processes do not differ by a factor of more than 2, which is much smaller than the scatter in the experimentally determined rates of the thermal decomposition of methane.[40] The activation energy of the decomposition of methane in this system (72 ± 3 kcal mol^{-1}) is close to the activation energy of the thermal decomposition of pure methane.[39,40] The good agreement between the rate of the thermal decomposition of pure methane, the rate of consumption of methane in the system and the rate of reduction of sulphur dioxide (with allowance for the stoichiometry of the reaction) shows that the thermal decomposition of methane is in fact the limiting stage of the process.

Figure 5 gives the kinetics of the reduction of sulphur dioxide by methane at a ratio $SO_2:CH_4 = 2:1$ and $T = 1200$ K. The similar behaviour of the starting materials can be clearly seen, indicating that their decompositions are limited by the same processes. As in the thermal decomposition of pure methane,[39] the kinetic curves show a section corresponding to acceleration of the reactions, that is the process is self-accelerating. The highest rate of decomposition of methane in this reaction is proportional to its concentration and depends very little on the concentration of sulphur dioxide. The maximum rate of change in the sulphur dioxide concentration is proportional to the concentration of sulphur dioxide and the concentration of methane, but only until the stoichiometric ratio $SO_2:CH_4 = 2$ is reached. At higher concentrations of methane it no longer influences the maximum rate of decomposition of sulphur dioxide.[37]

The principal primary product of the reduction of sulphur dioxide is carbon disulphide, and the start of appreciable formation of this product coincides with the end of the induction period; the highest concentration is reached at the same time as the highest rate of consumption of sulphur dioxide and methane. Its concentration subsequently decreases rapidly to almost zero. The highest concentration of carbon disulphide corresponds to almost 70% of the total change in the concentration of sulphur dioxide at that moment ($2[CS_2]_{max} \simeq 0.7\Delta[SO_2]_{t_{max}}$), and with allowance for its partial decomposition it can be stated that not less than 95% of the sulphur dioxide is converted initially into carbon disulphide. Thus carbon disulphide is not merely the principal but the only primary product of the reduction of sulphur dioxide by methane.

The formation of another sulphur-containing product, namely carbonyl sulphide, is observed much later, and its highest concentration is reached after the stage corresponding to the rapid decomposition of sulphur dioxide and methane. It is therefore a secondary product, formed most probably by the familiar reactions of carbon disulphide with other products of this process

$$CS_2 + CO_2 \longrightarrow 2COS,$$
$$CS_2 + H_2O \longrightarrow COS + H_2S.$$

In these reactions, only a small fraction of the carbon disulphide is apparently removed, since the highest concentration of COS is approximately one fifth of the highest concentration of carbon disulphide, although the concentration of carbon oxide sulphide decreases much more slowly than that of carbon disulphide, and COS is one of the stable end products.

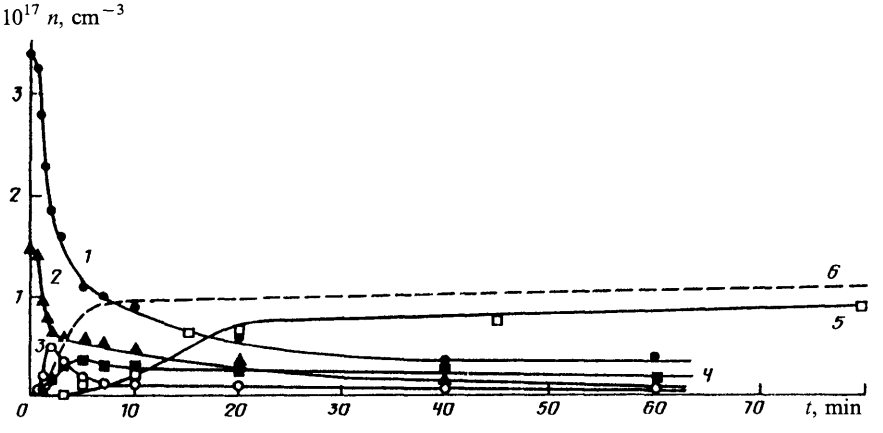


Figure 5. Kinetics of the change in the concentration of the products; $T = 1200$ K; $p = 440$ torr; $[SO_2] = 10\%$; $[CH_4]_0 = 5\%$;[38] *1*, SO_2; *2*, CH_4; *3*, CS_2; *4*, COS (relative units); *5*, H_2S; *6*, S_2 (estimated).

Hydrogen sulphide is a tertiary product of the reduction of sulphur dioxide by methane, since its formation begins after the highest concentrations of CS_2 and COS have been reached and is apparently directly related to their decomposition. In a large excess of sulphur dioxide, the formation of hydrogen sulphide is not observed at all, or takes place after a long time as a result of reactions between secondary reaction products. The highest yield of hydrogen sulphide (about 100%) is observed only with identical concentrations of sulphur dioxide and methane.

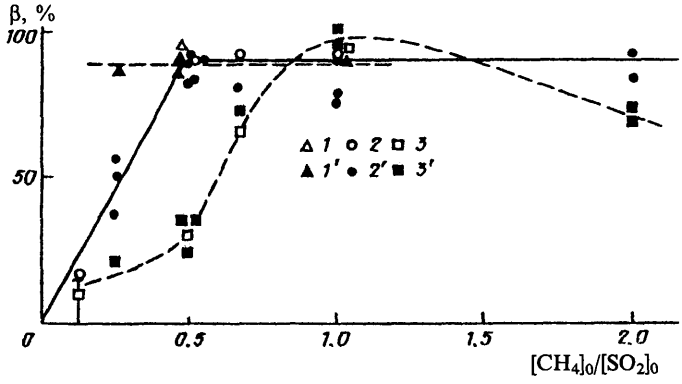


Figure 6. Dependence of the extent of the transformation of the reagents (β) on the ratio $[CH_4]_0/[SO_2]_0$; T = 1200 K; p = 440 torr;[38] *1*, $\Delta CH_4/(CH_4)_0$; *2*, $\Delta SO_2/(SO_2)_0$; *3*, $H_2S/\Delta SO_2$; reaction time: *1*–*3*, 30–50 min; *1'*, *2'*, *3'*, 60–80 min.

The formation of elemental sulphur begins at practically the same time as the formation of carbonyl sulphide. Thus sulphur is also a secondary product of this reaction, and its concentration fairly rapidly reaches a stationary level. For a ratio $SO_2:CH_4$ = 2, corresponding to the overall equation

$$2SO_2 + CH_4 \longrightarrow CO_2 + 2H_2O + S_2,$$

the distribution of sulphur in the principal products for fairly long reaction times at 1200 K is as follows: S_2 ~65, H_2S ~25, $SO_2 \leqslant 9$, and COS ~1%, that is the actual overall equation for the reaction is approximately:

$$4SO_2 + 2CH_4 \longrightarrow 2CO_2 + 3H_2O + H_2S + 5/4S_2 + 1/2SO_2.$$

At a higher concentration of methane, corresponding to a ratio $SO_2:CH_4$ = 1, the composition of the final products changes sharply towards the formation of hydrogen sulphide ($H_2S \geqslant 86\%$, $SO_2 \leqslant 9\%$, $COS \leqslant 4\%$, $S_2 + CS_2 < 1\%$), that is the relative yield of hydrogen sulphide $(H_2S/\Delta SO_2)_\infty$ tends to 100% (Fig. 6). This corresponds to the equation

$$SO_2 + CH_4 \longrightarrow CO + H_2O + H_2S.$$

With an even greater excess of methane, the relative yield of hydrogen sulphide again decreases. Here we should expect the appearance of the principal products of the thermal decomposition of methane, primarily hydrogen, C_2 hydrocarbons, and solid carbon.

Thus in the reduction of sulphur dioxide by methane, the following sequence of transformations of sulphur-containing products takes place:

$$SO_2 \rightarrow CS_2 \rightarrow COS \text{ and } S_2 \rightarrow H_2S.$$

The decomposition of carbon disulphide, which is the direct precursor of all other reaction products, is the next limiting stage of the process after the thermal decomposition of methane. It is therefore extremely important to determine the mechanism and rate of its transformation in this system. Published data[38] indicate that the decomposition of carbon disulphide involves its direct reaction with sulphur dioxide (Fig. 7). The rate of the thermal decomposition of pure carbon disulphide is one tenth of that in the $SO_2 + CH_4$ reaction. The presence of methane increases the rate of the decomposition of carbon disulphide at 1200 K by a factor of ~3, but only the reaction with sulphur dioxide can explain the observed kinetics of the decomposition of CS_2 in the $SO_2 + CH_4$ system.[38]

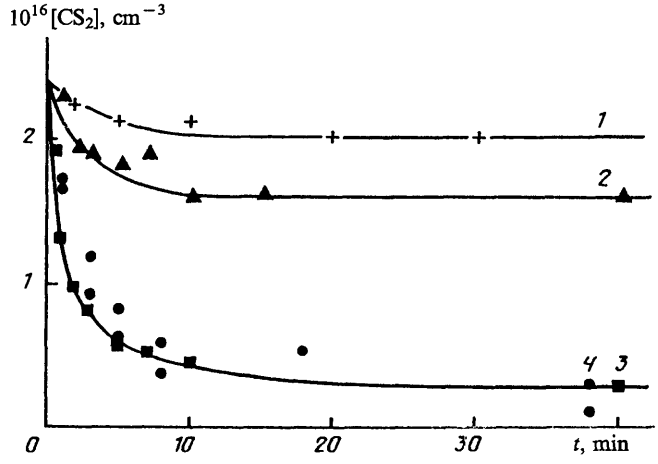


Figure 7. Kinetics of the decomposition of carbon disulphide; T = 1200 K, p = 440 torr; the initial concentrations of carbon disulphide are reduced to the same value $[CS_2]_0 = 2.4 \times 10^{16}$ cm^{-3};[38] *1*, thermal decomposition of CS_2; *2*, reaction of $CS_2 + CH_4$, $[CH_4]_0 = 1.75 \times 10^{17}$ cm^{-3}; *3*, reaction of $CS_2 + SO_2$, $[SO_2]_0 = 3.5 \times 10^{17}$ cm^{-3}; *4*, reaction of $SO_2 + CH_4$, $[SO_2]_0 = 3.5 \times 10^{17}$ cm^{-3}, $[CH_4]_0 = 1.75 \times 10^{17}$ cm^{-3}.

The extent of the transformation of sulphur dioxide in a deficit of methane increases regularly with increase in the concentration of methane in accordance with the stoichiometric ratio $\Delta[SO_2] = 2[CH_4]_0$. When this stoichiometric ratio and higher concentrations (an excess) of methane are reached, the degree of transformation of sulphur dioxide exceeds 90%.

The degree of transformation of sulphur dioxide into hydrogen sulphide (the relative yield of hydrogen sulphide) $H_2S/\Delta SO_2$ in a deficit of methane also increases regularly from $\leqslant 20\%$ at CH_4/SO_2 = 1:8 to ~30% at the stoichiometric ratio CH_4/SO_2 = 1:2 and to almost 100% at CH_4/SO_2 = 1:1, after which it

decreases again to 70% at $CH_4/SO_2 = 2:1$. Thus by controlling the ratio of methane and sulphur dioxide it is possible to control the ratio of the final concentrations of sulphur dioxide and hydrogen sulphide in the reaction products.

There are practically no published data on the kinetics of the reduction of sulphur dioxide by other gaseous hydrocarbons, except for acetylene.[41] The interest in acetylene is due to the fact that it is the principal hydrocarbon product of the thermal decomposition of methane,[39,40] and may play an important role in the high-temperature reduction of sulphur dioxide.

Studies in the temperature range 1000–1200 K[41] showed many common features in the reduction of SO_2 by methane and by acetylene, although acetylene reacts with SO_2 several times more rapidly. In this temperature range, simultaneous thermal decomposition of acetylene takes place,[42] and the rate of decomposition of acetylene under the conditions of the work cited[41] was much greater than the rate of change in the concentration of sulphur dioxide; the temperature dependence was approximately the same for these processes, and corresponded to an activation energy of ~45 kcal mol^{-1}. At lower temperatures (1000 K), a short period of auto-acceleration which is usually observed in the thermal decomposition of acetylene,[42] was noted.

The markedly different rates of the thermal decomposition of acetylene and the reduction of sulphur dioxide, together with the zeroth order of the rate of reduction of SO_2 with respect to acetylene, indicate that the reduction involves the reaction of sulphur dioxide with the thermal decomposition products of acetylene.

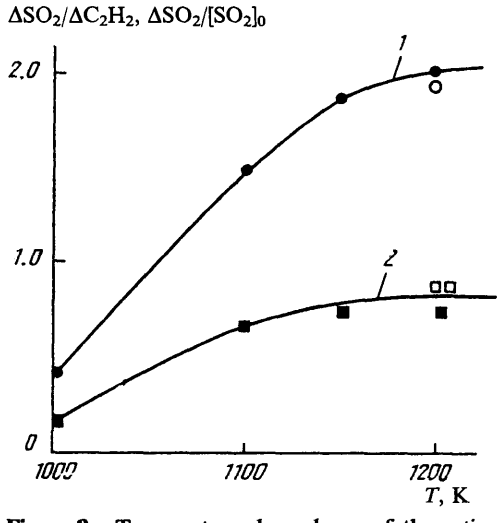


Figure 8. Temperature dependence of the ratios $\Delta SO_2/\Delta C_2H_2$ and $\Delta SO_2/[\Delta SO_2]_0$; black points—reactor with diameter 21 mm; open points—reactor with diameter 46 mm;[41] *1*, $\Delta SO_2/\Delta C_2H_2$; *2*, $\Delta SO_2/[SO_2]_0$.

In addition to sulphur, the principal sulphur-containing products of the process, recorded from their infrared spectra, are CS_2 and COS. As in the reaction of SO_2 with CH_4,[38] CS_2 is the principal and apparently the only primary product of the decomposition of sulphur dioxide. The formation of COS takes place much later, and is probably associated with the decomposition of CS_2 in the presence of SO_2. The highest concentrations $[CS_2]_{max}$ and $[COS]_{max}$ are apparently determined only by the rate of reduction of sulphur dioxide, and therefore are also independent of the initial concentration of acetylene. In an excess of acetylene, the formation of carbon is observed. Small quantities of methane are also formed, evidently by thermal decomposition.

Increase in temperature increases the ratio of the change in the concentration of sulphur dioxide to the change in the concentration of acetylene $\Delta SO_2/\Delta C_2H_2$ from 0.4 to 1000 K to 2.0 at 1200 K (Fig. 8). This may be related to a change in the mechanism and hence in the products of the thermal decomposition of acetylene, in which polymerisation products predominate at $T < 1200$ K, while at higher temperatures there is an increase in the contribution made by processes involving small radicals.[42] Another reason may be a change in the mechanism of the reaction of sulphur dioxide with the thermal decomposition products of acetylene. Evidence that the reduction of sulphur dioxide involves the thermal decomposition products of acetylene is provided by the change in the quantity $\Delta SO_2/\Delta C_2H_2$ during the reaction (Fig. 9). As the thermal decomposition products are used up, this ratio increases from zero to ~1.5 at 1100 K and ~2 at 1200 K. The degree of reduction of sulphur dioxide $\Delta SO_2/[SO_2]_0$ increases with increase in temperature is approximately the same way as the quantity $\Delta SO_2/\Delta C_2H_2$ (Fig. 8).

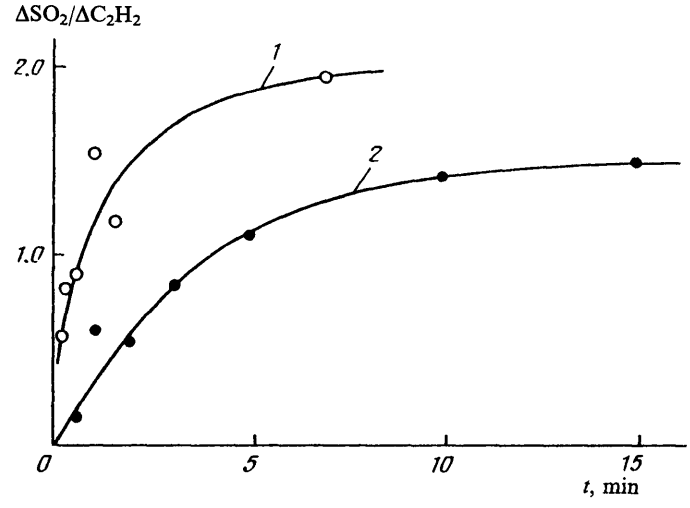


Figure 9. Time dependence of the ratio $\Delta SO_2/\Delta C_2H_2$; p = 440 torr, reactor diameter 21 mm; *1*, 1200 K; *2*, 1100 K.[41]

Thus the reduction of sulphur dioxide by acetylene and the reduction of sulphur dioxide with methane have a number of common features. From available data on the reaction of sulphur dioxide with methane and with acetylene, an attempt can be made to formulate some general conclusions about the mechanism of the reaction of SO_2 with hydrocarbons.

1. The limiting stage of the process is the thermal decomposition of the hydrocarbon.

2. The presence of sulphur dioxide does not lead to significant changes in the kinetics of the decomposition of the hydrocarbon.

3. A decisive role in the reduction is played by the reaction of SO_2 with the thermal decomposition products, primarily H_2.[43,44]

4. The rate of reduction is linearly dependent on the sulphur dioxide concentration.

5. The primary and apparently the only primary stable product of the reduction of SO_2 is CS_2. The sulphur-containing products are formed by the sequence

$$SO_2 \rightarrow CS_2 \rightarrow COS \text{ and } S_2 \rightarrow H_2S.$$

6. The subsequent decomposition of CS_2 involves its reaction with SO_2 to give COS, S_2, and other products.

7. The final degree of reduction of sulphur dioxide increases smoothly to 90–100% with increase in the hydrocarbon : sulphur dioxide ratio. At the same time the extent of the transformation of sulphur dioxide into elemental sulphur decreases.

IV. The formation of carbon disulphide and carbonyl sulphide in gas-phase processes

Carbon disulphide is one of the most important chemical products, and is required for the production of synthetic fibres, flotation reagents, vulcanisation accelerators, poisons, etc. In the nineteen-sixties, the intensive introduction of new industrial methods for obtaining carbon disulphide from natural gas and sulphur began, making it possible to establish large-scale fully automated processes.[12,45] The industrial process is carried out in the presence of a catalyst at a temperature up to 660 °C and a degree of transformation of methane up to 96%.[12] The kinetics of the process have been studied.[46] A large number of new studies are published annually on the technology of the production of carbon disulphide by this method using different modifications of the catalyst and different process conditions.[12,45] Heavier hydrocarbons containing three or more carbon atoms react readily with sulphur, and give a large quantity of carbon disulphide for every molecule of original sulphur and a correspondingly smaller quantity of hydrogen sulphide per molecule of carbon disulphide formed. The reaction of sulphur with higher hydrocarbons takes place much more rapidly with almost 100% conversion. In the catalytic process, however, the presence of propane and heavier hydrocarbons leads to the formation of carbon and tarry substances, including their formation on the catalyst, and also to the production of thiols, thiophens, and organic sulphides, so that the natural gas is purified beforehand to remove these hydrocarbons.[12]

In addition to catalytic methods, purely homogeneous methods have been proposed for carrying out this process at higher temperatures.[47–53] Patents have been published on the synthesis of carbon disulphide from paraffin hydrocarbons at 700–1300 °C,[47] accompanying petroleum gases,[48] and other hydrocarbons. A method for obtaining carbon disulphide by the reaction of saturated hydrocarbons with sulphur vapour and sulphur dioxide at 500–900 °C in 0.1–2 s has been described.[49] The disadvantages of this method are the low yield of CS_2 (42.5–50%) and the formation of side products. To eliminate these disadvantages, it is suggested that alkenes, dialkenes and heavier hydrocarbons be used as the carbon-containing starting material.[53] The process takes place at 500–900 °C at atmospheric or elevated pressure in 1.5–4 s with a yield of up to 80–91%. It is known, however, that unsaturated hydrocarbons, reacting with sulphur, give a large quantity of organic sulphur compounds as side products.[45] The kinetics of the gas-phase reaction of sulphur vapour with hydrocarbons have not been studied.

It has been suggested that carbon disulphide can be obtained by the reaction of sulphur vapour with carbon monoxide at 510–650 °C both in the gas phase[54] and in the presence of a catalyst.[55]

The use of various waste gases containing sulphur and hydrogen sulphide as the sulphur-containing starting material for the synthesis of carbon disulphide and carbon oxide sulphide is of considerable practical interest. A 26–70% yield of carbon disulphide at 1180 °C and 1280 °C without the use of a catalyst has been reported,[56] but other workers[57] obtained no carbon disulphide in the products of the homogeneous reaction in quartz tubes at temperatures of 900–1100 °C. Only the addition of a catalyst (kaolin impregnated with $K_2Cr_2O_7$) made it possible to obtain a 50% yield of CS_2,[57] so that it was suggested[45] that the quartz surface of the assembly in the work cited[56] had a catalytic action. Although the synthesis of CS_2 from methane and hydrogen sulphide has not yet found practical application, it has been suggested that this process may be promising if oxygen-containing gases or free oxygen are added to the reaction mixture.[45]

The formation of carbon disulphide and carbon oxide sulphide in the reaction of sulphur dioxide with methane was detected even in early studies.[31–33] This gas-phase process has been used with the simultaneous supply of sulphur vapour and sulphur dioxide for reaction by the hydrocarbon.[49,53] The kinetics of the formation of carbon disulphide and carbonyl sulphide by the reaction of sulphur dioxide with methane, acetylene, and carbon monoxide have been the subject of a series of detailed studies[37,38,41,58,59] (see sections III and V).

V. The kinetics and mechanism of the processes in the C–S–O system

The oxidation of carbon disulphide and carbonsyl sulphide is one of the most extensively studied gas-phase processes in the chemistry of sulphur. The available experimental data cover a wide range of temperatures (300–2000 K) and pressures (1–2000 torr) and include reactions under flow and static conditions, atomic flames, and experiments in shock tubes.[6] In addition, published data[13] on the rate constants of the elementary reactions in these processes have been used to construct a sufficiently adequate kinetic model, providing a satisfactory description of the published experiments.[6] An analysis of the kinetic model made it possible to select the most important reactions for the oxidation of CS_2:

$$CS_2 + O = CS + SO, \quad CS + O = CO + S,$$
$$CS_2 + O = COS + S, \quad S + O_2 = SO + O,$$
$$SO + O_2 = SO_2 + O,$$

and the oxidation of COS:

$$COS + O = CO + SO, \quad CO + SO = CO_2 + S,$$
$$COS + O = CO_2 + S, \quad CO_2 + S = CO + SO,$$
$$SO + O = S + O_2, \quad S + O_2 = SO + O.$$

Application of the mechanism being discussed to the conditions at low temperature $T \simeq 353$–493 K showed it to be inadequate. The calculated reaction rate was found to be too low. At low

temperatures, a fairly large contribution is apparently made by heterogeneous processes and reactions involving more complex intermediate species, not included in the kinetic scheme.

Since there is an extensive literature on the oxidation of CS_2 and COS, including reviews (see Ref. 6 and references therein), the kinetics and mechanism are examined in detail below for only one of the reactions in the C–S–O system, namely the thermal SO_2 + CO reaction.

The interest in carbon monoxide as reducing agent for sulphur dioxide is related to the fact that it is formed unavoidably when the reducing agent used is carbon or coke, whose use has been proposed for the preparation of sulphur from industrial gases containing SO_2.[60] As early as the eighteen-eighties, Berthelot and others showed that CO can reduce SO_2 slowly to give free sulphur. For example, the reaction of SO_2 and CO in a porcelain tube at 1000–1200 °C gave elemental sulphur and carbon dioxide, and also small quantities of carbonyl sulphide.[61] In the absence of a catalyst this reaction is slow, even at 800 °C, but is catalysed by almost any heated surface; the resulting reaction is of first order.[62]

Koval'skii and co-workers[63,64] showed by separate calorimetry that when Al_2O_3 is used as catalyst, the reduction of sulphur dioxide by carbon monoxide is a homogeneous reaction taking place by a chain mechanism, but chain initiation takes place on the surface of the catalyst. An appreciable quantity of carbonyl sulphide was formed in the reaction, and adding COS and sulphur increased the reaction rate.

From an analysis of the ESR spectra of the frozen products of the reaction of carbon monoxide and sulphur dioxide over bauxite at p = 1 atm and T = 600 °C it was concluded that SO is one of the species propagating the chain in the reduction of sulphur dioxide by carbon monoxide.[65] An excess of SO_2 relative to the stoichiometric ratio $CO:SO_2$ = 2 led to a decrease in the reaction rate, and an excess of CO to an increase.

The composition of a thermodynamicaly equilibrium SO_2–CO mixture at temperatures of 400–1000 K, including systems containing added water, oxygen, and carbon dioxide, has been calculated.[66] It was shown tht at 473 K almost complete reduction of sulphur dioxide by carbon monoxide is possible, but traces of water and oxygen lower the equilibrium yield of elemental sulphur.

The kinetics of the gas-phase CO + SO_2 reaction in static quartz reactors have been studied at temperatures of 1100–1360 K using infrared and ultraviolet spectroscopic analysis of the products.[58,59] Under these conditions, change in the surface:volume ratio of the reactor and in pressure in the range 60–300 torr had no influence on the reaction. The effective activation energy of the process, determined from the rate of removal of sulphur dioxide, was 46 kcal mol^{-1}. An interesting feature is that this value practically coincides with the activation energy of the formation of CO_2 in this reaction (E = 48.3 kcal mol^{-1}), obtained in shock waves at temperatures of 1770–2453 K.[67] It was established that the rate of change in the SO_2 concentration is independent of the concentration of SO_2 and is linearly dependent on the CO concentration. As in other studies,[64] the principal intermediate reaction product is carbonsyl sulphide. In contrast to the catalytic process at a lower temperature,[64] however, where the highest yield of COS reached 45%, in the gas-phase process at 1215 K and a reagent ratio $CO:SO_2$ = 2:1 the highest concentration of carbonyl sulphide was only 5–8% of the initial concentration of sulphur dioxide. At the moment when a highest COS concentration of 25–50% is reached, however, all the sulphur liberated at this stage by the decomposition of SO_2 is present as COS. An estimate taking account of the rate of decomposition of carbonyl sulphide itself showed that at least 80% of the SO_2 decomposed is converted initially into COS, and its lower concentration compared with published data[64] is due to the higher rate of its decomposition at a high temperature.

Experiments with the addition of carbonyl sulphide (up to 30% of the initial concentration of SO_2) to the original mixture showed[59] that in contrast to the catalytic process,[63,64] these additives have no significant influence on the kinetics of the decomposition of sulphur dioxide. The concentration of carbonyl sulphide itself decreased very rapidly, with practically the characteristic decomposition time of pure CO, to a quasi-stationary level close to the quasi-stationary concentration of COS in the reaction without the addition of this product. The decomposition of COS under these conditions apparently takes place to a considerable extent independently of the reduction of sulphur dioxide and does not make a significant contribution to the rate of radical initiation. The decomposition of COS in the presence of only one of the original reagents, SO_2 or N_2 (a five-fold excess relative to COS) was about three times more rapid than that in the reaction being studied. In the mixture with SO_2, a simultaneous slow decrease in the concentration of sulphur dioxide was observed. This is apparently related to the reaction of SO_2 with carbon monoxide formed by the decomposition of COS, taking place more rapidly than the decomposition of COS. The decrease in the quantity of CO_2 corresponded approximately to the stoichiometry of the reaction of SO_2 and the CO formed. Attempts to detect CS_2 in the decomposition of COS were unsuccessful, that is the reaction

$$2COS \rightleftharpoons CO_2 + CS_2$$

takes place to only a small extent, and the principal reaction is

$$COS \rightleftharpoons CO + S.$$

The extent of the decomposition of COS under these conditions was greater than 95%. The decomposition of COS is much slower in the presence of CO than in the presence of SO_2 or N_2. This may be a consequence of the influence of CO on the back reaction. Only traces of CS_2, corresponding to not more than 3% of ΔCOS, were detected. The presence of CO in the original mixture explains the slower rate of decomposition of COS in the reaction being studied, compared with the decomposition of pure COS. The extent of the decomposition also decreases as a result of the displacement of the equilibrium. Overall it can be stated that the reaction of CO and SO_2 takes place with the formation of COS and is accompanied by the subsequent and to a large extent independent decomposition of COS, mainly by the second reaction. The influence of the starting materials on the decomposition of COS reduces mainly to the influence of CO on the displacement of the equilibrium by the back reaction.

The estimated activation energy of the decomposition of COS lies in the range 30–46 kcal mol^{-1}. Since this value is approximately half the energy of the removal of a sulphur atom from a COS molecule (73.7 kcal mol^{-1}), it has been suggested[59] that the decomposition takes place by a bimolecular mechanism *via* the formation of a linear complex

$$OC-S + S-CO \longrightarrow CO + S_2 + CO,$$

which is endothermic to the extent of about 40 kcal mol^{-1}. This mechanism of the decomposition would indicate that the fact that added COS has no influence on the reaction rate is due to the absence of atoms and radicals from the reaction products.

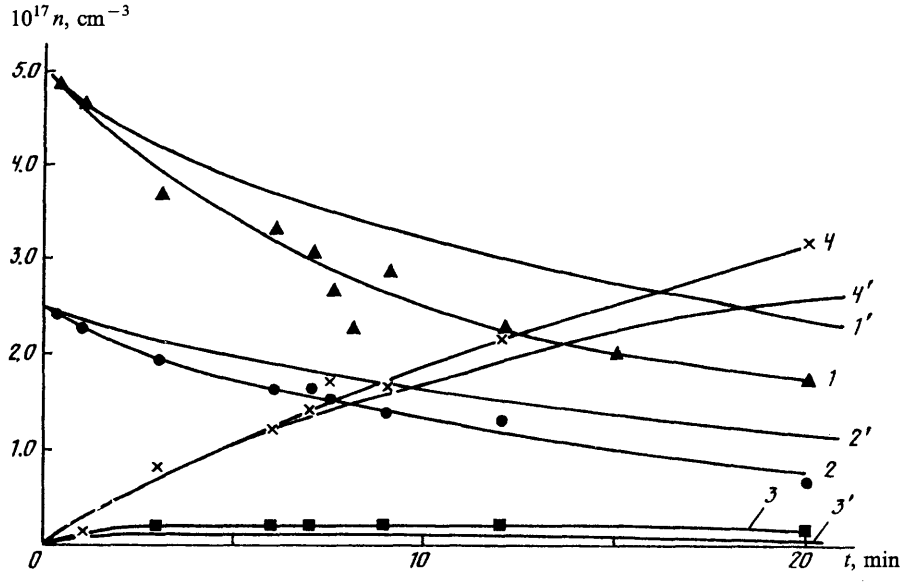


Figure 10. Kinetics of the change in the concentration (n) of the products of the reaction of sulphur dioxide with carbon monoxide at $CO:SO_2 = 2:1$ and $T = 1215$ K;[59] *1,1'*, CO; *2,2'*, SO_2; *3,3'*, COS; *4,4'*, CO_2; *1–4*, experiment; *1'–4'*, calculation.

Figure 10 gives the experimental kinetic curves for the reaction of sulphur dioxide with carbon monoxide. Attempts to detect the formation of other products, including S_2O, from infrared absorption at 679 cm^{-1} were unsuccessful. Only traces ($\leqslant 10^{15}$ cm^{-3}) of CS_2 were detected. Figure 10 also gives the results of calculations of the kinetics of this reaction using the kinetic model of the processes in the C–S–O system.[6] Satisfactory agreement was obtained between the experimental and calculated curves for all the observed products, confirming the reliability of the general model of the processes in the C–S–O system developed in the work cited.[6] Table 1[59] gives an abbreviated model of the reaction of CO and SO_2, obtained by selecting the most important reactions of the model[6] without introducing any changes to the values of their rate constants. Since the difference between calculations using the abbreviated scheme in Table 1 and calculations using the complete scheme does not exceed 15%, it can be stated that this simplified scheme gives the basic mechanism of the reduction of sulphur dioxide by carbon monoxide.

VI. The combined oxidation, photolysis, and radiolysis of carbon- and sulphur-containing compounds

The combined thermal oxidation, photolysis, and radiolysis of carbon- and sulphur-containing compounds is now being intensively studied. The aim of these studies is to find ways of processing sulphur-containing natural gas or purifying it from organosulphur compounds.

It has been shown that it is possible to carry out the chain thermal–radiation decomposition of hydrogen sulphide in the presence of carbon monoxide in the temperature range 60–650 °C;[68] the radiation-chemical yield of hydrogen $G(H_2)$ increased with increase in temperature, from 2 at 60 °C to 150 at 500 °C. According to the proposed scheme, carbon monoxide not only transfers excitation to the H_2S molecules but also reacts with the SH radical to give COS. Estimates[69] showed that it is possible to carry out the extensive purification of natural gas by the selective photodissociation of hydrogen sulphide by ultraviolet radiation to give hydrogen and elemental sulphur. This possibility was studied experimentally[70] in mixtures of hydrogen sulphide (0.5–10%) with CH_4, CO_2, and H_2 by irradiating with ultraviolet light with λ = 193 nm. Selective dissociation of H_2S took place down to concentrations lower than $10^{-3}-10^{-4}$ times the initial concentration. The formation of organosulphur compounds was not observed, and the concentration of methane remained unchanged. This result was attributed[70] to the small extent of the photodissociation of CH_4 and the low rate of the reactions of methane with the HS and S radicals formed by the photolysis of H_2S

$$HS + CH_4 \rightarrow H_2S + CH_3,$$
$$S + CH_4 \rightarrow HS + CH_3,$$

at $T < 600$ K. Because of their relatively low concentration, the reactions of S radicals with unsaturated compounds

$$S + C_2H_2 \rightarrow \text{products}$$

$$S + C_2H_4 \rightarrow \text{products}$$

have no significant influence on the purification process.

Experiments have been carried out on the combined incomplete oxidation of methane and hydrogen sulphide under static conditions at pressures of 350–440 torr and temperatures of 600–1000 K.[71] The process was carried out at concentrations of 0.3–10% hydrogen sulphide, 2.5–10% oxygen, and 5–90% methane (diluted with helium). The products were analysed from their infrared and

ultraviolet spectra (CH_4, H_2S, SO_2, CS_2, COS) and by chromatography (CH_3OH, C_2H_2, SO_2, and H_2O).

At temperatures of about 600 K it is possible to observe the kinetics of the consumption of H_2S and the accumulation of SO_2. In the absence of methane and with an excess of oxygen, practically all the H_2S is oxidised to SO_2. The presence of methane has little influence on the kinetics of the initial stage of the process, but the process becomes slower and stops at a certain residual stationary concentration of H_2S. Decrease in the oxygen concentration is accompanied by a decrease in the rate and extent of the oxidation of H_2S and the rate of formation and yield of SO_2, and by a decrease in the S_2/SO_2 ratio.

Table 1. Mechanism of the reduction of sulphur dioxide by carbon monoxide.[59]

Reaction	lg A, mol litre^{-1} s^{-1}	E, kcal mol^{-1}
$CO+SO_2 = CO_2+ SO$	9.78	55.0
$CO+SO = CO_2+ S$	9.78	10.9
$CO+S +M = COS+ M$	10.30*	1.8
$COS+M = CO+S+M$	11.28	64.0
$COS+SO = S_2 + CO_2$	8.40	8.3
$COS+S = CO + S_2$	9.23	4.0
$SO_2 + S = SO + SO$	9.78	16.8
$CO_2+S = CO + SO$	11.57	13.2

*mol^2 litre^{-2} s^{-1}.

With increase in temperature to 800 K there is a sharp increase in the rate of the decomposition of H_2S, and the SO_2 concentration passes through a maximum; both products reach stationary values of the concentration, which for H_2S correspond to half the initial value. At low concentrations (5%) of methane there is a slight decrease (~10%) in its concentration (Fig. 11). At a methane concentration of about 90% there is no change in its concentration within the accuracy of the measurements. The oxidation products contain an appreciable quantity of CS_2 and some COS; the concentrations of these products pass through a maximum when the stationary value of the concentration of SO_2 is reached. At the maximum the degree of transformation of H_2S into these products at $[H_2S] = [O_2] = [CH_4] = 10\%$ reaches the values $2CS_2/(H_2S)_0 \simeq 0.3$ and $COS/(H_2S)_0 \simeq 0.06$; the corresponding values for SO_2 and S_2 are about 0.3 and 0.35.

At even higher temperatures (900–1000 K) and concentrations $[H_2S] = [CH_4] = 10\%$ and $[O_2] = 5\%$, that is with a deficit of oxygen, H_2S decomposes completely ($t < 5$ s), but no formation of SO_2 is observed, that is the principal sulphur-containing product is now S_2.[71]

Depending on the ratio H_2S/O_2, two overall equations for the oxidation of hydrogen sulphide are possible:

$$2H_2S + O_2 \longrightarrow 2H_2O + S_2,$$
$$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2.$$

The fraction of hydrogen sulphide converted into sulphur dioxide naturally increases with the oxygen concentration. In the combustion of hydrocarbons containing a small quantity of sulphur compounds, practically all the sulphur is converted into SO_2.[16] Under the conditions of the work cited[71] in an excess of oxygen, the principal oxygen-containing product is again SO_2, but in the presence of methane the SO_2 formed is partly reduced to S_2 and even to H_2S, and this is a slower process than the actual oxidation of hydrogen sulphide (Fig. 11).

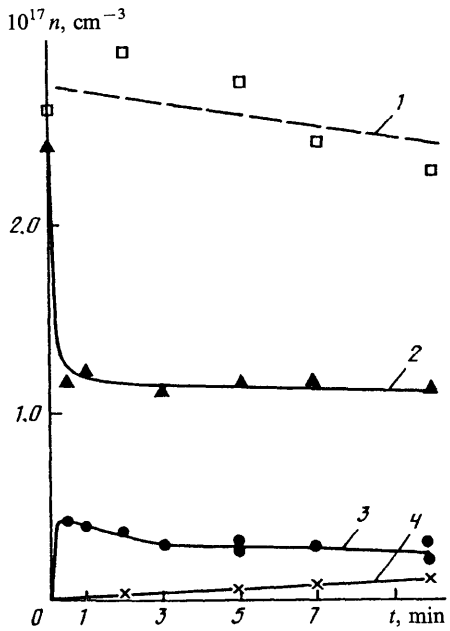


Figure 11. Kinetics of the oxidation of hydrogen sulphide in the presence of methane and the yield of products: *1*, CH_4; *2*, H_2S; *3*, SO_2; *4*, CS_2; T = 800 K, p = 440 torr, $[H_2S]$ = 5%, $[O_2]$ = 2.5%, $[CH_4]$ = 5%.[71]

Thus in the oxidation of methane containing a small quantity of hydrogen sulphide, the rapid partial oxidation of hydrogen sulphide to S_2 and SO_2, the ratio of which is determined by the oxygen concentration, is accompanied by the subsequent slower reduction by methane of the SO_2 formed to give S_2, and also by the reaction of S_2 with methane to give CS_2. It is only in a large excess of oxygen relative to hydrogen sulphide that almost complete transformation of H_2S with an almost 100% yield of SO_2 takes palce. The slow reduction of sulphur dioxide by methane (section III) limits the establishment of equilibrium in this system.

Figure 12 gives the dependence of the maximum rate of increase in the pressure W_{max} and the yield of products on the H_2S concentration. The presence of even 0.3% H_2S lowers the highest

reaction rate by a factor of 2, and 2% H_2S lowers it by a factor of about 4. The yield of methanol also decreases slightly.[71] Figure 13 gives the kinetics of the formation of the reaction products for a mixture containing 2% H_2S. In all the mixtures the concentration of methanol passes through a maximum. An interesting feature is that the transformation of H_2S is complete well before the end of the whole process.[17]

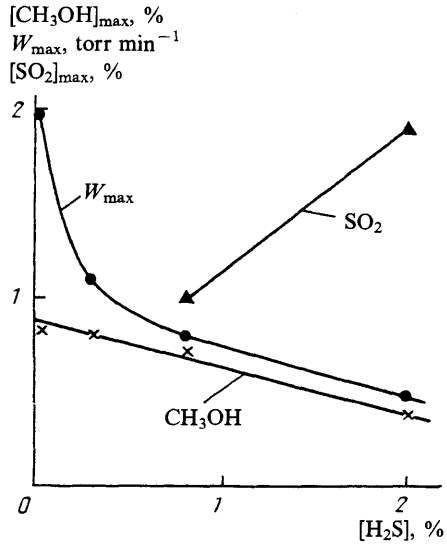


Figure 12. Dependence of the highest rate of oxidation of methane (W_{max}) and the highest yields of methanol [CH_3OH] and sulphur dioxide [SO_2] on the concentration of hydrogen sulphide; T = 723 K, p = 350 torr, [CH_4] = 80%, [O_2] = 10%, [H_2S] = 0.3–2%, remainder helium.[71]

Figure 12 shows that up to H_2S concentrations of 0.8% the highest concentration of methanol decreases by not more than 15%, indicating that it may be possible to use natural gas with a low sulphur concentration for its partial oxidation to methanol. Kinetic modelling of the incomplete oxidation of natural gas with a low sulphur concentration to give methanol at high pressures (100 atm) showed that in addition to a sharp decrease in the reaction time, even a slight increase in the yield of methanol can be expected. Even at a concentration [H_2S] $\simeq$ 1%, however, the conversion of hydrogen sulphide into sulphur dioxide is not complete. In view of the low reliability and incomplete nature of the kinetic data on the reactions of sulphur-containing compounds, however, it is difficult, without appropriate experimental studies, to evaluate the conclusions reached by modelling.

VII. The reaction of carbon- and sulphur-containing molecules in atmospheric processes

Sulphur is a relatively widespread element, and plays an important role in the circulation of the lithosphere and the atmosphere. On the earth's surface it is concentrated mainly in sulphide and sulphate ores, and in the ocean it is present mainly as dissolved sulphates. The principal sulphur-containing compounds in the atmosphere are sulphur dioxide, hydrogen sulphide, and other reduced compounds of sulphur, and also sulphate aerosols. Sulphur compounds do not accummulate in the atmosphere. Chemical cycles ensure a fine balance between the supply of sulphur to the atmosphere and its return to the earth's surface, although the increasing flux of sulphur originating from man's activities (207 million tons of SO_2 in 1976, 41.4% of the total supply of sulphur to the atmosphere[72]) is possibly displacing this equilibrium slightly.

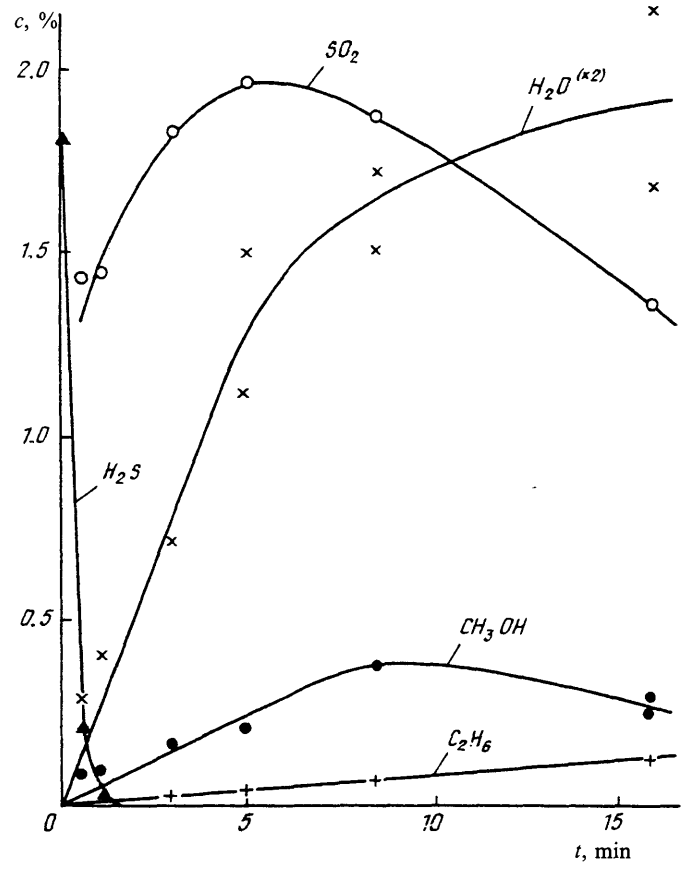


Figure 13. Kinetics of the formation of the products of the oxidation of methane in the presence of added hydrogen sulphide; T = 723 K, p = 350 torr, [CH_4] = 80%, [O_2] = 10%, [He] = 8%, [H_2S] = 2%.[71]

Most of the carbon in the atmosphere is present as carbon dioxide (~340 p.p.m.), methane (1.6–1.7 p.p.m.), and carbon monoxide (0.04–0.20 p.p.m.).[1]

Reduced carbon- and sulphur-containing molecules, whose concentration in the atmosphere is low, are oxidised mainly by

hydroxyl radicals to give finally carbon dioxide and more highly oxidised compounds of sulphur

$$OH + COS \rightarrow CO_2HS,$$
$$OH + COS \rightarrow CO + SOH,$$
$$OH + CS_2 \rightarrow COS + HS,$$
$$OH + CS_2 \rightarrow CS + SOH,$$
$$OH + CH_3SCH_3 \rightarrow \text{products}.$$

The photolysis of these compounds in the troposphere plays a relatively minor role. The hydroxyl radical is also involved in the conversion of SO_2 into H_2SO_4.

Methane also reacts initially with the hydroxyl radical to give methyl radicals

$$CH_4 + OH \longrightarrow CH_3 + H_2O,$$

which are then oxidised by O_2 in a series of reactions to give formaldehyde, whose subsequent photolysis gives carbon monoxide. Carbon monoxide from this source, and carbon monoxide entering the atmosphere directly, is oxidised further by OH radicals in a cyclic series of reactions, beginning with the reaction

$$CO + OH \longrightarrow CO_2 + H,$$

giving CO_2 as the final product. In the troposphere, about 70% of the OH radicals are used up in the reaction with CO, and 30% in the reaction with CH_4. Both processes give peroxide radicals:

$$H + O_2 + M \longrightarrow HO_2 + M,$$

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M,$$

which can react with sulphur dioxide:

$$ROO + SO_2 \longrightarrow RO + SO_3,$$

whose concentration in the atmosphere reaches about 1.1×10^{-10}.[1] If the rate constant of the reaction

$$CH_3OO + SO_2 \longrightarrow CH_3O + SO_3$$

were about $(5-10) \times 10^{-15}$ $cm^3 molecule^{-1} s^{-1}$, as has been reported,[73,74] it might play a decisive role in the sulphur cycle. Later work,[75,76] however, gave a much lower value for the rate constant of this reaction (5×10^{-17} $cm^3 molecule^{-1} s^{-1}$), so that this reaction apparently does not play a significant part in the sulphur cycle.

Among the reduced compounds of sulphur, entering the atmosphere mainly from the ocean surface, a relatively important part in the global sulphur cycle is played by organosulphur compounds, primarily dimethyl sulphide CH_3SCH_3, which annually supplies about 40 million tons of sulphur to the atmosphere.[77] Recently, therefore, considerable attention has been paid to the mechanism of the oxidation of dimethyl sulphide, dimethyl disulphide CH_3SSCH_3, and other organosulphur compounds in the atmosphere.[77,78] As in the case of other reduced compounds of sulphur, the principal chemical process responsible for the decomposition of CH_3SCH_3 and CH_3SSCH_3 in the atmosphere is their reaction with OH, and the principal product of the complex processes involved in their atmospheric oxidation is SO_2.[78]

The reaction of carbon- and sulphur-containing molecules may play a much greater role in the atmospheres of planets such as Venus, where the concentrations reach 96.5% CO_2, 0.003% CO, and 0.015% SO_2.[1] They apparently play a predominant role in the region of the atmosphere of Venus below the cloud layer. In view of the high temperatures (732 K on the surface of Venus) and pressures (90 atm) and the proximity of the surface, which catalyses the approach to equilibrium, it may be assumed in a first approximation that the thermodynamically equilibrium composition, perturbed by vertical transport processes, is established in this region. This equilibrium is apparently in fact established at the surface, but with increase in the distance from the surface the equilibrium begins to break down to a considerable extent, increasing the part played by kinetic processes in the formation of the composition of the atmosphere. As a result, the ascending and descending streams apparently have different chemical compositions. The ascending streams contain components originating in Venus' crust (for example COS, S_2, H_2S, etc.), and the descending streams contain the products of photolysis in the upper cloud layer (SO_3, Cl_2, O_2, etc.). On the surface, chemical equilibrium is apparently established for all the gases except CO and O_2, which in the tropospheres are not in equilibrium with one another or with the COS/SO_2 system.[1] The next most important elementary stages, beginning with the formation of SO, can describe the interconversion of various components:

$$SO_2 + CO \longrightarrow SO + CO_2, \qquad CO + S + M \longrightarrow COS + M,$$
$$SO + CO \longrightarrow S + CO_2, \qquad S + COS \longrightarrow S_2 + CO,$$
$$SO + SO_2 \longrightarrow S + SO_3, \qquad SO + COS \longrightarrow S_2 + CO_2.$$

Spectroscopic data obtained by cosmic probes confirm indirectly the presence of S_2, S_3, and subsequent oligomers of sulphur S_x up to the stable S_8.[1] The photo-dissociation of these molecules

$$S_x + h\nu \longrightarrow S^* + S_{x-1}$$

may be the source of excited S* atoms capable of reacting with molecules of water and carbon dioxide

$$S^* + H_2O \longrightarrow SH + OH,$$
$$S^* + CO_2 \longrightarrow SO + CO.$$

Excited atoms and molecules play an important part in the chemistry of the atmosphere. In particular, the reaction of excited molecules of sulphur dioxide with hydrocarbons may play an important role in the formation of sulphur-containing aerosols in industrial regions with a relatively high atmospheric concentration of hydrocarbons and sulphur dioxide. The high bond energy in the SO_2 molecule practically excludes the dirct photo-dissociation of this molecule in the atmosphere, and also all other reactions except further oxidation.[79] The formation of excited SO_2^* molecules in the atmosphere may open up alternative pathways in the reaction of SO_2 with carbon-containing molecules. It has been reported[80] that a large quantity of sulphur-containing products is formed when an air/sulphur dioxide/butane mixture is irradiated.

A study of the photochemical reactions in mixtures of SO_2 with alkanes on irradiation with light with $\lambda = 3130$ Å[81] showed the absence of processes involving the rupture of C–C bonds, since the products of the photolysis of SO_2 with isobutane and n-butane did not contain methane, ethane, or propane. A small quantity of C_8 hydrocarbons was detected. Only traces of oxygen-containing compounds—alcohols, aldehydes, and ketones—were detected. The principal products include sulphinic acids RS(=O)OH and other organic acids. Their low quantum yield and the low yields of hydrogen and the products of the recombination and disproportionation of alkyl radicals show that the reaction of SO_2 with RH does not involve radical chain reactions. For the most part the mechanism of the reaction of excited SO_2^* with hydrocarbons remains unclear.

A more obvious process is the reaction of SO_2^* with carbon monoxide

$$SO_2^* + CO \longrightarrow CO_2 + SO,$$

where the spin-allowed character of the formation of SO in the triplet ground state $X^3\Sigma^-$ and the excess excitation energy make the reaction in this direction possible, although the low quantum yield shows that the removal of oxygen, even from the excited SO_2^* molecule, is difficult[81] and still requires an activation energy of 4 kcal mol^{-1}.[82]

Calvert and co-workers carried out a series of studies of the reaction of the triplet excited molecules $SO_2(^3B_1)$ with alkanes,[83,84] alkenes, and aromatic hydrocarbons.[85,86] The activation energy of the quenching of $SO_2(^3B_1)$ by paraffinic hydrocarbons decreases regularly in the order: ethane, neopentane, propane, n-butane, cyclohexane, and isobutane, which corresponds to the decrease in the strength of the C–C bond in the molecule. These and other data indicate that for these compounds chemical quenching, probably involving the removal of a hydrogen atom, predominates. The rate constants of the quenching of $SO_2(^3B_1)$ by alkenes and aromatic hydrocarbons depend little on temperature and correspond closely to the number of binary collisions. These data confirm the hypothesis that the initial act of the reaction, determining the rate of the process, is the reaction between $SO_2(^3B_1)$ and the π-system in these compounds. The subsequent addition of $SO_2(^3B_1)$ to the double bond of the alkene gives a triplet biradical as an intermediate complex,[83] as in the reaction of $O(^3P)$ atoms with alkenes.[87] The principal stable products of the reaction of $SO_2(^3B_1)$ with alkenes are sulphinic acids, formed with an efficiency of 0.14–0.5 per collision.[85]

---o0o---

The practical importance of the chemical reactions of carbon- and sulphur-containing compounds requires a deeper understanding of the kinetics of these reactions. New data in this field may lead to the improvement of a number of processes of technical importance.

References

1. R P Wayne *Chemistry of Atmospheres*, Oxford Sci. Publ., Clarendon Press, Oxford, 1985
2. G S Tyndall, A R Ravishankara *Int. J. Chem. Kinet.*, 1991, **23** 483
3. J C Kramlich, P C Malte, W L Grosshandler *XVIII Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1981, p. 151
4. A Demerdache, T M Sugden *The Mechanism of Corrosion by Fuel Impurities* (Edited by H R Johnson, D J Littler), Butterworths, London, 1963
5. A V Chernysheva, V Ya Basevich, V I Vedeneev, V S Arutyunov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, (9) 1956
6. A V Chernysheva, V Ya Basevich, V I Vedeneev, V S Arutyunov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1992, (4) 812
7. M A Berlin, V G Gorechenkov, N P Volkov *Pererabotka Neftyanykh i Prirodnykh Gazov* (The Processing of Petroleum and Natural Gases), Khimiya, Moscow, 1981, 472 pp
8. *Ochistka Gazov ot Sernistykh Soedinenii pri Ekspluatatsii Gazovykh Mestorozhdenii* (The Purification of Gases from Sulphur-Containing Compounds in the Exploitation of Gas Deposits), Nedra, Moscow, 1985, 270 pp
9. M A Menkovskii, V T Yavorskii *Tekhnologiya Sery* (The Technology of Sulphur), Khimiya, Moscow, 1985, 327 pp
10. *Avtogennye Protsessy v Tsvetnoi Metallurgii* (Autogenic Processes in Non-ferrous Metallurgy), Metallurgiya, Moscow, 1991, 413 pp
11. V R Grunval'd *Tekhnologiya Gazovoi Sery* (The Technology of Gasoeus Sulphur), Khimiya, Moscow, 1992, 272 pp
12. *Khimiya i Tekhnologiya Serougleroda* (The Chemistry and Technology of Carbon Disulphide), Khimiya, Leningrad, 1986, 224 pp
13. A V Chernysheva, V S Arutyunov, V Ya Basevich, V I Vedeneev *Khim. Fiz.*, 1990, **9**(1) 98
14. W T Reid *External Corrosion and Deposits, Boilers and Gas Turbines*, Elsevier Publ., America, 1971
15. C F Cullis, M F R Mulcahy *Combust. Flame*, 1972, **18** 225
16. M R Zachariah, O I Smith *Combust. Flame*, 1987, **69** 125
17. C P Fenimore, G W Jones *J. Chem. Phys.*, 1965, **69** 3593
18. A S Kallend *Combust. Flame*, 1972, **19** 227
19. A S Kallend *Trans. Faraday Soc.*, 1967, **63** 2442
20. H Egsgaard, L Carlsen, H Florencio, et al. *Chem. Phys. Lett.*, 1988, **148** 537
21. J Chamboux, V Viossat, F Jorand, K Sahetchian *J. Chim. Phys.*, 1985, **82** 499
22. G Whittingham *Trans. Faraday Soc.*, 1948, **44** 141
23. C F Cullis, R M Henson, D L Trimm, *Combust. Flame*, 1967, **11** 150
24. G M Johnson, C J Matthews, M Y Smith, D J Williams *Combust. Flame*, 1970, **15** 211
25. S F Evlanov *Tsvetnye Metally*, 1979, (4) 53
26. US P. 1 919 342 1933; US P. 1 917 687, 1933
27. US P. 2 270 427, 1942; US P. 2 388 259, 1945; US P. 24 312 336, 1947
28. E P Fleming, T C Fitt *Ind. Eng. Chem.*, 1950, (11) 2249
29. T D Averbukh, N P Bakina, A A Radivilov, et al. *Khim. Promst. (Moscow)*, 1968, (10) 33
30. A V Avdeeva, V A Karzhavin, N F Yushkevich *Khim. Promst. (Moscow)*, 1934, **1**(2) 33
31. J Zawadzki, S Ostrauch, G Kwiecinski *Przem. Chem.*, 1938, **22**(11–12) 558
32. C W Walker *Ind. Eng. Chem.*, 1946, **38**(9) 906
33. Ya P Berkman, S V Kushnir *Zh. Prikl. Khim.*, 1959, **32**(6) 1211
34. A S Bobrin, V I Anikeev, A Ermakova, et l. *React. Kinet. Catal. Lett.*, 1989, **40** 357
35. A S Bobrin, V I Anikeev, A Ermakova, V A Kirillov *React. Kinet. Catal. Lett.*, 1989, **40** 363
36. L D Shishkina, Summary of Candidate's Thesis, State Scientific Research Institute for Non-Ferrous Metals, Moscow, 1982
37. V S Arutyunov, V Ya Basevich, V I Vedeneev, et al. *Kinet. Katal.*, 1991, **32**(5) 1240
38. V S Arutyunov, V Ya Basevich, V I Vedeneev, O V Sokolov *Kinet. Katal.*, 1991, **32**(6) 1295
39. V S Arutyunov, V I Vedeneev, R I Moshkina, V A Ushakov *Kinet. Katal.*, 1991, **32**(2) 267
40. V S Arutyunov, V I Vedeneev *Usp. Khim.*, 1991, **60**(12) 2663 [English translation in *Russ. Chem. Rev.*, 1991(12)]
41. V S Arutyunov, V Ya Basevich, V I Vedeneev, O V Sokolov *Kinet. Katal. (in the press)*

42. J H Kiefer, W A Von Drasek *Int. J. Chem. Kinet.*, 1990, **22** 747
43. V S Arutyunov, V I Vedeneev, V A Ushakov, V V Shumova *Kinet. Katal.*, 1990, **31**(1) 13
44. V S Arutyunov, V Ya Basevich, V I Vedeneev, et al. *Kinet. Katal.*, 1991, **32**(5) 1236
45. V S Smurov, B S Aranovich *Proizvodstvo Serougleroda* (The Production of Carbon Disulphide), Khimiya, Moscow–Leningrad, 1966
46. C M Thacker, E Miller *Ind. Eng. Chem. Ind. Ed.*, 1944, **2** 182
47. BRD P. 1 122 046, 1962
48. BRD P. 1 122 047, 1962
49. French P. 2 053 879, 1971
50. USSR P. 295 247; *Byull. Izobr.*, 1971, (7) 185
51. US P. 3 699 215, 1972
52. US P. 3 927 185, 1975; US P. 4 057 613, 1977; US P. 4 073 868, 1978
53. US . 3 932 595, 1976
54. French P. 2 463 744, 1981
55. French P. 2 463 745, 1981
56. H I Waterman, C van Vlodrop *J. Soc. Chim. Ind.*, 1939, **58** 109
57. E Luzarreta, J Garaud *Compt. Rend. 78^e Cong. Socs. Savantes. Paris et Depts. Sect. Sci.*, 1953, p. 365; *Chem. Abs.*, 1955, 9239a
58. V S Arutyunov, V Ya Basevich, V I Vedeneev, et al. *Kinet. Katal.*, 1990, **31**(5) 1053
59. V S Arutyunov, V Ya Basevich, V I Vedeneev, et al. *Kinet. Katal.*, 1992, **33**(3) 487
60. R Lepsoe *Ind. Eng. Chem.*, 1938, **30** 92
61. J B Ferguson *J. Am. Chem. Soc.*, 1918, **40** 1626
62. R Lepsoe *Ind. Eng. Chem.*, 1940, **32** 910
63. M L Bogoyavlenskaya, A A Koval'skii *Zh. Fiz. Khim.*, 1946, **20** 1325
64. A A Koval'skii, Doctoral Thesis, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1946
65. V T Minasyan, A B Nalbandyan *Dokl. Akad. Nauk SSR*, 1974, **218** 393
66. V C Okay, W L Short *Ind. Eng. Chem. Process. Des. Dev.*, 1973, **12** 291
67. S H Bauer, P Jeffers, A Lifshits, B P Yadava *XIII Symp. (Int.). on Combustion. Pittsburgh: Combust. Institute*, 1971, p. 417
68. M A Kurbanov, V Kh Mamedov, V R Rustamov *Khim. Vys. Energ.*, 1988, **22** 218
69. V V Vasilevskii, E I Gutsevich, B V Potapkin, et al. *Khim. Vys. Energ.*, 1990, **24** 41
70. V V Vasilevskii, E I Gutsevich, B V Potapkin, et al., *Khim. Vys. Energ.*, 1991, **25** 455
71. V S Arutyunov, V I Vedeneev, L V Nikisha, et al. *Kinet. Katal.* (in the press)
72. C F Cullis, M M Hirschler *Atmospheric Environment*, 1980, **14** 1263
73. C S Kan, R D McQuigg, M R Whitbeck, J G Calvert *Int. J. Chem. Kinet.*, 1979, **11** 921
74. E Sanhueza, R Simonaitis, J Heicklen *Int. J. Chem. Kinet.*, 1979, **11** 907
75. S P Sander, R T Watson *Chem. Phys. Lett.*, 1981, **77** 473
76. L V Nikisha, S S Polyak, V S Arutyunov, V I Vedeneev *Kinet. Katal.*, 1992, **33**(5,6) 1010
77. F Yin, D Grosjean, J H Seinfeld *J. Atmospher. Chem.*, 1990, **11** 309
78. F Yin, D Grosjean, R C Flagan, J H Seinfeld *J. Atmospher. Chem.*, 1990, **11** 365
79. H Okabe *Photochemistry of Small Molecules* (Translated into Russian), Mir, Moscow, 1981, 504 pp
80. H S Johnston, K D Jain *Science*, 1960, **131** 1523
81. R B Timmons *Photochem. Photobiol.*, 1970, **12** 219
82. G E Jackson, J G Calvert *J. Am. Chem. Soc.*, 1971, **93** 2593
83. F B Wampler, K Otsuka, J G Calvert, E K Damon *Int. J. Chem. Kinet.*, 1973, **5** 669
84. C C Badcock, H W Sidebottom, J G Calvert, et al. *J. Am. Chem. Soc.*, 1971, **93** 3115
85. H W Sidebottom, C C Badcock, J G Calvert, et al. *J. Am. Chem. Soc.*, 1971, **93** 3121
86. K L Demerjian, J G Calvert *Int. J. Chem. Kinet.*, 1975, **7** 45
87. V D Knyazev, V S Arutyunov, V I Vedeneev *Int. J. Chem. Kinet.*, 1992, **24** 545

Received 23rd April 1992

Translated from *Uspekhi Khimii* 61 2105–2125 (1992) U.D.C. 541.49:632.952

The influence of metal coordination compounds on the ionic conductivity of bilayer lipid membranes

B A Bovykin, A M Omel'chenko, T V Sytnik
Dnepropetrovsk Institute of Chemical Engineering

ABSTRACT. The results of studies on the problem of the effect of metal coordination compounds on biological and bilayer lipid membranes are surveyed. The authors' later data, defining the mechanism of the action of metal complexes which are significant in the development of specific syntheses of physiologically active substances used in medicine and agriculture, are presented.

The bibliography includes 50 references.

Contents

I. Introduction 1156
II. Interaction of metal complexes with biological membranes 1156
III. The mechanism of the influence of coordinatively unsaturated compounds on the ionic conductivity of bilayer lipid membranes 1159
IV. The mechanism of the influence of coordinatively saturated metal complexes on the ionic conductivity of bilayer lipid membranes 1163
V. Conclusion 1165

I. Introduction

One of the most important problems in modern chemistry is that of the creation of the foundation for the specific synthesis of compounds with a specified biological activity. Its solution can be achieved only by establishing the relation between the physiological activity, on the one hand, and the molecular structure and properties of substances on the other. Despite certain advances in this field, there is at present no scientificially-based theory which would make it possible to construct effective biologically active compounds.

One of the causes of this is that the manifestation of activity is frequently inferred from the final results of the activity of substances manifested in the alteration of some kind of properties and features of the living organism as a whole (at least the living cell). The deep-seated processes at a molecular level, which are in fact the cause of the change in the normal functioning of the organism, are hardly investigated under these conditions.

The problem of creating the foundations for a specific synthesis of biologically active compounds must be solved by imparting to them properties which would enable them to act on the most important molecular mechanism among the enormous number of mechanisms of the normal vital activity of the living cell.

Among such mechanisms, it is essential to differentiate those which are linked directly to the functioning of cell membranes. Lipids, among which phospholipids predominate, constitute the structural basis of the membranes of living organisms. Bilayer lipid membranes (BLM), which are completely adequate models of the cell membranes of living organisms,[1] are therefore convenient objects for the study of the mechanisms of the action of compounds on biological membranes. Using this model, the mechanism of the action of various substances, including metal ions, has been investigated. On the other hand, only isolated studies have been devoted to the action of coordination compounds, including biologically active ones, on cell membranes.

A characteristic features of unmodified BLM is their extremely low permeability to the majority of inorganic ions, especially multicharged ions, and as a rule the absence of an appreciable selectivity among the ions. The low permeability of BLM to inorganic cations is due to the high activation energy for their transfer (of the order to 120 kJ mol^{-1} for singly charged cations[2]). At the same time, it is well known that biological membranes exhibit a high permeability (higher by 5–6 orders of magnitude than that of BLM) and manifest ion-selective properties.

The mechanisms of ionic conduction and selectivity of biological and artificial membranes have not been ultimately elucidated despite the large number of relevant studies. The accumulated literature and the authors' own data on the effect of metal cations on the lipid membranes have been surveyed[3] taking into account their physicochemical properties. It was indicated in the review that, when metal cations are bound to BLM and other membrane systems, it is necessary to take into account a series of factors: hydrolysis, the behaviour of metal compounds at different pH of the solution, in particular their solubility, their complex forming capacity, and other properties,

The subdivision of metal cations into classified groups taking into account their covalent characteristics makes it possible to estimate the sequence in which the metal cations are bound to membranes using models of the adsorption centre in lipid bilayers of different composition.

The available data suggest that the transport of metal cations through biological membranes is achieved with the aid of special transferring molecules. Evidently the transport of transition metal cations, which are important for the physiology and toxicology of living organisms, should involve the participation of organic compounds—bioligands capable of coordination interaction with these metal cations. In this connection, studies on the molecular mechanisms of the interaction of metal complexes with cell membranes have become particularly timely.

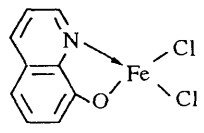
II. Interaction of metal complexes with biological membranes

Insufficient attention has been devoted hitherto to the question of coordination compounds.

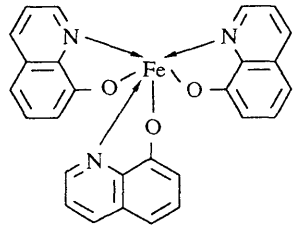
It has been assumed that the role of the metal in the complex consists in creating a suitable transport form for the ligands or, if

the metal ion itself exhibits a biological activity, then the complex is necessary for the transport of the metal through the cell membrane.[4]

Albert[5] showed that the iron(III) complex of 8-hydroxyquinoline (HQ) has the 1 : 3 composition. Neither the ligand nor the iron(III) ion possess biological activity but are very effective in suppressing pathogenic microorganisms when combined in a 1 : 1 complex.



$Fe(HQ)Cl_2$



$Fe(HQ)_3$

The author suggested that the compound containing three deprotonated 8-hydroxyquinoline molecules $Fe(HQ)_3$ is the only one among all the possible complexes which is capable of penetrating through the cell membranes of the microorganism. He believes that coordinatively unsaturated complexes are bound too strongly to membranes. After entering the cell, $Fe(HQ)_3$ decomposes with formation of 1 : 1 and 1 : 2 complexes, which exhibit a biological activity. The view that the most lipophilic complex exhibits a toxic activity on pathogenic microorganisms is supported by the fact that the introduction of hydrophobic groups into the 8-hydroxyquinoline molecule weakens the antibacterial activity of the complex.

Similar conclusions were reached in a study[6] confirming that only coordinatively saturated and neutral copper(II) complexes with low-molecular-weight lipophilic plasma components can permeate through cell membranes.

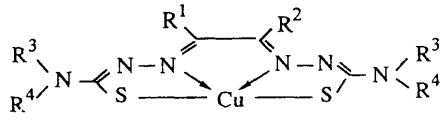
It has been shown[7] that the copper(II) complex of ceruloplasmin (CPL), which is a copper-containing serum α-2-glycoprotein, is synthesised in the liver and then enters the serum and the blood plasma. The physiological functions of ceruloplasmin involve oxidase and ferroxidase enzyme activities and participation in the iron and copper metabolisms in the organism involving transport of copper(II) ions through plasmatic membranes.

It is stated in the above monograph that bisthiosemicarbazones, which tetradentate complex-forming substances, exhibit an appreciable antitumour activity. The derivative in which R^1 = ethoxyethyl and $R^2 = R^3 = R^4 = H$ [ketoxal bisthiosemicarabazone (H_2KTS)] has been most thoroughly investigated. The effect of these compounds is due to the binding of copper(II) ions with formation of a therapeutically active complex:

$$H_2KTS + CuX_2 \longrightarrow CuKTS + H_2X.$$

This complex has been isolated and investigated in solutions and in the solid state. According to X-ray diffraction data, it has a square planar structure.

By virtue of its high stability ($\lg\beta = 18.4$), the complex is almost incapable of forming axial adducts and of entering into substitution reactions. It can therefore be regarded as coordinatively saturated.



CuKTS

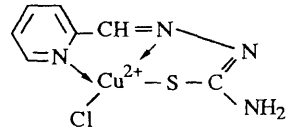
It has been demonstrated by polarographic and potentiometric methods that the compound is capable of undergoing one-electron reduction. The reaction with thiols (for example, glutathione) proceeds via a mechanism involving three stages:

$$Cu^{(II)}KTS + RSH \longrightarrow Cu^{(I)}SR + {}^1/_2RSSR + H_2KTS,$$
$$CuKTS + RS^- \rightleftharpoons CuKTSRS^-,$$
$$CuKTSRS^- + RSH \longrightarrow Cu^{(I)}SR + HKTS^- + RS^{\cdot},$$
$$2RS^{\cdot} \longrightarrow RSSR.$$

It has been noted that the rate of oxidation of thiols is correlated with the cytotoxic activity of the complexes. It is believed that H_2KTS enters the cell only as a result of the complex formation reaction with copper(II). If the reaction does not occur, then the ligand is localised in the lipophilic part of the membrane. On reduction of the complex in the cell and the formation of $Cu^{(I)}SR$, the copper is probably distributed between the cell thiols and moves to the interior of the cell, while the H_2KTS ligand emerges from the cell. This inhibits the synthesis of DNA and the mitochondrial oxidative phosphorylation, which constitutes ultimately the cytotoxic activity of the complex.

The example analysed above describes the mechanism of the action of the coordinatively saturated complex on the cell membrane, complex formation occurring on the surface of the membrane with participation of the metal ion located within the components of the tumour cell. Only as a result of this process is the physiologically active complex transported through the biological membrane.

The case of a coordinatively unsaturated complex occurs when 2-formylpyridine thiosemicarbazone (Hα) reacts with copper(II). In contrast to CuKTS, the complex $[Cu\alpha Cl]^0$, where α is the tridentate ligand



enters readily into adduct formation reactions, for example, with ethylenediamine. The stability of the complex [CuαenCl] is indicatated by $\lg\beta = 5.53$. The complex $[Cu\alpha Cl]$ is reduced on interaction with thiols within the cell, but does not decompose, in contrast to CuKTS, and affords an adduct.

The effect of platinum and platinum group metal complexes, which exhibit an appreciable antitumour activity, on biological membranes is of special interest. It was noted in 1969 that certain platinum complexes exhibit an anticarcinogenic activity. The influence of the charge, geometrical structure, stability, etc. of the complexes on their antitumour activity was investigated. It was noted that the absence of antitumour activity in charged platinum complexes is associated with their inability to permeate through cell membranes. The interaction of *cis*-dichlorodiamineplatinum(II) with a phosphate transferring agent in mitochrondia has been investigated.[8] It was suggested that the fully or partly hydrolysed complex interacts in mitochondria with a phosphate transferring agent and modifies the SH group in the latter. According to the authors, such interaction can partly account for the antitumour activity of the complex.

Interesting data have been obtained by Stetsenko et al.[9] in a study of the electrical conductivity of a NaCl solution ($c = 1 \times 10^{-2}$–0.15 M) on treatment with $[Pt(NH_3)_2Cl_2]$ isomers ($c = 3 \times 10^{-3}$ M). The reason why *cis*-$[Pt(NH_3)_2Cl_2]$ influences the electrical

conductivity of the solution is the associative interaction of the ion–dipole type between the Cl^- ions and the polar molecules (of the *cis*-isomer). The existence of a direct relation between the antitumour activity and the ability of *cis*-$[Pt(NH_3)_2Cl_2]$ to reduce the electrical conductivity of the electrolytes suggests that the association of the biologically active *cis*-isomer promotes its retention within the extracellular liquid, where the concentration of chloride ions is high, and its supply in an unchanged form through the cell membrane to the site of the reaction with the DNA of the tumour cell.[9]

Bearing in mind the size of the complex molecule (the distance between the chlorine atoms is 340 pm) and the pore radius in the cell membrane (400 pm), through which the solutes pass in either direction relative to the concentration gradient, it has been suggested[7] that *cis*-$[Pt(NH_3)_2Cl_2]$ permeates the cell as a result of passive diffusion. This mechanism has been confirmed by experiments which make it possible to distinguish passive diffusion from active transport. The rate of accumulation of *cis*-$[Pt(NH_3)_2Cl_2]$ in the cells of the Ehrlich ascites tumour has been determined and the data were analysed on the basis of the kinetic Michaelis–Menten equatiion. The hypothesis that *cis*-$[Pt(NH_3)_2Cl_2]$ passes through membranes by means of diffusion is supported by the finding that the rate of accumulation of the preparation in the cells is not affected by substances promoting membrane permeability.[7]

The biological activity of compounds is in many respects determined also by their ability to alter the functional activity of membrane structures. The complexes inhibit the activity of membrane enzymes, interacting with the surface or deep-seated SH groups of ATPase. Thus in the anionic Pt^{2+} and Pd^{2+} complexes having the composition $K_2[MX_4]$, where X = NO_2^-, Cl^-, Br^-, I^-, or SCN^-, the inhibiting properties vary in different ways with increase in the ability of the ligands to redistribute the electron density from the complex-forming ion in the above series of ligands X. For palladium(II), the inhibiting activity of the complexes increases, while for platinum(II) it diminishes. This indicates different mechanisms of the activity of the complexes. The Pt^{2+} compounds are reduced to zerovalent platinum on contact with the enzyme, forming "couplings". On the other hand, the Pd^{2+} compounds act as electron acceptors, forming complexes with the electron-donating groups of the enzyme.[10]

It has been noted that in the series of compounds $Q_2[PdBr_4]$, where Q = K^+, $(CH_3)_3NH^+$, or $N(C_2H_5)_4^+$, the inhibiting activity of the membrane ATPase diminishes with increase in the size and hydrophobicity of the cation. The large dimensions of the cations and ionic associated species probably hinder the approach through complexes to the active centre of the enzyme, as a result of which $[N(C_2H_5)_4]_2[PdBr_4]$ does not have an inhibiting activity. The same behaviour has been observed for copper(II) complexes—$[(CH_3)_3NH]_2[CuCl_4]$ and other compounds.

The intensification of studies on substances the mechanism of the biological activity of which is associated with their interaction with biological membranes has been promoted by the studies of Mueller et al.[1] They were able to develop a method for the formation of bilayer lipid membranes constituting an adequate model of the lipid matrix of the membranes in any living organisms.

A number of investigations of the effects of various reagents on BLM have been carried out using this model.[11] However, only isolated communications have been devoted to studies on coordination compounds.

Thus it has been shown[12] that, in the presence of Cu^{2+}, Zn^{2+}, Ni^{2+}, and Hg^{2+} ions as well as tetrachlorotrifluoromethylbenzimidazole (TTFB), the bilayer lipid membranes comprising brain lipids have an N-shaped voltage–current characteristic (VCC). The decrease in the conductivity of the BLM with increase in voltage has been explained by the formation of coordination compounds of the type $[M(TTFB)_n]^{2+}$ It has been suggested[13] that the agent effecting transfer through the membrane is in this case the complex of the metal cations with TTFB and the reason for the appearance of the descending section on the voltage–current characteristic is the decomposition of the complex under the influence of the potential difference between the lipid phase of the membrane and the aqueous solution.

There have also been a few studies on the transport of metal cations through the lipid bilayers of liposomes which takes place with participation of organic ligands. For example, free aliphatic acids increase the permeability of liposomes to Yb^{3+}, Tb^{3+}, Fe^{3+}, Fe^{2+}, and Co^{2+}.[14]

It has been shown[15] that hypoglycemic sulphonylureas (glibenclamide and gliclazide) increase the permeability of sonicated dipalmitoylphosphatidylcholine vesicles to Pr^{3+} and Ca^{2+}.

In view of the inadequacy of the published factual data and the lack of systematic studies of the membrane activity of coordination compounds of metals, which constitute one of the most important preconditions for the creation of a theory of the specific synthesis of biologically active substances, we undertook a study of the molecular mechanisms of the interaction of coordination compounds of metals and planar BLM to which a number of studies have been devoted.[16–30] In each specific case, the principal problem which had to be solved was that of the composition of the membrane-active form of the complex.

In order to investigate the nature of the absorbing and permeating species, use was made of the methods for the generation of a transmembrane electrical potential differences (EPD) for an asymmetric addition of the reagents to the BLM,[31] the method based on the VCC for BLM which also exist under asymmetric conditions as regards the concentration of the reagents, as well as the method involving the measurement of the intramembrane electrical potential difference based on the conpensation for the second harmonic of the alternating current.[32]

In many instances the central ion in the complex can be coordinatively unsaturated in relation to the ligand. It is then possible to postulate the formation of a membrane-transport form having the compositions central ion–organic ligand–electrolyte anion. When this is taken into account, the mechanisms of the effect of coordinatively saturated and unsaturated compounds on BLM should differ significantly. We carried out an experimental test of these hypotheses in chloride solutions and investigated the mechanisms of the transport of chloride anions by coordinatively unsaturated metal-containing compounds.

It must be emphasised that substances which function as transferring agents for chloride anions through a membrane should undoubtedly exhibit an appreciable biological activity. This is indicated by data showing the importance of maintaining a chloride homeostasis for the normal functioning of the living cell. For example, the membrane potentials of mitochondria and liver cells have a chloride basis.

III. The mechanism of the influence of coordinatively unsaturated compounds on the ionic conductivity of bilayer lipid membranes

Complexes with various biological properties were chosen as objects for the study of the activity of coordinatively unsaturated compounds. Thus the copper(II) complex of ε-caprolactam (CL)—the preparation phyton (kartocid)—exhibits a high fungicidal activity against the agent responsible for false mildew.[33]

Phyton L (a laboratory preparation) was obtained by refluxing copper(II) chloride and ε-caprolactam in molar proportions of 1 : 3 in dry alcohol over a period of 1 h. According to X-ray diffraction data, a single crystal of phyton L has an ionic structure.[34] The molecule consists of the cations $[Cu(CL)_6]^{2+}$, having a crystallographic symmetry such that the Cu^{2+} cation is a centre of symmetry, and of the anions $[Cu(CL)Cl_3]_2^-$. Thus the formula of phyton L is $[Cu(CL)_6][Cu(CL)Cl_3]_2$. ε-Caprolactam is a monodentate ligand and is coordinated to Cu^{2+} via the oxygen atom.

Phyton T (technical preparation) is dichloroaquotricaprolactamcopper(II) $Cu(CL)_3Cl_2H_2O$. Phyton T is synthesised by fusing together the initial components.

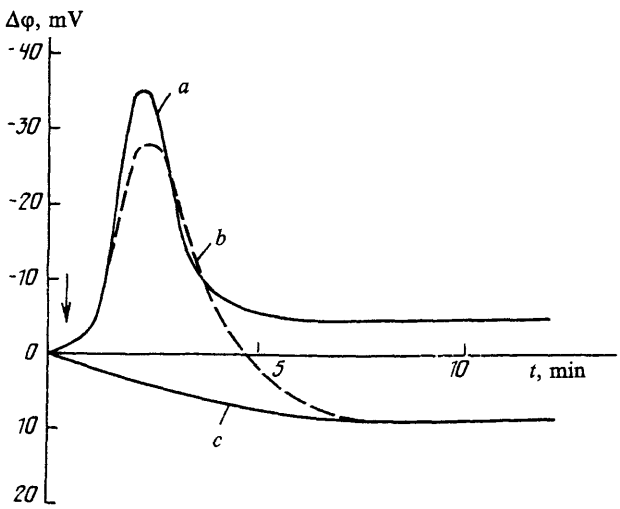


Figure 1. Typical curves for the generation of the transmembrane electrical potential difference following the introduction of reagents on one side of a brain lipid BLM; the arrow indicates the instant of the introduction of the reagents: *a*, $CuCl_2$; *b* and *c*, phyton; electrolyte—0.01 M KCl.

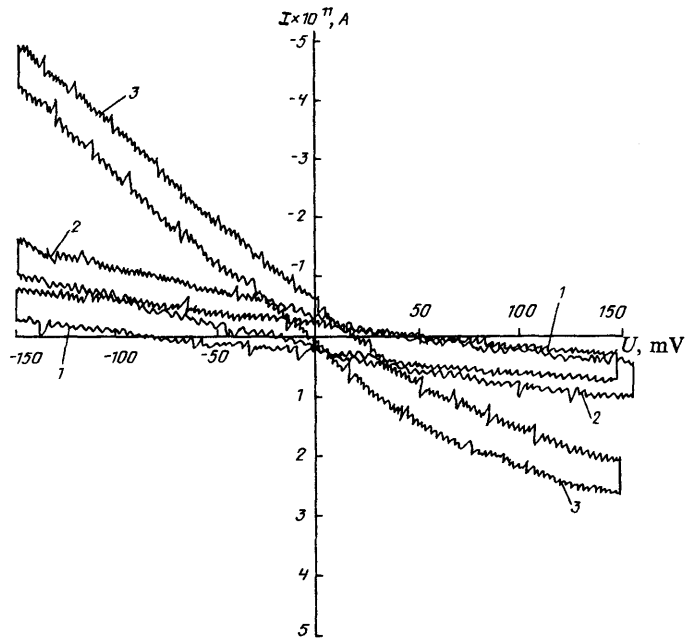


Figure 2. The voltage—current cyclic characteristics of brain lipid BLM in the presence of various concentrations of phyton on one side: *1*, in the absence of phyton; *2*, 1.7 × 10^{-4} M; *3*, 5.4 × 10^{-4} M; rate of scanning of the potential 1 mV s^{-1}; electrolyte—0.01 M KCl.

Fig. 1 presents typical curves for the generation of the transmembrane electrical potential difference when $CuCl_2$ and phyton are introduced on one side of the BLM. The introduction of ε-caprolactam did not generate a potential difference, which indicates its non-ionic nature. The nature of the transmembrane potential difference, generated on the BLM after the introduction of membrane-active agents on one side, has been studied in detail in relation to ionogenic detergents.[31,35] It was shown that the form of the potential growth—potential decrease curve depends significantly on the magnitude and sign of the charge on the adsorbing species and on the surface area of the BLM and is determined by two processes—the adsorption on the BLM of ions of membrane-active substances as well as the transmembrane transfer of these ions and the ions contained in the electrolyte solutions. The stationary potential is diffusional in nature and arises as a consequence of the transmembrane gradient of the adsorbing ions. The rate of generation of the potential is determined by the rate of adsorption of Cu^{2+} on the surface of the BLM, while the rate of dissipation of the charge is determined by the rate of the transmembrane transport (i.e. by the resistance of the membrane). The maximum on the potential growth—potential decrease curve shows that the transfer of ions through the membrane is slower than their adsorption. The existence of an excess negative charge on the BLM comprising cattle brain lipids[36] apparently determines the specific adsorption of the ions on the membrane surface.

For the asymmetric addition of dimethylformamide solutions of phytons L and T to the electrolyte surrounding the BLM, a positive charge arose also in the compartment with the phyton (Fig. 1*b*). The positive sign of the stationary potential difference indicated the preferential passage through the BLM of the negatively charged (anionic) form of phyton. Such a species was likely to have been $[Cu(CL)Cl_3]^-$. Sometimes a negative potential was recorded in the compartment with phyton and was then reversed in the course of 5—10 min (Fig. 1*c*). In this case, the curve representing the

variation of the membrane potential had a maximum, which is apparently associated with the adsorption of the coordinatively saturated complex cations $[Cu(CL)_6]^{2+}$.

The anionic nature of the membrane-transport form of phyton is indicated also by the symmetrical form of the voltage–current characteristics recorded in the presence of phyton (Fig. 2). Evidently, in the absence of the modifying agent, the voltage–current characteristic for the BLM is linear in the potential range ±150 mV. In the presence of phyton on one side, the BLM acquired rectifying properties. For the negative polarisation of the compartment with phyton, the current was greater than for the positive polarisation, which indicated the appearance of preferential anionic conductivity in the BLM.

The addition of phyton affected also the electrical conductivity of the BLM. The unmodified BLM has a low conductivity of the order of $10^{-9}-10^{-8}$ S cm^{-2}. The introduction of $CuCl_2$ diminished slightly the electrical conductivity while the addition of ε-caprolactam did not affect the conductivity of the BLM. Under the influence of dimethylformamide solutions of phytons L and T, the electrical conductivity of the BLM increased approximately by a factor of 100 (Fig. 3). The non-linearity of the dependence of the electrical conductivity of the BLM on the concentrations of the reagents is noteworthy. At a phyton concentrate close to 10^{-2} M, the structure of the BLM was affected and became unstable.

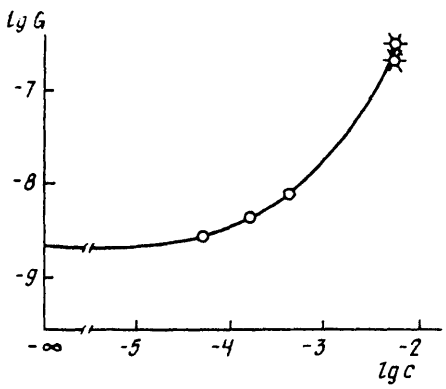


Figure 3. Dependence of the conductivity (G, S cm^{-2}) of the BLM on the phyton concentration (c, M) on one side (the points represented by stars denote the conductivity of BLM measured 20 min after the introduction of the reagent).

The solubility of the permeating anion in lipids may be imparted to it by the presence in its composition of a ε-caprolactam molecule, which exhibits definite lipophilic properties. The logarithm of the partition coefficient of ε-caprolactam in the octanol–water system, which is usually adopted as a measure of the lipophilicity, is $\lg K_{o/w} = 1.03$.[37]

The set of data obtained suggested that the coordinatively unsaturated complex between $CuCl_2$ and ε-caprolactam should be capable of combining with chloride ions and of transporting them across the membrane, whereas the coordinatively saturated complex of the above substances does not possess this property.

By altering the conditions in the synthesis, the coordinatively unsaturated compound $[Cu(CL)Cl_2(H_2O)]$ (yellow colour, lamellar form of the crystals) was isolated from the aqueous or aqueous ethanol solution with the ratio $CuCl_2$:CL = 1:3. The coordinatively saturated compounds $[Cu(CL)_6Cl_2](CL)_2$ (green colour, acicular form) was obtained from benzene solutions after adding to $CuCl_2$ an excess (more than 3 mol per mole of $CuCl_2$) of ε-caprolactam.[21] The study of the membrane activity of these compounds showed that $[Cu(CL)Cl_2(H_2O)]$ does indeed possess membrane activity similar to that of phyton T, i.e. it forms an ionic membrane-transport form having apparently the composition $[Cu(CL)Cl_3]^-$. On the other hand, the effect of $[Cu(CL)_6Cl_2](CL)$ reduced to the adsorption of the cationic complex on the surface of the BLM and did not differ qualitatively from the effect of the simple Cu^{2+} salt.

Another important biologically active compound is the zinc complex of ethylenethiourea. Ethylenethiourea (ETU) is the main product of the metabolism of metal-containing zineb and maneb,[38] which exhibit an appreciable fungicidal activity.[39] It has been suggested that, having entered the interior of the cell, zineb and maneb undergo acid hydrolysis with formation of ethylenethiourea, which exhibits a toxic activity.[40] The absence of fungicidal activity in ethylenethiourea itself can be explained by its poor capacity for permeation through cell walls. Zineb and maneb are regarded as a kind of depot of ethylenethiourea. On the other hand, no account has been taken whatsoever of the role in transport through the cell membrane of the metal cations in the $ZnCl_2$–ethylenethiourea complex.

Up to a concentration of 2 mM, ethylenethiourea does not alter the conductivity and capacity of the BLM. It has been shown by the method of trial hydrophobic ions[41] that ethylenethiourea molecules are incorporated in the solution/BLM boundary.[25]. Under these conditions, the ethylenethiourea dipoles are oriented parallel to the dipoles of the phospholipid molecules, which increases the dipole-induced jump in the BLM potential.

The study of the complex formation reaction between $ZnCl_2$ and ethylenethiourea in aqueous solutions by spectrophotometric and conductimetric methods showed[26] that, at an ethylenethiourea concentration below 10^{-4} M, the complex is not formed even in the presence of a 60-fold excess of zinc ions. At $ZnCl_2$ and ethylenethiourea concentrations of 10^{-3} and 10^{-4} M respectively, the tetrahedral complex $[Zn(ETU)Cl_2]$, in which ethylenethiourea is a bidentate ligand, is formed. At higher ethylenethiourea concentrations, a second ethylenethiourea molecule adds to the zineb ion with formation of the tetrahedral complex $[Zn(ETU)_2Cl_2]$. Under these conditions, ETU behaves as a monodentate ligand.

The study of the effect of the complex on the BLM established[27] that it induces an appreciable growth of membrane conductivity (Fig. 4). This occurs at a concentration of the complex close to 10^{-3} M, so that, in combination with data obtained in the study of the complex formation reaction with ethylenethiourea in aqueous solutions, this shows that at a concentration less than 10^{-3} M the complex decomposes in the solution into its component parts and that the increase in the conductivity of the BLM is induced by the effect of the complex species. The threshold character of the dependence of the electrical conductivity of the BLM on the concentration of the complex suggested the possibility, in principle, that a membrane-active complex is formed from $ZnCl_2$ and ethylenethiourea directly in the electrolyte solution. The results for the influence of $ZnCl_2$ on the properties of the BLM formed in the presence of ethylenethiourea are presented in Fig. 4. Evidently, as in

the case where the complex is catalytically active, here too the conductivity of the BLM increases after the attainment of a $ZnCl_2$ concentration of about 10^{-3} M. This indicates the formation of permeating complex ions directly from simpler species either in the bulk of the electrolyte or at the membrane/solution interface.

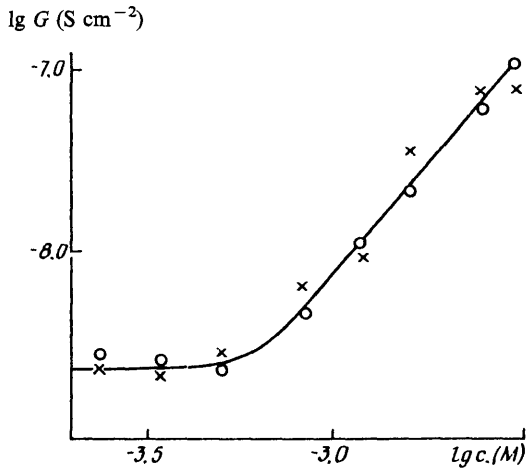


Figure 4. Dependence of the conductivity of the BLM on the concentration of the complex (circles) and $ZnCl_2$ in the presence of 2.4×10^{-3} M ethylenethiourea (crosses).

In order to determine the sign of the charge of the permeating species, a study was made of the voltage–current characteristics of BLM under asymmetric conditions. The BLM was then formed in the presence of ethylenethiourea on either side of the membrane, while $ZnCl_2$ was added on one side. Under these conditions, the voltage–current characteristics had an asymmetric form, the current being higher at a negative potential in the $ZnCl_2$ compartment. This showed that the permeating species are anions.

Measurement of the intramembrane potential difference with the aid of the second harmonic of the alternating current made it possible to determine the sign of the charge of the adsorbing species. It is seen from Fig. 5 that the position of the current I minimum (II) does not change under the influence of ethylenethiourea. This showed that ethylenethiourea does not by itself alter the intramembrane potential difference and confirmed its non-ionic nature. When $ZnCl_2$ is introduced at a concentration of 6.8×10^{-4} M in the cell compartment where ethylenethiourea had been added previously, a difference between the boundary potentials amounting to +14 mV is generated. This indicates a change in the surface charge on the *cis*-side of the BLM in the positive direction as a result of the adsorption of the Zn^{2+} cations. On subsequent increase of the $ZnCl_2$ concentration to 7.5 mM, the sign of the intramembrane potential difference is reversed, which indicates a change in the sign of the charge and hence in the nature of the species adsorbed on the membrane surface.

In this case, the anionic transport complex is apparently formed as a result of the addition of chloride anions to the coordinatively unsaturated complex $[Zn(ETU)Cl_2]$ with formation of the anion $[Zn(ETU)Cl_3]^-$. The most characteristic coordination number for Zn^{2+} cations is 4. The coordinative unsaturation of $[Zn(ETU)Cl_2]$ is associated with the impossibility of altering the denticity of the ligand. Thus one can postulate that the permeating charged species is the anion $[Zn(ETU)Cl_3]^-$. The presence of ethylenethiourea in the complex imparts a certain lipophilicity to the latter (for ethylenethiourea, $\lg K_{o/w} = 0.35$ [37]), whilst chloride anions impart to the complex a negative charge, which is more favourable for transport across the BLM. It is well known that lipophilic anions have a much greater permeating capacity than cations, because the hydrophobic region of the BLM is subject to the influence of a positive electric potential.[42]

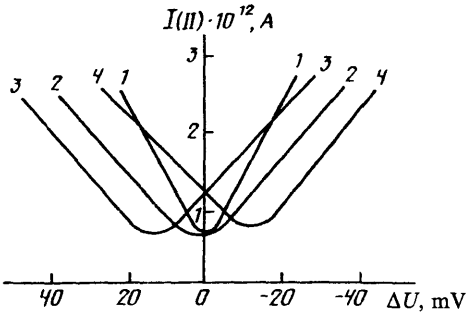


Figure 5. Dependence of the current of the second harmonic and the applied potential in the presence of 1.7×10^{-3} M ethylenethiourea on the *cis*-side: *1*, BLM in the absence of modifying agents; in the presence of modifying agents on one side: *2*, 1.7×10^{-3} M ethylenethiourea; *3*, 6.8×10^{-4} M $ZnCl_2$; *4*, 7.5×10^{-3} M $ZnCl_2$; brain lipid BLM; electrolyte—0.01 M KCl + 0.002 M acetate buffer.

Coordination compounds of cobalt(II) with *o*-phenanthroline (phen) have aroused much interest among the series of new biologically active substances.[43,44] Their appreciable catalytic activity in the oxidation reactions of biological substrates and their influence on the respiratory electron transport chain in mitochondria and on the photosynthetic apparatus of chloroplasts have been observed. Growth regulating and bactericidal activities have been found for a number of complexes. However, the membrane activity of these compounds has not been studied. At the same time, *o*-phenanthroline is appreciably lipophilic ($\lg K_{o/w} = 1.83$ [37]). This suggests a definite possibility of transmembrane transport of cobalt ions as part of coordination compounds with *o*-phenanthroline.

We investigated the effect of *o*-phenanthroline and of its coordinatively unsaturated compounds $[Co(phen)(H_2O)_2](NO_3)_2$ and $[Co(phen)Cl_2].HCl$ on BLM made up of ox brain lipids.[23,29] It was shown that, in the presence of simple salt $CoCl_2$, at a concentration of 10^{-3} M, the electrical conductivity of the BLM is reduced by 20%. On the other hand, the effect of *o*-phenanthroline or the coordination compounds $[Co(phen)(H_2O)_2](NO_3)_2$ and $[Cl(phen)Cl_2].HCl$ on BLM led to an increase in the electrical conductivity of the latter. The kinetics of this change are illustrated in Fig. 6. The effect of *o*-phenanthroline is apparently a consequence of its

lipophilic properties. In order to determine the site of location of *o*-phenanthroline in the BLM structure, the method of trial hydrophobic ions was used. It demonstrated, that, in constrast to ethylenethiourea, *o*-phenanthroline molecules do not have a particular location relative to the normal to the BLM plane. This is probably associated with the more pronounced lipophilic properties of *o*-phenanthroline compared with ethylenethiourea. The protonated form of *o*-phenanthroline, formed in the weakly acid electrolyte (pH 4.5) surrounding the membrane, is apparently the carrier of electricity through the BLM. *o*-Phenanthroline plays the role of the protonophor in this system.

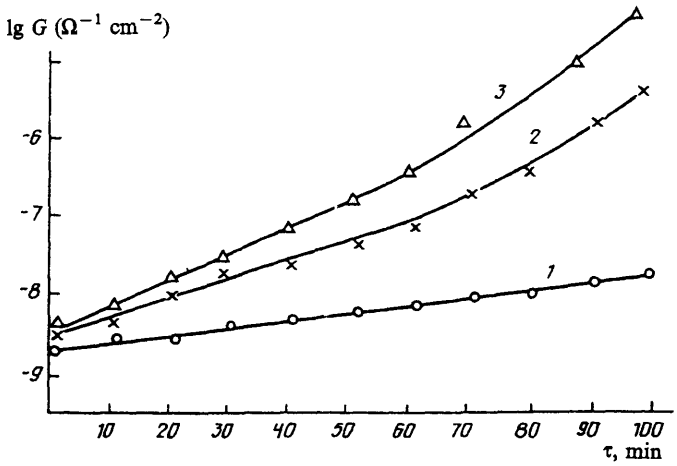


Figure 6. Kinetics of the variation of the conductivity of the BLM after the introduction of 2×10^{-4} M reagents on one side of the membrane: *1*, *o*-phenanthroline; *2*, $[Co(phen)(H_2O)_2](NO_3)$; *3*, $[Co(phen)Cl_2]HCl_2.HCl$; electrolyte—0.01 M KCl + 0.002 M acetate buffer.

The increase in the electrical conductivity of the BLM in the presence of $[Co(phen)Cl_2].HCl$ and $[Co(phen)(H_2O)_2](NO_3)_2$ is apparently induced by the passage through the BLM of lipid-soluble membrane-transport forms comprising coordination compounds.

In order to establish the sign of the charge of the permeating species, a study was made of the voltage–current characteristics of the BLM under asymmetric conditions. Fig. 7 shows that the voltage–current characteristics are asymmetric and that for $[Co(phen)Cl_2].HCl$ the current is greater at a negative potential in the cell compartment where the reagent had been added (*cis*-compartment), while in the case of $[Co(phen)(H_2O)_2](NO_3)_2$ the current is greater at a positive potential in the cell compartment. This shows that anions and cations are the permeating species in the former and latter cases respectively.

As stated above, the complexes investigated are coordinatively unsaturated. The maximum coordination number of cobalt(II) is 6, while in the given complexes it is 4, since *o*-phenanthroline is a bidentate ligand. There is therefore a possibility of a further addition to the central ion of chloride ions, a large number of which are present in the electrolyte. However, here it is necessary to bear in mind that the permeating capacity of the ions through the BLM diminishes greatly with increase in their charge, i.e. the transport of a singly-charged ion is preferred to that of a doubly-charged ion. In the case of $[Co(phen)Cl_2].HCl$, the permeating species are probably the anions $[Co(phen)Cl_3]^-$, while in the case of $[Co(phen)(H_2O)_2].(NO_3)_2$ they are the cations $[Co(phen)(H_2O)_2Cl]^+$. In the latter case, the coordination of a single chloride anion diminishes the positive charge of the ion transported. Such forms of the complex ions probably exhibit an enhanced stability in the membrane phase, i.e. in a medium with a low dielectric constant, whereas in the bulk of the electrolyte they are less stable and dissociate with elimination of chloride anions. Thus, under the influence of the electric field gradient there may be induced transport of chloride anions from one side of the membrane to the other. The greater electrical conductivity of BLM in the presence of $[Co(phen)Cl_2].HCl$ compared with $[Co(phen)(H_2O)_2](NO_3)_2$ is apparently associated with the difference between the charges of the permeating ions.[42]

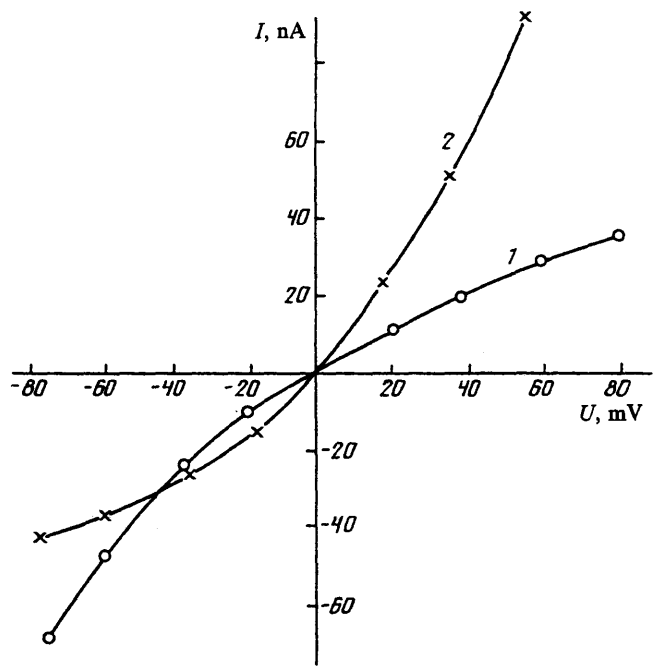


Figure 7. The voltage–current characteristics of a BLM in the presence of $[Co(phen)Cl_2].HCl$ (curve *1*) and $[Co(phen)(H_2O)_2].(NO_3)_2$ (curve *2*) on one side; the sign of the potential is indicated relative to the cell compartment to which the reagent has been added; electrolyte—0.01 M KCl + 0.002 M acetate buffer.

The chloride selectivity of BLM in the presence of the given complexes is indicated by measurements of the potential arising when a transmembrane electrolyte concentration gradient is established. For example, in the presence of 2×10^{-4} M $[Co(phen)(H_2O)_2](NO_3)_2$ with the ratio of the concentrations of the

KCl electrolyte on the two sides of the membrane amounting to 10, an ionic potential of 53 mV is developed, which corresponds to the transport number of the anions $t_{Cl^-} = 0.91$.

The influence of the coordinative saturation of the Co^{2+} ions and of the lipophilic properties of the ligands on the membrane activity of the complex compounds was investigated with the aid of the coordinatively saturated complex $[Co(phen)_2Cl_2].3.5(H_2O)$ and the coordinatively unsaturated complex $[Co(dimphen)Cl_2].HCl$, where dimphen is 2,9-dimethylphenanthroline. The lipophilic properties of 2,9-dimethylphenanthroline are more pronounced ($\lg K_{o/w} = 2.49$ [37]) than those of *o*-phenanthroline. It is striking that, in the presence of the coordinatively saturated complex $[Co(phen)_2Cl_2].3.5H_2O$, the electrical conductivity of the BLM does not increase. It is also seen that the more lipophilic cobalt(II) complex of the dimethyl derivative of *o*-phenanthroline is more effective than $[Co(phen)Cl_2].HCl$. In the presence of $[Co(dimphen)Cl_2].HCl$ on one side of the membrane, the voltage–current characteristics of BLM are asymmetric (the membrane current at a negative potential in the *cis*-compartment is greater than at a positive potential).

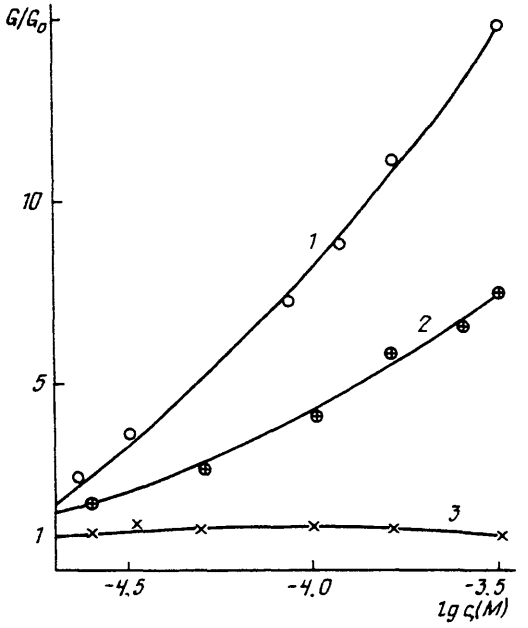


Figure 8. The influence of cobalt(II) complexes of *o*-phenanthroline and its dimethyl derivatives on the relative conductivity of the brain lipid BLM: *1*, $[Co(dimphen)Cl_2].HCl$; *2*, $[Co(phen)Cl_2].HCl$; *3* $[Co(phen)_2Cl_2].3.5H_2O$; electrolyte—0.01 M KCl + 0.002 M acetate buffer.

The study of the ionic selectivity of BLM in the presence of the given complexes by the method involving the measurement of the diffusion potential under conditions where a transmembrane chloride ion gradient has been established demonstrated the chloride selectivity of BLM in the case of coordinatively unsaturated complexes (the Cl^- transport numbers were 0.91–0.93) and the absence of ionic selectivity in the case of the coordinatively saturated complex. The results permit two conclusions: firstly, the coordinatively saturated complexes are unable to transport chloride ions through BLM and, secondly, an increase in the lipophilicity of the coordinatively unsaturated complexes improves their membrane-transport properties in relation to chloride anions.

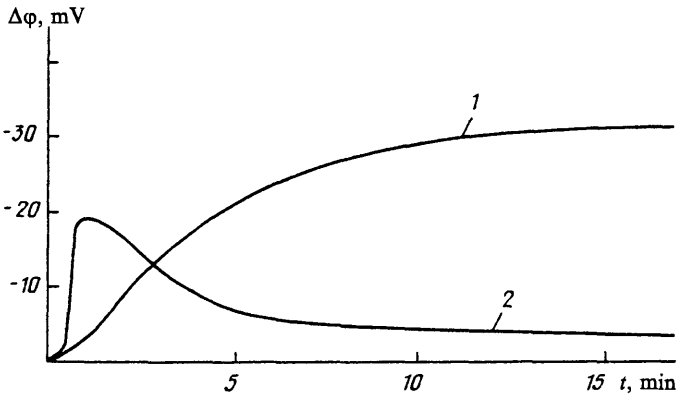
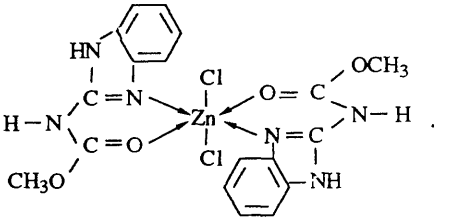


Figure 9. Generation of the transmembrane potential difference after the introduction of 2.7×10^{-6} M $[Zn(BMC)_2Cl_2]$ (curve *1*) and 2.5×10^{-4} M $ZnCl_2$ (curve *2*) on one side of the membrane.

IV. The mechanism of the influence of coordinatively saturated metal complexes on the ionic conductivity of bilayer lipid membranes

The coordinatively saturated complex of $ZnCl_2$ with *N*-methyl-(2-benzimidazolyl)carbamate (BMC) exhibits a fungicidal activity.[45] Its structure and properties have been described.[46] The complex $[Zn(BMC)_2Cl_2]$, where BMC is a bidentate ligand, has an octahedral configuration:



In order to determine the sign of the charge of the membrane-active species, a study was made of the generation of the transmembrane potential difference after the introduction of $[Zn(BMC)_2Cl_2]$ and $ZnCl_2$ on one side of the BLM (Fig. 9). When both reagents were added, the potential difference had a minus sign in the *cis*-compartment. The form of the curve in the case where $ZnCl_2$ was introduced indicated a facilitated adsorption of the cations and a negatively charged surface of the BLM made up of ox brain lipids. The absence of a maximum following the introduction of $[Zn(BMC)_2Cl_2]$ indicated the retardation of the stage involving the adsorption of ions formed on dissociation of the above complex compared with the stage involving their transport. The sign of the generated potential difference shows that the permeating ions are cations.

Additional evidence indicating that the permeating species are cations on exposure of the membrane to $[Zn(BMC)_2Cl_2]$ was provided by the voltage–current characteristics of the BLM recorded after the introduction of the reagent on one side only. They had the rectification form—the current corresponding to positive polarisation in the *cis*-compartment was higher than that corresponding to the negative polarisation. The cationic transport complex is apparently formed as a result of the hydrolysis involving the elimination of a chloride ion:

$$[Zn(BMC)_2Cl_2] + H_2O \rightleftarrows [Zn(BMC)(H_2O)Cl]^+ + Cl^- .$$

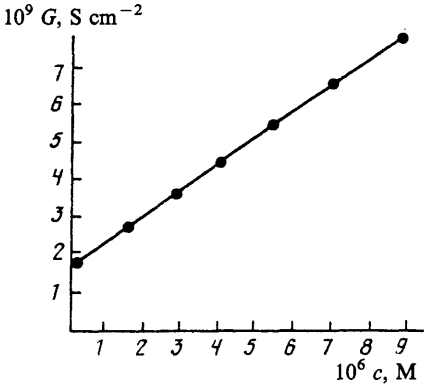
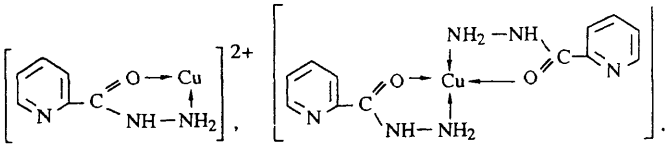


Figure 10. The influence of the $[Zn(BMC)_2Cl_2]$ concentration on the conductivity of the ox brain lipid BLM; electrolyte—0.01 M KCl + 0.002 M acetate buffer.

The transport of cations is ensured by the lipophilic properties of the BMC molecules ($\lg K_{o/w}$ = 0.35 [37]) and also by the low electric charge on the complex (+1) and apparently proceeds via a mechanism involving the direct passage of hydrophobic ions through the BLM. Evidence for this mechanism of the transmembrane transport of the cations $[Zn(BMC)_2(H_2O)Cl]^+$ is provided by the linear dependence of the conductivity of the BLM on the concentration of the cations (Fig. 10). Such linear dependence is characteristic of the direct passage of hydrophobic ions through the BLM.[41]

The complex of gallium(III) chloride with isonicotinic acid hydrazide (INAH), having the formula $[Ga(INAH)_3]Cl_3.H_2O$, is coordinatively saturated. Isonicotinic acid hydrazide (isoniazide) inhibits the growth of tuberculosis bacteria. The main side effect of isoniazide therapy is liver damage. On the other hand, the use of isoniazide in a complex with copper ions makes it possible to reduce greatly the negative side effect of the preparation. The copper(II) complex of INAH is an active antitumour agent. The protonated forms of the complex exhibit a biological activity:



It is believed [7] that the role of the metal reduces to creating a liposoluble compound which enhances the transport of the physiologically active ligand through the biological membrane. The use of isoniazide in a complex with the triply charged gallium cation can probably lead to new effects in therapy using this preparation.

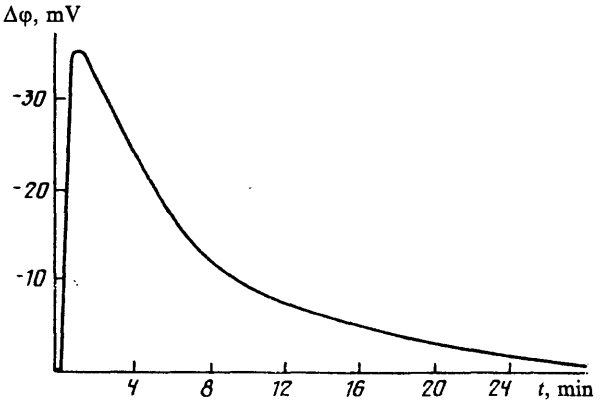


Figure 11. Generation of the transmembrane potential difference following the introduction of 1.6×10^{-6} M $[Ga(INAH)_3]Cl_3$ on one side of the membrane; the instant of the introduction of the reagent was adopted as the zero time; electrolyte—0.01 M KCl + 0.002 M acetate buffer.

We investigated the membrane activity of the $GaCl_3$ complex with isoniazide in relation to ox brain lipid BLM.[28] A typical potential difference generation curve after the introduction of the complex on one side of the BLM is illustrated in Fig.1. The minus sign of the potential difference in the *cis*-compartment of the cell indicates the adsorpton of the positively charged complex species on the BLM surface. It is seen that the residual (diffusion) potential diminishes almost to zero, which indicates the absence of the transmembrane transport of any kind of ionic form of the reagent. The maximum on the curve indicates an appreciable adsorption capacity of the complex, which is associated with the presence in its composition of the complex cation with the +3 charge.

The presence of the lipophilic isoniazide organic ligand ($\lg K_{o/w}$ = −0.5 [37]) leads to an increased adsorption capacity of the complex compared with the simple gallium salt $Ga(NO_3)_3$ (Fig. 12). When account is taken of the equality of the charges on the adsorbing species (+3), the higher value of $\Delta\varphi$ corresponds to a greater amount of cations bound to the BLM surface.

Studies on the ionic selectivity of BLM in the presence of the $GaCl_3$ complex with isoniazide demonstrated the absence of the ability of the latter to combine with and transport chloride anions to the BLM. On the other hand, comparison of the concentration variations of the relative conductivities and capacities of the BLM formed from n-octane and n-tetradecane solutions of lipids showed that, with increase in the concentration of the reagent, the properties of the BLM vary as a consequence of structural rearrangements in them (Fig. 13). It is essential to note the qualitative difference between the concentration variations of the capacities of the

membranes formed from n-octane and n-tetradecane lipid solutions, which is due to the different contents of the hydrocarbon solvent in the BLM.[22]

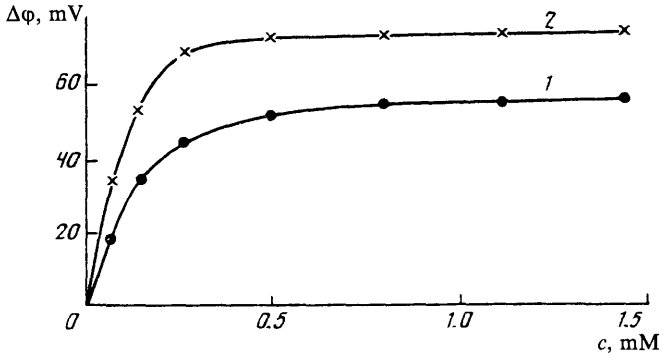


Figure 12. Dependence of the difference between the boundary potentials of the brain lipid BLM on the concentrations of $Ga(NO_3)_3$ (curve *1*) and $[Ga(INAH)_3]Cl_3$ (curve *2*); electrolyte—0.01 M KCl + 0.002 M acetate buffer.

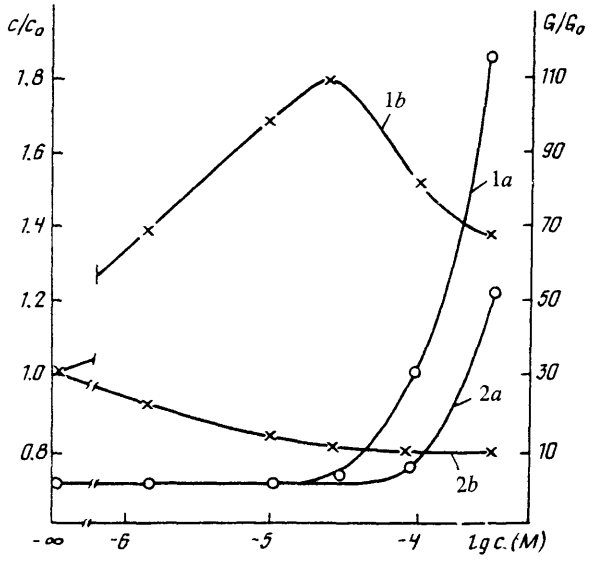


Figure 13. Dependence of the change in the relative conductivity (*a*) and relative capacitance (*b*) of the BLM in n-octane (curve *1*) and n-tetradecane (curve *2*) on the $[Ca(INAH)_3]Cl_3$ concentration; c_0 and G_0—the capacitance and electrical conductivity of the unmodified membranes.

V. Conclusion

The systematic studies which have been carried out make it possible to put forward the following considerations concerning the mechanisms of ion transport through biological membranes with participation of metal coordination compounds. There is no doubt about the validity of the hypothesis that the complex species is more favourable as a transport form for the transfer of both heavy metal ions and lipophilic ligands through the cell membrane.

However, the mechanisms of their action depend on a number of factors: coordinative unsaturation, charge, and stability of the complex, the lipophilicity of the ligands, etc. Under these conditions, the mechanism of the actual interaction of the complexes with the biological membrane, frequently accompanied by a change in its structure, is quite distinct.

Allowance for these phenomena is a necessary precondition for the specific synthesis of physiologically active substances with a wide range of therapeutic activities.

Experimental data for the effects of different complexes on BLM have shown that the most important factor in the interaction is the coordinative saturation of the complexes and the lipophilic ligands. It is known that the effect of hydrophilic heavy metal salts is associated with adsorption on the surface of the biological membrane. An increasing number of data have appeared recently showing that the specific chemical properties of the metal cations as well as the structure and properties of the adsorption centres are strongly manifested in this kind of binding process. Here it must be emphasised that in the case of BLM the above interaction does not entail an increase in the conductivity of the BLM.

However, an increase in the lipophilicity of the reagent should lead to an increase in the membrane activity of the heavy metal salts. Thus on coordination of the lipophilic ε-caprolactam, the complex $[Cu(CL)Cl_2(H_2O)]^0$ causes an appreciable increase in the activity of the BLM.

The use of the lipophilic 8-hydroxyquinoline ($\lg K_{o/w} = 1.13$) as the ligand and the formation of the compound $[Cu(HQ)_2]^0$ increase the electrical conductivity of BLM approximately by an order of magnitude. The membrane activity of the trichlorophenol (TCP) complex of copper(II) $[Cu(TCP)_2]^0$, where the lipophilicity of each TCP molecule is $\lg K_{o/w} = 3.7$, increases even further.

All the complexes indicated are coordinatively unsaturated but even the coordinatively saturated compound $[Zn(BMC)_2Cl_2]^0$, in which the BMC molecule has a definite lipophilicity $\lg K_{o/w} = 0.35$, constitutes an energetically favourable transport form whereby transfer through a biological membrane is effected.

On the other hand, the complexes which do not include lipophilic molecules do not exhibit a membrane activity. Thus in the presence of $[Cu(NH_3)_4]SO_4$ there is no change in the electrical conductivity and capacity of BLM up to a concentration of 2 mM. The lipophilicity parameter for ammonia molecules is low, amounting to $\lg K_{o/w} = -1.5$. The low membrane activity of $[Cu(NH_3)_4]SO_4$ compared even with $CuSO_4$ is associated with the stability of the complex ion whose instability constant is 10^{-12}.

The effect of ligands (ethylenethiourea, BMC, 8-hydroxyquinoline, ε-caprolactam, *o*-phenanthroline, etc.) does not alter the permeability of BLM to K^+ and Cl^- ions, which is associated with their non-ionic nature and probably with the absence of a marked surface activity of such species. On the other hand, polar molecules are able to be incorporated in the BLM structure. The dipoles of such molecules are then oriented in a different manner relative to the dipoles of the lipid molecules. By becoming incorporated similarly in BLM, polar molecules alter the dipole-induced potential jump at the BLM/aqueous solution interface, which may affect the change in the permeability of membranes to metal cations.

A significant difference between the mechanisms of the action of coordinatively unsaturated and saturated complexes is that, as

observed for the first time by ourselves, the coordinatively unsaturated complexes become transferring agents for chloride anions and probably other anionic substrates via a diffusional mechanism.

The substance synthesised as the agent transferring chloride anions through membranes must possess a number of properties which make possible, firstly, the addition of chloride anions to the complex-forming ion via a coordinate bond and, secondly, the transport of the chloride ions through the internal hydrophobic region of a BLM as a part of the composition of the lipophilic transport complex. This imposes definite requirements on the central ions and ligands which are determined by calculating the energy of the transport of species through BLM. The theoretical foundations of the specific synthesis of biologically active substances, inducing the transport of chloride anions through BLM, have been described in detail.[24,30] We shall describe only the main ones.

The principal property of the ligand molecules in the process indicated is their ability to impart lipophilic properties to the transport complexes formed, which enables them to permeate through the internal hydrophobic region of the BLM. On the other hand, it has been shown[48] that the permeability of the membrane to extremely hydrophilic and extremely hydrophobic molecules is very low. The optimum partition coefficient $\lg K$ in the organic solvent/water system, adopted as a measure of the hydrophobicity of the molecule, is in the range $-1 \leqslant \lg K \leqslant 1.5$.

The coordinatively unsaturated complex species, with which the anionic substrate combines, must have a positive electrical charge or, in the absence of the latter, a dipole moment. On the basis of electrostatic considerations, a +1 charge is optimum. In the absence of electrostatic attraction of chloride anions to the coordinatively unsaturated complex, one can assume, taking into account the non-equivalence of the coordination, that combination with chloride ions does not occur. This is indicated by the results of a study[9] where it was shown that the addition of chloride anions is observed for the polar *cis*-$[Pt(NH_3)_2Cl_2]$ and is not observed for the non-polar *trans*-$[Pt(NH_3)_2Cl_2]$ if it is assumed that both compounds are coordinatively unsaturated.

One can postulate that the mechanism described plays a definite role in the transport systems of biological membranes. A complex transport form having the composition coordinated ion–lipophilic ligand–hydrophilic substrate is then created. Aminoacids, polypeptides, as well as purine and pyrimidine bases, which are components of protein molecules, can play the role of ligands.[7] By virtue of their lipophilic and polar properties, the above ligands can be incorporated in the lipid bilayer and, furthermore, are able to interact with transition metal cations. This results in the formation of a compound, coordinatively unsaturated by the ligand, which can combine with chloride anions and effect their transfer. In a real biological system, other hydrophilic substrates (dihydrogen phosphate, hydrogen carbonate, carboxylate, etc. anions) can also take the place of chloride ions.

Hydrolytic enzymes, in particular carbonic anhydrase and carboxy- peptidase, which are coordinatively unsaturated compounds of zinc and histidine or with histidine and glutamic acid, can probably serve as examples of such systems in living organisms. Proof of the direct binding of a chloride anion to zinc in carbonic anhydrase was obtained from line broadening in the ^{35}Cl NMR spectra.[49] Similar results have been obtained for other anionic substrates and in the case of carboxypeptidase.

Another mechanism of the interaction of coordination compounds with cell membranes is that involving a change in the structure of the membranes. The change in the structure of membranes, in particular BLM, is associated with the charge of the active complex species. It is noteworthy that anionic complexes do not interact with BLM because of the presence of a negative charge on its surface. In the presence of highly lipophilic ligands, the latter can only be incorporated in the lipid bilayer.

Coordination compounds with a +2 charge and above are adsorbed on the BLM surface and the adsorption is stronger the higher the charge of the adsorbing species for identical lipophilicities of the ligands in the coordination sphere of the complex.

We have shown,[22,28] in relation to the interaction of the gallium complex of isonicotinic acid hydrazide $[Ga(INAH)_3]^{3+}$ with BLM, that the properties of the bilayers change as a consequence of the compaction of their structure caused by the decrease in the electrostatic forces repelling the polar heats of the lipid molecules in the adsorption of complex cations on the BLM surface. The concluding stage of the increase in the electrical conductivity of BLM with increase in the concentration of the complex involves the phase transition of the BLM from the liquid-crystal to the gel state. The increase in the permeability of bilayers in such phase transitions has been pointed out.[50] This results in an increase in the thickness of BLM, which do not contain the solvent, this being explained by the transition from the *gauche*-conformation to the fully *trans*-conformation in the lipid molecules. The increase in the conductivity of BLM under the influence of a cationic complex in the phase transitions can be induced by the local formation of micellar and hexagonal phases, whose permeability is high, and also by the appearance of lipid domains at the boundaries of which there is a possibility of the diffusion of ions. For the BLM obtained from individual lipids, the change in conductivity during the phase transition has a discrete character. In our case, the change becomes more marked slowly and smoothly, which is a characteristic feature of the phase transitions in BLM formed from a mixture of lipids. Under these conditions, the conductivity increases significantly only in the region of high concentrations of the complex.

The data obtained for the mechanisms of the action of complexes are important for the development of the specific synthesis of biologically active substances and must be taken into account in discussing the physiological properties of such compounds.

References

1. P Mueller, D O Rudin, H J Tien, W C Wescott *J. Phys. Chem.*, 1963, **67**(2) 534
2. R C McDonald *Biochem. Biophys. Acta*, 1976, **448**(2) 193
3. A M Omel'chenko *Itogi Nauki i Tekhniki. Ser. Biofizika* (Advances in Science and Engineering. Biophysics Series), Izd. VINITI, Moscow, 1991, Vol. 41, 105 pp
4. K B Yatsimirkii *Vvedenie v Bioneorganicheskuyu Khimiyu* (Introduction to Bioinorganic Chemistry), Naukova Dumka, Kiev, 1976, 143 pp
5. A Albert *A Strategy in Chemotherapy* (Translated into Russian), Mir, Moscow, 1967, 87 pp [This may be a reference to *Selective Toxicity* by this author (Ed. of Translation)]
6. G E Jackson, P M May, D R Williams *J. Inorg. Nucl. Chem.*, 1978, **40**(6) 1189
7. E E Kriss, I I Volchenskova, A S Grigor'eva, et al. *Koordinatsionnye Soedineniya Metallov v Meditsine* (Metal Coordination Compounds in Medicine), Naukova Dumka, Kiev, 1986, 216 pp

8. E Tračova, S Kuzela *Neoplasma*, 1985, **32**(6) 679
9. A I Stetsenko, L B Sel'derkhanova *Dokl. Akad. Nauk SSSR*, 1981, **259**(6) 1378
10. I A Zakharova *Biofizika*, 1977, **22**(3) 418
11. Yu A Ovchinnikov, V T Ivanov, A M Shkrob *Membrano-Aktivnye Kompleksy* (Membrane-Active Complexes), Nauka, Moscow, 1974, 150 pp
12. A V Babakov, V V Demin, S D Sokolov, et al. *Biofizika*, 1968, **13**(6) 1122
13. E A Liberman, V P Topoly *Biofizika*, 1968, **13**(6) 1025
14. R I Simpson, R Moore, T G Peters *Biochem. Biophys. Acta*, 1988, **941**(1) 39
15. M Deleers, M Gelbcka, W J Malaisee *Acta Int. Pharmacodyn.*, 1983, **262**(2) 313
16. A M Omel'chenko, B A Bovykin, S S Kukalenko, et al. *Sel'skokhozyaistvennaya Biologiya*, 1984, (5) 75
17. A M Omel'chenko, B A Bovykin *Biofizika*, 1985, **30**(1) 168
18. S S Kukalenko, B A Bovykin, S I Shestakova, A M Omel'chenko *Usp. Khim.*, 1985, **65**(7) 1152 [English translation in *Russ. Chem. Rev.*, 1985(7)]
19. B A Bovykin, A M Omel'chenko, N M Lepekhina *Voprosy Khimii i Khimicheskoi Tekhnologii* (Problems of Chemistry and Chemical Engineering), Vishcha Shkola, Kharkov, 1985, No. 79, p. 32
20. B A Bovykin, A V Polikarpov, A M Omel'chenko, et al. *Sel'skokhozyaistvennaya Biologiya*, 1987, (8) 54
21. B V Bovykin, R M Sharonina, A I Zanina, et al. *Voprosy Khimii i Khimicheskoi Tekhnologii* (Problems of Chemistry and Chemical Engineering), Vishcha Shkola, Kharkov, 1985, No. 79, p. 26
22. A M Omel'chenko, B A Bovykin *Biofizika*, 1987, **33**(3) 456
23. A M Omel'chenko, B A Bovykin, T V Sytnik, et al. *Dokl. Akad. Nauk SSSR*, 1988, **301**(5) 1238
24. B A Bovykin, A M Omel'chenko, T V Sytnik *Teoreticheskie Osnovy Napravlennogo Sinteza Biologicheski Aktivnykh Koordinatsionnykh Soedinenii, Indutsiruyushchikh Transport Anionov Khlora Cherez Bisloinye Lipidnye Membrany* (Theoretical Foundations of the Specific Synthesis of Biologically Active Coordination Compounds inducing the Transport of Chloride Anions through Bilayer Lipid Membranes), Dnepropetrovsk, 1988, 60 pp. Deposited at UkrNINTI, 19.09.88, No. 2408-Uk88
25. A M Omel'chenko, B A Bovykin *Biologicheskie Membrany*, 1989, **6**(4) 404
26. B A Bovykin, A M Omel'chenko, I A Zanina *Koord. Khim.*, 1990, **16**(5) 587
27. A M Omel'chenko, B A Bovykin, P A Grigor'ev *Dokl. Akad. Nauk SSSR*, 1989, **309**(1) 236
28. A M Omel'chenko, B A Bovykin, T V Sytnik, et al. *Molekulyarnaya Genetika i Biofizika. Respublikanskoi Mezhduvedomskii Nauchnyi Sbornik* (Molecular Genetics and Biophysics. All-Republic Interdepartmental Science Collection), Vishcha Shkola, Kiev, 1990, No. 15, p. 13
29. A M Omel'chenko, B A Bovykin, G N Novodarova, USSR P. 1 637 811; *Byull. Izobret.*, 1991, (12)
30. B A Bovykin, A M Omel'chenko, T V Sytnik *Teor. Eksp. Khim.*, 1991, **27**(3) 382
31. O S Ksenzhek, A M Omel'chenko *Molekulyarnaya Genetika i Biofizika. Respublikanskoi Mezhduvedomskii Nauchnyi Sbornik* (Molecular Genetics and Biophysics. All-Republic Interdepartmental Science Collection), Vishcha Shkola, Kiev, 1979, No. 4, p. 37
32. V S Sokolov, V G Kuz'min *Biofizika*, 1980, **25**(1) 168
33. S I Shestakova, S S Kukalenko, E I Andreeva, et al., USSR P. 782 350; *Byull. Izobret.*, 1983, (26)
34. S S Kukalenko, Yu T Struchkov, S I Shestakova, et al. *Koord. Khim.*, **9**(3) 312
35. W D Seufert *Biophys.*, 1972, **10**(4) 281
36. A V Babakov, I V Myagkov, P S Sotnikov, et al. *Biofizika*, 1972, **17**(2) 347
37. C Hansch, A Leo *Substituent Constants for Correlation Analysis in Chemistry and Biology*, John Wiley, New York, 1979, p. 339
38. R Engst, W Z Schnaack *Lebensmittel. Untersuch. und Forsch.*, 1970, **143**(3) 99
39. N P Mel'nikov, K V Nozozhilov, S R Belan, et al. *Spravochnik po Pestitsidam* (Handbook of Pesticides), Khimiya, Moscow, 1985, 352 pp
40. V N Lobov, G A Efimov *Pestitsidy* (Pesticides), Gos. Izd. Tekh. Lit. Ukr. SSR, Kiev, 1963, 276 pp
41. A M Omel'chenko, B A Bovykin *Molekulyarnaya Genetika i Biofizika. Respublikanskoi Mezhduvedomskii Nauchnyi Sbornik* (Molecular Genetics and Biophysics. All-Republic Interdepartmental Science Collection), Vishcha Shkola, Kiev, 1983, No. 8, p. 62
42. D A Haydon, S B Hladky *Quart. Rev. Biophys.*, 1972, **5**(2) 187
43. B M Anic, H Van der Goot, W K Nauta, et al. *Eur. J. Med. Chem.*, 1977, **12**(6) 573
44. G N Novodarova, E M Kolosova, L L Kiseleva, et al. *Problemy Svoremennoi Bioneorganicheskoi Khimii* (Problems of Modern Bioinorganic Chemistry), Nauka, Novosibirsk, 1986, p. 67
45. S S Kukalenko, S D Volodkovich *Sistemnye Fungitsidy i Protraviteli Semyan* (Systemic Fungicides and Seed Pickling Agents), Izd. NIITEKhIM, Moscow, 1981, 51 pp
46. B E Zaitsev, V M Palishkin, T M Ivanova, et al. *Koord. Khim.*, 1985, **11**(11) 1490
47. V G Ivkov, G N Berestovski *Dinamicheskaya Struktura Lipidnogo Bisloya* (The Dynamic Structure of the Lipid Bilayer), Moscow, 1981, 293 pp
48. A Kotyk, K Janacek *Biomembranes, Vol. 9, Membrane Transport* (Translated into Russian), Mir, Moscow, 1980, 250 pp
49. M Hughes *The Inorganic Chemistry of Biological Processes* (Translated into Russian), Mir, Moscow, 1983, 408 pp
50. H Träuble, H Eibl *Proc. Nat. Acad. Sci. USA*, 1974, **71**(2) 214

Received 28th January 1992

Translated from *Uspekhi Khimii* **61** 2129–2171 (1992) U.D.C. 541.63 + 547.23

Some problems in the stereochemistry of nitrogen compounds in the gas phase

N I Sadova, L S Khaikin, L V Vilkov
Moscow State University

ABTRACT. Data on the geometry of free molecules containing a nitrogen atom have been reviewed. Most attention has been paid to compounds of amines with a nitrogen–metal bond, nitro-compounds, and complex compounds. The applicability of various ideas on the relationship between the electronic structure and geometry of molecules has been analysed.

The bibliography contains 193 references.

Contents

I. Introduction 1169
II. Amino-derivatives 1169
III. Imino-, carbodi-imido-, and azino-derivatives 1175
IV. Nitro-compounds 1176
V. Complex compounds of nitrogen 1184
VI. Summary 1190

I. Introduction

The stereochemistry of nitrogen compounds is rich in different forms of valence state of the nitrogen atom and different types of bond between nitrogen and other elements. A large number of publications[1–8] have been devoted to the systematisation of data on the geometry of molecules in the gas phase and the discovery of structural regularities. The present review is restricted to a few classes of nitrogen compound, and most of the data systematised are not in the works cited above.

The analysis was based on two sections of Landolt–Bornstein[9] containing the results of electron diffraction (GE) and microwave (MW) studies of the structure of molecules in the gas phase up to and including 1985, and original publications for the following year. For the values of the parameters given in the text, the following dimensions are used: bond lengths in Ångstrom units (Å) and valence and dihedral angles in degrees (°). Their experimental errors in the last significant figures are given in brackets.

Since different methods of studying the structure were used, the geometric parameters, in particular the bond lengths, have slightly different physical significance, because of the slight (generally up to ~0.01 Å) influence of vibrational corrections (see for example Ref. 2).

II. Amino-derivatives

1. Amines with hydrocarbon substituents and halogenoamines

In the examination of the structure of amines, particular attention is usually paid to the geometry of the amine fragment, that is to the configuration of the bonds formed by the nitrogen atom and the lengths of the "nitrogen–substituent" bonds.

Table 1. Geometric parameters of alkylamine molecules.

Compound	N–C, Å	C–N–C, °	Method,* type of parameter	Refs.
CH_3NH_2	1.472(3)	–	GE+MW, r_g	[10]
$(CH_3)_2NH$	1.455(6)	111.8(8)	GE, r_a	[11]
	1.462(7)	112.2(5)	MW, r_s	[12]
$(CH_3)_3N$	1.458(4)	110.9(6)	GE, r_α	[13]
$(CF_3)_3N$	1.426(6)	117.9(4)	GE, r_0^δ	[14]
$C_2H_5NH_2$	1.470(10) *trans*	–	GE+RC+NC, r_g	[15]
	1.475(10) *gauche*			
$(CH_3)_3CNH_2$	1.493(6)	–	GE, r_g	[16]
$CH_2CH_2CHNH_2$	1.452(7)	–	MW, r_s	[17]
$(CH_3)_2NC_2H_5$	1.452(6)	111.3(10)	GE, r_a	[18]
$CH_2N(CH_3)_2$	1.449(4)	110.7(10)	GE, r_α	[19]
$[(CH_3)_2CH]_2NH$	1.470(4)	120.1(10)	GE+VS+MM, r_g	[20]
$[(CH_3)_3C]_2NH$	1.467(15)	135(3)	GE, r_a	[21]
$(CH_3)_3CNHCH_2CH_3$	1.476(1) (C″)	117.6(11)	GE+VS+NC, r_g	[22]
	1.465(1)			
$(CF_3CF_2CF_2)_3N$	1.459(8)	120.0(2)	GE, r_g	[23]

*Notation: GE = gas-phase electron diffraction, MW = microwave spectroscopy, RC = rotational constants, NC = non-empirical calculations, VS = vibrational spectroscopy, MM = molecular mechanics.

The geometric parameters of a number of alkylamines are given in Table 1. The bonds formed by the nitrogen atom in ammonia and methylamines have a pyramidal configuration. The replacement of the hydrogen atoms in NH_3 by CH_3 groups increases the average valence angle α_N by ~3°:

Amine	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
$\bar{\alpha}_N$, °	106.7	110	108.6	110.9

In the methylamine series the N–C bond length tends to decrease on going from the primary to the tertiary amine. This trend is also observed in a series of alkylamines with heavier substituents, such as $C_2H_5NH_2$ [N–C 1.472(10) Å] and $C_2H_5N(CH_3)_2$ [N–C 1.452(6) Å].

On going from CH_3NH_2 to $C_2H_5NH_2$ the N–C bond length remains unchanged, but the presence of the bulky t-butyl substituent in $(CH_3)_3CNH_2$ increases the N–C bond length to 1.493(6) Å.

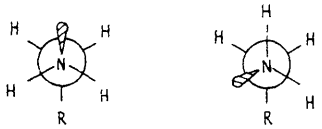
Replacing the electron-donor CH_3 groups in the trimethylamine molecule by the electron-acceptor CF_3 groups leads to flattening of the configuration of the nitrogen atom [the CNC angle is 117.9(4)°]. At the same time the N–C bonds are shorter [1.426(6) Å] than those in methylamines.

On going from $(CF_3)_3N$ to $(CF_3CF_2CF_2)_3N$ the configuration of the bonds formed by the nitrogen atom becomes completely planar, with a CNC angle of 120.0(2)°, and the N–C bond length increases by ~0.03 Å.

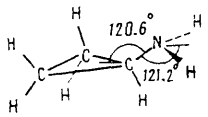
The steric interactions between the t-butyl groups in the $HN[C(CH_3)_3]_2$ molecule increase the CNC angle to 135(3)° compared with the corresponding angle [120.1(10)°] in $NH[CH(CH_3)_2]_2$, indicating that the steric repulsion of the t-butyl groups is greater than that of the isopropyl groups.

Thus the configuration of the bonds formed by the amine nitrogen atom in alkylamines depends on the type of substituent and on steric factors.

In the study of the structure of more complex aliphatic amines such as $CH_3CH_2NH_2$, $CH_2CH_2CHNH_2$, $(CH_3)_2CHNH_2$,[24] $(CH_3)_2NC_2H_5$, $NH[C(CH_3)_3]_2$, $NH[CH(CH_3)_2]_2$, and $CH_2[N(CH_3)_2]_2$, the conformations of the molecules, in particular the rotational isomerism about the N–C bond, is also examined in detail. It has been shown, for example, that ethylamine consists of a mixture of *gauche*- and *trans*-isomers (~1:1) and that $\Delta H(gauche-trans)$ = 306(200) cal mol^{-1}.



In cyclopropylamine the amino-group is in the staggered "perpendicular" conformation relative to the cyclopropane ring†.



The conformations of the molecules of secondary amines are characterised by the two angles of rotation about the N–C bonds. For the $NH[CH(CH_3)_2]_2$ molecule these angles are the same and equal to 52(4)°, whereas in $NH[C(CH_3)_3]_2$ the t-butyl groups are rotated slightly differently (19° and 30°) relative to the N–C bond, and the axes of symmetry of these groups deviate from the direction of the N–C bonds by 2.5 ± 1.5°.

†According to the definition given by the authors cited, the term "perpendicular" conformation indicates that the lone pair of electrons of the nitrogen atom is situated above the three-membered ring and is projected on to the bisector of the CCC angle.

The geometric parameters of a number of halogenoamines are given in Table 2. A distinguishing feature of halogenoamines compared with ammonia and methylamines is the decrease in the valence angles XNX and XNY, and hence in the average valence angle at the nitrogen atom.

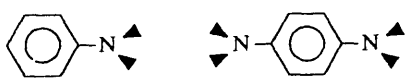
Table 2. Geometric parameters of halogenoamine molecules.

Compound	Bond lengths, Å		Valance angles, °		Method,* type of parameter	Refs.
NF_3	N—F	1.365(2)	FNF	102.4(3)	MW, r_e	[25]
NH_2F	N—F	1.400(2)	FNH	99.8(2)	ME, r_s	[26]
	N—H	1.026(2)	HNH	102.9(2)		
NF_2Cl	N—F	1.382(9)	FNF	103(1)	GE, r_a	[27]
	N—Cl	1.730(8)	FNCl	105(1)		
NF_2CF_3	N—F	1.371(4)	FNF	105.3(5)	GE+MW, r_{av}	[28]
	C—N	1.476(5)	CNF	104.1(7)	r	
$NF(CF_3)_2$	N—F	1.378(12)	CNC	116.6(6)	GE, r_α^0	[28]
	C—N	1.446(4)	CNF	104.8(7)		
NCl_3	N—Cl	1.754(2)	ClNCl	107.8(4)	MW, r_s	[29]
	N—Cl	1.759(2)	ClNCl	107.1(5)	GE, r_g	[30]
NCl_2CH_3	N—Cl	1.74(2)	ClNCl	108(2)	GE	[9]
	C—N	(1.47)*	CNCl	109(2)		
$NCl(CH_3)_2$	N—Cl	1.749(1)	CNCl	108.0(1)	MW, r_0	[31]
	C—N	1.476(1)	CNC	(110.7)*		
$NHClCH_3$	N—Cl	1.750(3)	ClNC	109.4(2)	MW, r_s	[32]
	C—N	1.474(5)	ClNH	102.8(2)		
NH_2Cl	N—Cl	1.748(1)	ClNH	103.7(3)	MW, r_s	[33]
	N—H	1.017(5)	HNH	107(2)		

*Accepted value.

The N–C bond lengths decrease systematically in the fluoroamine series CF_3NF_2 > $(CF_3)_2NF$ > $(CF_3)_3N$ (Tables 1 and 2).

The configuration of the bonds formed by the nitrogen atom in aromatic amines is sensitive to the influence of substituents. According to microwave data, the molecule of aniline $C_6H_5NH_2$ (A) is non-planar.[34] The angle of displacement of the N–C_{arom} bond from the plane NX_2 (Φ) is 37.5°, and the angle HNH is 113°, indicating that the configuration of the bonds formed by the nitrogen atom is pyramidal:

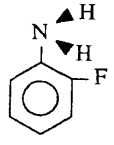


(A) (B)

For the related molecule of *p*-diaminobenzene (B),[35] the angle Φ characterising the pyramidal character of the configuration of the bonds formed by the nitrogen atom is slightly greater [43(4)°] than that in aniline (37.5°), but the conformation of the molecule (B) is similar to that of aniline. Of the other geometric parameters of these molecules, the N–C bond lengths [1.402(2) Å in (A) and 1.424(5) Å in (B)] and the $CC_{NH_2}C$ valence angles [119.4(2)° in (A) and

119.8(2)° in (B)] are noteworthy. The N–C bond length in arylamines is much shorter than that in alkylamines and halogenoalkylamines. The deformation of the valence angle in the benzene ring at the amine nitrogen atom is slight.

Microwave data have been published, characterising the configuration of the bonds formed by the amine nitrogen atom in the molecules of *o*-, *m*-, and *p*-$XC_6H_4NH_2$ (X = F,[36–38] Cl[39–41]), *p*-$FC_6H_4NHCH_3$,[42] $C_6H_5NHCH_3$,[43,44] and $C_6H_5N(CH_3)_2$‡.[45] The complete structures of these molecules have not been determined, however. Of all the fluorine-substituted anilines, *o*-$FC_6H_4NH_2$ [36] is the one for which the parameters characterising the geometry of the amino-group are closest to those for non-substituted aniline; it is followed by *m*-$FC_6H_4NH_2$,[37] and the greatest deviations are observed for *p*-$FC_6H_4NH_2$.[38] It is suggested[36] that since an intramolecular hydrogen bond H...F may be formed, the conformation of the *o*-$FC_6H_4NH_2$ molecule probably differs from that of aniline.



When one or two H atoms in the amino-group of *p*-$FC_6H_4NH_2$ are replaced by a CH_3 group, the configuration of the bonds formed by the nitrogen atom is flattened considerably.

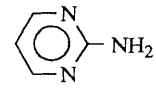
Molecule	$C_6H_5NH_2$	*m*-$FC_6H_4NH_2$	*n*-$FC_6H_4NH_2$	*n*-$FC_6H_4NHCH_3$	*n*-$FC_6H_4N(CH_3)_2$
Angle HNX, ° (X=H, CH_3)	113.1(2)	115.0	112	115.6	114
Angle of displacement of the N–C_{arom} bond $\bar{\phi}$, °	37.5(2)	36.2	46.4	18.3	27

In the series of chloro-substituted anilines, on going from *o*-$ClC_6H_4NH_2$ [39] to *p*-$ClC_6H_4NH_2$ [41] the angle Φ characterising the pyramidal nature of the configuration of the bonds formed by the nitrogen atom increases from 34.5° to 41.4°.

The structure of another two arylamines, $(C_6H_5)_3N$ [47] and $C_6H_5NCH_2CH_2$,[48] can be considered. In the triphenylamine molecule the valence angles at the nitrogen atom are 116(2)°, that is the configuration of the bonds formed by the nitrogen atom is flattened considerably, as in N-fluoromethylamines, but in the N-phenylethyleneimine molecule the nitrogen atom, firmly fixed in the ring, has a pyramidal structure, and the angle of displacement of the N–C_{arom} bond from the plane of the three-membered ring is ~55°. The conformation of the $C_6H_5NCH_2CH_2$ molecule is similar to that of aniline and dimethylaniline. The electron diffraction studies of the $(C_6H_5)_3N$ and $C_6H_5NCH_2CH_2$ molecules, however, were carried out in the sixties, with an accuracy lower than that now attainable.

‡ The $C_6H_5N(CH_3)_2$ molecule has also been studied by electron diffraction,[46] but the accuracy of the determination of the parameters is low.

2-Aminopyrimidine



is stereochemically similar to arylamines.[49] The molecule of this compound is flatter than the aniline molecule, and the angle of displacement of the N–C_{arom} bond from the plane of the NH_2 group is 27°. The N_{amine}–C bond length [1.33(1) Å] is shorter than that in $C_6H_5NH_2$.

Thus the configuration of the bonds formed by the nitrogen atom in arylamines varies from pyramidal to almost planar, depending on the substituents on the nitrogen atom and to some extent on the substituents in the benzene ring.

Comparison of aliphatic and aromatic amines shows that $r(N-C)_{aliph} > r(N-C)_{arom}$ and $\bar{\alpha}_N(aliph) < \bar{\alpha}_N(arom)$ ($\bar{\alpha}_N$ is the average value of the valence angle at the nitrogen atom).

There are almost no published data on enamines of the type $R^1R^2N-CR^3=CR^4R^5$ in the gas phase. In a microwave study of vinylamine $CH_2=CHNH_2$,[50] the complete structure could not be determined. By making a number of assumptions it was possible to obtain, with a low accuracy, only the N–C bond lengths [1.397(30) Å and the C=C–N angle [125.2(20)°], and also the angle between the N–C bond and the continuation of the bisector of the HNH angle [θ = 34(5)°].

The amides of carboxylic acids $RC(O)NH_2$ and their derivatives form a separate class of compound. The central fragment in amide molecules contains the N–C(O) bond. A knowledge of the geometry of this fragment is of considerable importance for establishing the structure of the peptide group in polypeptides.

The geometry of the molecules of the simplest amides has been studied by spectroscopic and diffraction methods and in considerable detail. The nitrogen atom in the >NC(O) group has a planar bond configuration. The N–C(O) bond is ~0.1 Å shorter than the N–CH_3 bond. The bond lengths in the molecules are different in the gas phase and in the crystal; the N–C(O) bond is 0.07 Å longer, and the C=O bond ~0.4 Å shorter, in the gas phase than in the crystal.

Detailed data on the structure of amides in the gas phase are given in a book by Naumov and Kitaeva.[51]

2. Monomeric compounds of amines with metals

Electron diffraction studies, carried out mainly abroad in the late eighties, provide material for generalising the characteristics of the geometric structure of monomeric compounds of amines with metals, chiefly compounds in which the metal has a low coordination number (CN).

A large proportion of these data relate to compounds containing two-coordinate metals of groups II (the *s*-elements Be and Mg, and the *d*-elements Zn, Cd, and Hg), VII, and VIII (the *d*-elements Mn, Fe, and Co), and also to compounds with the *p*-elements of group IV Ge, Sn, and Pb (Table 3). Data have also been published on compounds of amines with three-coordinate Sc, La, Ce, and Pr (*d*-elements of group III and lanthanides), and on tetra-amino-compounds of Ti, Zr, and V, a penta-amino-compound of Ta, and a hexa-amino-compound of W (*d*-elements of groups IV–VI, Table 4).

The two-coordinate state is not characteristic of the atoms of the lighter group II metals. Their compounds with amines tend to associate to give bridged systems, and the CN of the metal may reach four or more. In the compounds studied, the stability of the two-coordinate states of the atoms of these metals is ensured by the

large volume of the substituent $N[SiMe_3]_2$. Only the Hg atoms are distinguished by their inability to extend greatly their coordination sphere. The following mechanism has been proposed[61] to explain this difference in the coordination properties of the *d*-elements of group II. If the nitrogen atoms form σ-bonds with the sd_{z^2}-hybrid orbitals of the two-coordinate atoms of these elements, then since the 6*s*- and 5*d*-energy levels of the Hg atom are close to one another, there is more complete mixing for this atom, so that the Hg–N bonds are stronger than the Zn–N or Cd–N bonds. When adducts are formed, however, the degree of mixing of the *s*- and *d*-orbitals of the Hg atom decreases, the primary Hg–N bonds become weaker, and there is probably no energy gain as a reuslt of additional coordination to the metal atom, that is the structure of the adduct is unstable.

Table 3. Parameters (r_a) of monomeric amino-derivatives of two-coordinate metal atoms, obtained by gas-phase electron diffraction.

Molecule	Bond lengths, Å		Valence angles, °			Refs.
	E–N	N–Y	NEN	ENY	YNY	
			Group II			
$Be[N(SiMe_3)_2]_2$	1.562(24)	1.722(7)	180	115.4(4)	129.2(7)	[52]
$Mg[N(SiMe_3)_2]_2$	1.91(3)	1.703(6)	180	114.0(12)	132(2)	[53]
$Zn[N(SiMe_3)_2]_2$	1.824(14)	1.728(7)	180	114.8(10)	130.4(20)	[54]
$Cd[N(SiMe_3)_2]_2$	2.03(2)	1.727(7)	180	114.0(6)	132.0(12)	[55]
$Hg[N(SiMe_3)_2]_2$	2.01(2)	1.732(9)	180	116.0(10)	128(2)	[56]
			Groups VII and VIII			
$Mn[N(SiMe_3)_2]_2$	1.95(2)	1.718(6)	180	114.0(6)	132.1(12)	[57]
$Fe[N(SiMe_3)_2]_2$	1.84(2)	1.723(5)	180	114.4(5)	131.2(10)	[57]
$Co[N(SiMe_3)_2]_2$	1.84(2)	1.730(7)	180	114.7(7)	130.6(14)	[57]
			Group IV			
$Ge[N(SiMe_3)_2]_2$	1.89(1)	1.743(6)	101(2)	121.1(7)	117.8	[58]
$Sn[N(SiMe_3)_2]_2$	2.089(10)	1.74	96,0	117.3	125.4	[59]
$Sn(NMe_2)_2$*	1.996(4)	1.483(3)	95(1)	118.1(3)	123.8	[60]
$Pb[N(SiMe_3)_2]_2$	2.20(2)	1.75(1)	91(2)	119.6(8)	120.8	[58]

*The parameter r_g is given.

The presence of bulky substituents is apparently no less important for the stabilisation of monomeric structures with the two-coordinate *d*-atoms Mn, Fe, or Co and *p*-elements of group IV. The tendency of these compounds to associate is revealed by the formation of dimers in the crystal and in the gas phase. The gas-phase structure of one of these compounds, namely the dimer of the amino-derivative of tin(II) $\{Sn[NMe_2]_2\}_2$, will be examined in Section V.

For the atoms of group III metals (Sc, La, and the lanthanides), the usual CN are 7, 8, and 9, and with small bidentate ligands such as the nitrate group, even CN of 10 and 12 are possible. The bulky nature of the $N(SiMe_3)_2$ ligands is also of decisive importance for stabilising the fairly uncommon three-coordinate states of the atoms of these elements.

a. Amino-derivatives of *s*- and *d*-elements of group II and *d*-elements of groups VII and VIII

Important common characteristics of these compounds are the linearity of the N–E–N fragment, the planar configuration of the bonds formed by the amine nitrogen atom, and the orthogonal arrangement of the two pairs of terminal substituents $SiMe_3$ in the stable molecular form.

For the structures of the *d*-elements of group II (Zn, Cd, and Hg), the first two of these characteristics also follow from an analysis of the vibrational spectra of solutions[62] and the utlraviolet spectra of the gas phase.[63] The spectral data, however, do not make it possible to make a choice between the orthogonal (D_{2d}) and planar eclipsed (D_{2h}) conformations of the $Si_2N-E-NSi_2$ core. Electron diffraction data show that the equilibrium form has D_{2d} symmetry. At the same time there is a torsional motion of large amplitude round the linear chain N–E–N. The heights of the potential barriers (V_2) in the planar transition state D_{2h}, obtained for amino-derivatives of Mg, Zn, Cd, and Hg, are relatively small [3(1), 2.5(1.5), 1–2, and 2(1) kcal mol^{-1} respectively] and practically constant, at least for the derivatives of the *d*-elements.

The production of the barrier to rotation in this case might be due to the presence of dative π-bonds in the N–E–N fragment, van der Waals interactions between the ligands, or a combination of these factors. Force field calculations based on the vibrational spectra[62] show that in the molecules being considered the E–N bonds should be essentially single bonds. At the same time, if it is assumed that the other geometric parameters (other than the angle of rotation) remain unchanged in the process of internal rotation, then in the planar form D_{2h} the shortest of the distances between the Me groups, although shorter than those in the equilibrium form D_{2h}, are nevertheless greater than the sum of the van der Waals radii. Thus the existence of the barrier to internal rotaiton could be attributed to the effects of dative π-interaction rather than to steric factors. Although these electronic effects are very small, in this case they are apparently responsible for the stabilisation of the linear form of the N–E–N fragment.

It is possible to take as a geometric criterion of the multiplicity of the metal–nitrogen bond the difference between its length and that of the corresponding metal–chlorine bond.

	Be	Mg	Zn	Cd	Hg	Cl
r(E–Cl), Å	1.75	2.18	2.06	2.21	2.25	1.99
r(E–N), Å	1.56	1.91	1.82	2.03	2.01	1.76
Δ, Å	0.19	0.27	0.24	0.18	0.24	0.23

Since the nitrogen and chlorine atoms have equal electronegativities, the polar corrections for the corresponding bonds with a metal should also be equal. Since the accuracy of the determination of the Be–Cl, Be–N, Cd–Cl, Cd–N, and Hg–N bond lengths is low, it can be taken that the effect of replacing the chlorine atom by the nitrogen atom remains practically constant, and the actual changes Δ can be related to the difference between the covalent radii of the chlorine and nitrogen atoms. For metal chlorides, significant multiplicity of the metal–chlorine bonds is unlikely, since the chlorine atom cannot be a strong electron donor for a metal atom.

From the general principle that the atomic radius increases on going from a lighter to a heavier element in a group, the changes in the bond lengths E–N in the compounds of the group II elements show two anomalies (Table 3), on going from the *s*-atom Mg to the *d*-atom Zn and on going from the Cd atom to the Hg atom. Thus the Mg–N bond is 0.35 Å longer than the Be–N bond, and the Cd–N bond is 0.2 Å longer than the Zn–N bond. However, since

the effective charge on the nucleus of the Zn atom, which has a full *d*-level, is much larger, the Zn–N bond length is ~0.1 Å shorter than the Mg–N bond length. The Hg–N bond length in turn differs little from the Cd–N bond length, apparently due to a combination of the effects of *d*-contraction, *f*-contraction, and relativistic concentration.

The relatively short Be–N bond is possibly a consequence of a slight increase in dative π-interaction, if the small radius of the Be atom and its fairly high acceptor power are taken into account. Together with the increase in the inter-ligand interactions, this should lead to an increase in the barrier to internal rotation in the $Be[N(SiMe_3)_2]_2$ molecule compared with the amino-derivatives of the other group II metals.

In the compounds of the group VII and VIII metals of period IV, the change in the E–N bond lengths corresponds to the change in the atomic radius on going from a lighter to a heavier element. A characteristic feature is that within the large experimental errors the Mn–N bond length still approaches the Mg–N bond length, whereas the Fe–N and Co–N bond lengths are almost the same as the Zn–N bond length.

For the parameters of the ligand $N(SiMe_3)_2$, the Si–N bonds in some of the compounds examined are shorter than that in the $HN(SiMe_3)_2$ molecule [r_a = 1.738(5) Å[64]], whereas in others they are almost equal to this value. The observed decrease in the Si–N bond lengths is usually attributed to an increase in the polarity of the corresponding E–N bonds, which leads to an increase in the dative π-interaction between the N and Si atoms. The changes in the SiNSi valence angles in the amino-derivatives of the metals being considered relative to $HN(SiMe_3)_2$ [131.3(15)°] are slight. The large value of this angle, characteristic of these compounds, in this case is apparently determined chiefly by intra-ligand steric factors. Comparison of the data being considered with the dimeric structures of amino-derivatives of Mn and Co in the crystals shows that dimerisation is accompanied by a considerable increase in the length of the terminal E–N bonds and a decrease in the Si–N–Si valence angles in the terminal ligands by ~10°.

b. Structures with two-coordinate atoms of *p*-elements of group IV

It was noted above that the use of the bulky substituents $N(SiMe_3)_2$ makes it possible to obtain more stable monomeric compounds with two-coordinate Ge, Sn, or Pb atoms in the gas phase and in crystals. When $N(SiMe_3)_2$ groups in an Sn^{II} derivative are replaced by NMe_2, the concentration of the monomer in the gas phase decreases to 76 ± 1%.

Unlike the amino-derivatives of metals of groups II, VII, and VIIII, the monomers of the *p*-elements of group IV contain non-linear N–E–N fragments (Table 3). At the same time, the planar configuration of the bonds formed by the amine nitrogen atom is preserved. Both NY_2 planes are practically perpendicular to the NEN plane.

The valence angles NEN do not exceed 101°. They decrease regularly with increase in the atomic number of E, as is characteristic of many other compounds of the elements of the main sub-groups. This corresponds to the familiar Bent's rule, according to which an increase in the difference between the electronegativities of the atom E and the substituent is accompanied by an increase in the *s*-character of the non-bonding orbitals of the atom E. It is also possible that a decisive role is here played by inter-ligand steric repulsions which are weaker for longer E–N bonds. Steric effects, however, probably have a greater influence on the E–N bond lengths. Thus the Sn–N bond in the $Sn(NMe_2)_2$ molecule is almost 0.1 Å shorter than that in the $Sn[N(SiMe_3)_2]_2$ molecule, whereas the NSnN valence angles are almost equal in the two molecules. The difference between the E^{II}–N and E^{IV}–N bond lengths obtained for Ge and Sn derivatives is half of this value (see Table 3 and Ref. 2). Comparison shows that the Sn–N bond in the $Sn(NMe_2)_2$ molecule is only ~0.05 Å shorter than that in the $Sn(NMe_2)_4$ molecule. Overall, the change in the E^{II}–N bond lengths in the structures being considered reflects the gradual increase in the atomic radius on going from a lighter to a heavier element.

In the crystalline phase the E–N bond lengths of the monomers are practically the same as those in the molecules in the gas phase, whereas the NEN angles are larger by 10° or more and become less sensitive to the nature of the atom E. This is probably related to a change in the orientation of the ligands in the crystal, since the form of the molecule produced in the gas phase is not favourable for effective packing. This change leads to the production of shorter intramolecular contacts, and the resulting strain is compensated by an increase in the angle NEN. The relative ease of the change in the orientation of the $N(SiMe_3)_2$ groups on going from the gas to the crystalline phase may indicate that the potential function of the internal rotation is flat.

c. Amino-derivatives of *d*-elements of group III and the lanthanides

X-Ray diffraction data show that the amino-derivatives of group III elements $E[N(SiMe_3)_2]_3$ are monomeric. All the compounds $E[N(SiMe_3)_2]_3$ can be divided into two groups differing in the configuration of the EN_3 fragments. This separation also corresponds to the characteristics of the electronic structure of the metal atom. The derivatives of the *p*-elements (Al, Ga, In, Tl) have a planar core EN_3, and D_3 symmetry for the molecule as a whole. In the derivatives of the group III *d*-elements and the lanthanides studied, the configuration of the EN_3 fragment is pyramidal, with valence angles NEN equal to 115.5 (Sc), 117.8(1) (Nd), and 116.6° (Eu).

On going to the gas phase there are appreciable changes in the configuration of the environment of the atoms of the group III *d*-elements and the lanthanides (Table 4).

Electron diffraction data show that in the Sc derivative the configuration of the ScN_3 fragment becomes almost planar, whereas in the compounds of La, Ce, and Pr (nearest neighbours of Nd in the periodic table) the EN_3 fragment is much more pyramidal than in the crystal. The measured dipole moments and the infrared spectra also indicate that the solutions contain molecules with a planar ScN_3 fragment,[72] and the vibrational spectra of the derivatives of the lanthanides Pr and Nd confirm that their structures are non-planar in the crystal, in the gas phase, and in solutions.[73] The values of the valence angles NEN found in the crystal are very close to one another, and possibly determine the molecular form most favourable for crystal packing. The relative ease with which changes take place in these angles with change in the state of the substance apparently indicates a flat form for the potential function of the inversion of the central atom E in these systems.

The pyramidal configuration of the ScN_3 fragment, produced in the solid phase by the effects of crystal packing forces, is accompanied by a change in the geometry of the ligands. The Si–N bonds become much longer [1.751(2) Å], and the angle SiNSi

Table 4. Parameters of monomeric amino-derivatives of metals with coordination numbers from three to six, obtained by gas-phase electron diffraction.

Molecule	Parameter	Bond lengths, Å		Valence angles, °			Refs.
		E–N	N–Y	NEN	ENY	YNY	
				Group III			
$Sc[N(SiMe_3)_2]_3$	r_a	2.02(3)	1.715(8)	119.5(15)	116(1)	128(2)	[65]
$La[N(SiMe_3)_2]_3$	r_a	2.36(3)	1.692(13)	110(3)		128(4)	[66]
$CeN(SiMe_3)_2]_3$	r_a	2.33(4)	1.696(15)	112(3)	108(2)*anti* 123(2)*syn*	129(4)	[67]
$Pr[N(SiMe_3)_2]_3$	r_a	2.31(4)	1.705(15)	113(3)	108(2)*anti* 123(2)*syn*	129(4)	[67]
				Group IV			
$Ti(NMe_2)_4$	r_a	1.917(3)	1.461(2)	114.2(17) 2-fold 107.2(9) 4-fold	124.3(3)	113.3	[68]
$Zr(NMe_2)_4$	r_g	2.071(11)	1.461(4)	110.5(25) 4-fold 107.4(48) 2-fold	124.3(6)	111.3(12)	[69]
				Groups V and VI			
$V(NMe_2)_4$	r_a	1.879(4)	1.457(3)	114.1(1) 4-fold 100.6(5) 2-fold	123.2(3)	113.6	[68]
$Ta(NMe_2)_5$	r_g	1.922(12)ax. 2.034(12)bas.	1.461(11)	114.1(35)ax.-bas. 75.5(2)bas.		110.7(40)	[70]
$W(NMe_2)_6$	r_g	2.035(5)	1.453(4)	180	125.6(4)	108.9(8)	[71]

Note. The prefixes anti- and *syn*- are used to characterise the relative arrangement of the $SiMe_3$ groups and the atom of the metal E relative to the N_3 plane in the triamino-derivatives of Ce and Pr; ax. and bas. denote the axial and basal Ta–N bonds in the pentakis(dimethylamino)tantalum molecule and the valence angles between them; 2-fold and 4-fold denote the two-fold and four-fold valence angles NEN in the tetra-amino-derivatives of Ti, Zr, and V (S_4 symmetry); the difference between them is that the S_4 axis lies in the planes of the two-fold angles.

becomes much smaller [121.6(4)°]. These changes are apparently due to Me...Me contact repulsion between neighbouring $N(SiMe_3)_2$ groups.

A consequence of the steric requirements of the bulky $N(SiMe_3)_2$ ligands may be their propeller-like configuration, found in the gas phase, relative to both the planar EN_3 fragment in $Sc[N(SiMe_3)_2]_2$ [angle of rotation 55(2)°] and the pyramidal EN_3 fragment in the derivatives of Ce [42(5)°] and Pr [47(5)°]. In the crystalline phase the configuration is practically unchanged, and the angle of rotation is ~50°.

d. Amino-derivatives of *d*-elements of groups IV–VI

The stability of the monomeric structures of the derivatives of the *d*-elements of groups IV–VI decreases on going from a lighter to a heavier element in a group, and this is usually related to the change in the covalent radii. Studies of benzene solutions of amino-derivatives of Ti and Zr showed, in particular, that the $Ti(NMe_2)_4$ molecules are monomeric in solution, whereas $Zr(NMe_2)_4$ gives an equilibrium monomer–dimer mixture.

Many derivatives of tantalum and tungsten in higher oxidation states also exist as binary or pseudo-binary compounds. Data on the structure of the stable monomeric amino-derivatives of these elements are therefore of considerable interest. The study of the structure of $V(NMe_2)_4$ is also important in relation to the influence of change in the configuration of the electron cloud of the central atom on the structure on going from the d^0-compounds of Ti and Zr to the d^1-compound of V.

One of the most significant characteristics of the state of amine nitrogen atoms, namely the bond configuration, is practically planar in all the structures studied (Table 4); this is apparently determined by the $p_\pi - d_\pi$-interaction of the nitrogen atom with the metal atom. At the same time, changes in the covalent radius of the metal atoms and also in their coordination numbers may have a significant influence on the form of the potential function of the wagging–inversion motion of the amino-group, which may be more or less flat, depending on steric factors.

The covalent radius of the Zr atom (1.45 Å) is much larger than those of the atoms of Ti (1.32 Å) or W (1.30 Å). The flatter potential function of the inversion of the amino-group in the $Zr(NMe_2)_4$ molecule compared with $W(NMe_2)_6$ is indicated by the much larger mean amplitude of the vibrations for the distances Zr...C [0.162(8) Å] compared with W...C [0.085(1) Å], whereas the amplitude of the vibrations for the C...C distances is almost the same in the two molecules.

The observed difference in the Zr–N and Ti–N bond lengths (0.154 Å) corresponds closely to the difference between the covalent radii given above. At the same time, for the bonds Zr–N and W–N the value of this difference obtained experimentally (0.036 Å) is much smaller than the estimated value. Thus the actual radius of the W atom in the $W(NMe_2)_6$ molecule is underestimated, and the

deviation is possibly due to inter-ligand steric interactions. The W–N bond length in the gas phase [2.035(5) Å] agrees with that found in crystalline $W(NMe_2)_6$ [2.032(25) Å[71]]. The $W(NMe_2)_6$ molecules in both phases have core symmetry T_h, with orthogonal planar $C_2N-W-NC_2$ fragments and linear N–W–N chains.

The molecular structures of the tetra-amino-derivatives of Ti, Zr, and V studied have S_4 symmetry. The configuration of the EN_4 fragment in these derivatives deviates considerably from T_d symmetry, particularly in the V compound. This is confirmed by spectral data.[74] The dihedral angles NENC characterising the rotation of the plane of the amino-group relative to the NEN plane containing the S_4 axis varies in these structures from 51(1) (Ti) to 69(9) (Zr) and 71(2)° (V).

The increase in the radius of the central metal atom on going from Ti to Zr possibly explains the slightly smaller deviation of the NZrN valence angles from the tetrahedral value (109.47°). It has been pointed out[69] that the deviation of the symmetry of the core of the $Zr(NMe_2)_4$ molecule from T_d cannot be regarded as statistically significant. Moreover, the large error in the determination of the valence angles of the ZrN_4 fragment and the fact that changes in these angles (not exceeding ±2°) have no influence on the values of the other parameters suggest that the ZrN_4 fragment is appreciably non-rigid and easily deformed.

The results of the X-ray diffraction study of the diamagnetic d^2-structure of $Mo(NMe_2)_4$ are of interest.[75] The crystal cell contains two independent molecules having symmetry close to D_{2d} (angle N–Mo–N–C ~90°). The value of the NMoN angles in these molecules, however, varies completely arbitrarily from 107.3(2)° to 112.5(2)° [average value 109.5(19)°], that is it is determined chiefly by intermolecular forces. The influence of the d^2 electron configuration of the central Mo atom on the structure of $Mo(NMe_2)_4$ is apparently less significant.

Table 5. Microwave and electron diffraction data for imino-derivatives.

Molecule	Method	Parameter	N=C, Å	X–N=C, °	Refs.
$HN=CH_2$	MW	r_s	1.273	110.4	[76]
$FN=CF_2$	MW+GE	r_α^0	1.274(6)	107.9(2)	[77]
$ClN=CCl_2$	GE	r_α^0	1.266(5)	117.1(4)	[78]
$Me_3CN=CH-CH=NCMe_3$	GE	r_a	1.283(6)	122.8(15)	[79]

In the opinion of authors cited,[68,69] the conclusion that the EN_4 core of tetra-amino-derivatives of Ti, Zr, and V undergoes deformations of large amplitude is confirmed by the appreciable values of the mean amplitudes of the vibrations obtained for the N...N distances [0.22(3), 0.14(3), and 0.19(4) Å in the derivatives of Ti, V, and Zr respectively]. However, the large experimental error most probably reflects the fact that the contribution of the N...N distances to the diffraction pattern is too small to be determined reliably against the background of the stronger or more numerous E...C, C...C, and N...C contributions.

The same feature apparently makes meaningless the discussion of the observed differences in the ratios between the values of the two-fold and four-fold valence angles NEN in the compounds studied (see Table 4), including the discussion of the possible influence of change in the configuration of the electron cloud of the central atom.

The $Ta(NMe_2)_5$ molecule has C_{2v} symmetry, and the TaN_5 fragments form a distorted square pyramid. A characteristic feature of the structure is that the axial Ta–N bond is 0.1 Å shorter than the basal bonds.

Table 6. Electron diffraction data (r_a) for carbodi-imide derivatives.

Molecule	N=C, Å	X–N=C, °	τ, °*	Refs
$H_3SiN=C=NSiH_3$	1.206(5)	150.6(12)**	—	[80]
$Me_3SiN=C=NSiMe_3$	1.216(4)	142.0(11)	44(2)	[81]
$H_3GeN=C=NGeH_3$	1.184(9)	138.0(5)	75	[82]
$Me_3GeN=C=NGeMe_3$	1.219(5)	131.4(9)	59(4)	[81]
$F_2PN=C=NPF_2$	1.240(5)	132.8(5)	55	[83]

*Dihedral angle between the planes XNC and CNX.
**The authors cited[80] assume that the equilibrium value of the Si–N=C valence angle is 180°, so that the Si–N=C=N–Si fragment is linear.

III. Imino-, carbodi-imido-, and azino-derivatives

In the imino-derivatives (Table 5) the N=C bond length changes little under the influence of substituents. The valence angle at the nitrogen atom, however, increases considerably on going from the $FN=CF_2$ molecule to $ClN=CCl_2$ and then to $Me_3CN=CH-CH=NCMe_3$, because of the appreciable steric interactions.

In the carbodi-imides (Table 6) the carbon atom forms bonds of the cumulene type, so that the N=C bonds in these compounds are shorter than those in the imines. The marked increase in the valence angle X–N=C (X = Si, Ge, P) compared with that in the imines may be due to the steric and electronic effects of the attachment of the Si, Ge, and P heteroatoms to the nitrogen atom. An interesting feature is that on going to the bulkier $SiMe_3$ and $GeMe_3$ substituents the X–N=C angle becomes much smaller than that in the SiH_3 and GeH_3 derivatives. Thus the observed increase in the valence angles Si–N=C and Ge–N=C is apparently due to the stereoelectronic effects of the Si and Ge atoms.

The cumulene bond system in allene $H_2C=C=CH_2$ has D_{2d} symmetry, with a dihedral angle H–C=C=C–H of 90°. In the carbodi-imide derivatives, however, the arrangement of the terminal groups is characterised by a much smaller dihedral angle. The investigation of this feature requires more systematic studies and quantum-chemical calculations.

Azino-derivatives (Table 7) are diene systems, that is classical conjugated double bond systems. As in derivatives of butadiene, the central N–N bond in these compounds is shorter than that in hydrazine [1.449(2) Å[88]]. The decrease in the length of the N–N bond in the molecule of the azine of formaldehyde $H_2C=N-N=CH_2$ (~0.05 Å), however, is smaller than the decrease in the length of the C–C bond in butadiene compared with ethane (0.07 Å^2). This can be attributed to the smaller coordination number of the N atom. The experimental average values of the N–N bond lengths (r_g, r_a) in halogen-substituted azines of formaldehyde (Table 7) were determined with a fairly large uncertainty, so that regularities in the changes cannot be established.

Table 7. Electron diffraction data for azino-derivatives.

Molecule	Parameter	Bond lengths, Å		Angles, °		Refs.
		N=C	N–N	N–N=C	C=N–N=C	
$H_2C=N-N=CH_2$	r_g	1.280(2)	1.402(4)	114.5(4)	180*	[84]
$F_2C=N-N=CF_2$	r_a	1.264(7)	1.421(12)	112.7(9)	153(5)**	[85]
$Cl_2C=N-N=CCl_2$	r_g	1.267(4)	1.389(9)	117.3(10)	139(7)*	[84]
$Br_2C=N-N=CBr_2$	r_g	1.274(10)	1.381(23)	117.4(27)	121(9)*	[84]
$MeH_2=N-N=CHMe$	r_a	1.277(4)	1.436(12)	110.5(7)	160–180**	[86]
$F_3C-C=N-N=C-CF_3$ $F_2C-CF_2-CF_2$	r_a	1.257(11)	1.349(19)	121.9(7)	52.4	[87]

*The value of the dihedral angle at the minimum of the potential function of the internal rotation is given (the angle 180° corresponds to the planar *anti*-form). For $H_2C=N-N=CH_2$, an MP2/6-31GF** calculation[84] gave another shallower minimum at an angle C=N–N=C of ~90° (see text).

**The effective value corresponding to averaging with respect to the twisting vibration of large amplitude relative to the N–N bond is given (see text).

Non-empirical quantum-chemical calculations in the Hartree–Fock approximation with 6-31GF** [85] and 6-31GF* [84] basis sets indicate a regular decrease in the length of this bond in the equilibrium *trans*- or close to *trans*-conformations of the azine of formaldehyde and its tetrafluoro- and tetrachloro-derivatives (from 1.40 to 1.39 and 1.37 Å respectively). According to these calculations, the change in the N–N bond length in the internal rotation is 0.04 Å. In the case of the azine of formaldehyde, the N–N bond length is shortest in the *gauche*-form (1.37 Å), and in the planar *cis*- and *trans*-forms with a predisposition towards conjugation it increases to 1.41 Å and 1.40 Å, whereas in the halogen derivatives there is a regular change from the smallest value in the *cis*-form to the largest value in the *trans*-form.

The conformation of C=N–N=C is of considerable interest. The results of experiments and calculations indicate that the potential functions of the internal rotation of the azine of formaldehyde and its halogen derivatives have a fairly flat surface in a wide region close to the *trans*-form and a high barrier in the *cis*-position. The height of the barrier is 14.6 kcal mol^{-1} for the molecule of the azine of formaldehyde (MP2/6-31GF** calculation), and 14.2 kcal mol^{-1} and 26.5 kcal mol^{-1} for the tetrafluoro- and tetrachloro-derivatives (MP2/6-31GF*//6-31GF*).[84] Calculation at the Hartree–Fock level gives a value for the barrier which is only 2 kcal mol^{-1} higher. These values are 2–3 times the values obtained by calculations at the Hartree–Fock level for the heights of the barriers in butadiene, glyoxal, and their fluoro-derivatives (see Ref. 85 and references therein). The form of the potential curve in the flat region and the position and number of the minima on it depend to a significant extent on the substituents present in the molecule. Thus for the molecule of the azine of formaldehyde, in addition to the principal minimum corresponding to the planar *trans*-form, non-empirical calculation[84] also gives a weak minimum in the region of the *gauche*-form (the dihedral angle C=N–N=C is ~90°), with an energy 0.75 kcal mol^{-1} higher. The barrier to the transformation from the *trans*- to the *gauche*-form is very low, only 0.85 kcal mol^{-1}.

In contrast to this, according to the calculations,[84] for the $F_2C=N-N=CF_2$ molecule the minimum corresponding to the *trans*-position is the only one. An electron diffraction study of the fluorinated azine of formaldehyde[85] gave for the angle C=N–N=C the effective value 153(5)°, due to averaging with respect to a twisting vibration of large amplitude. This non-planarity of the average configuration is related to the fact that the equilibrium *trans*-form has planar symmetry. In the twisting vibrations, rotation through the same angle in different directions from the plane of symmetry leads to two equivalent configurations. Thus the averaging with respect to configurations which is obtained in the analysis of the electron diffraction data without allowance for the vibration of large amplitude (using the so-called static model) leads to an effective non-planar configuration of the molecule.

The potential function of the internal rotation of the $Cl_2C=N-N=CCl_2$ molecule has a minimum in the region of the *gauche*-form. The experimental value of the dihedral angle C=N–N=C at the positon of the minimum [139(7)°], obtained by analysis with allowance for the twisting vibration of large amplitude (using the so-called dynamic model), shows good agreement with the value obtained in a quantum-chemical calculation.[84] Estimation of the height of the barrier in the transition state corresponding to the planar *trans*-form, however, gives a value not exceeding 0.1 kcal mol^{-1}.

According to electron diffraction data, the height of the barrier to rotation in the planar *trans*-form [1.4(12) kcal mol^{-1}] in the $Br_2C=N-N=CBr_2$ molecule should be much greater than that in the chlorine analogue, and the minimum of the potential function in the *gauche*-position corresponds to a greater deviation from the *trans*-form [121(9)°].

In the *trans*-conformations of the Cl- and Br-derivatives of the azine of formaldehyde there is considerable steric repulsion between the Cl or Br atoms and the lone pairs of the N atoms in the *cis*-position to them. The importance of steric factors is indicated by the appreciable increase, found by calculations,[84,85] in the N–N=C valence angles on going from the *trans*- to the *cis*-form for the azine of formaldehyde and its tetrafluoro- and tetrahcloro-derivatives (by 10, 15, and 20° respectively).

IV. Nitro-compounds

C-, N-, and O-nitrocompounds, with CNO_2, NNO_2, and ONO_2 groups, are distinguished. Structural data on nitro-compounds, obtained up to 1979, have already been reviewed.[89] The present

Table 8. Principal geometric parameters of the molecules of various nitro-compounds in the gas phase, from gas-phase electron diffraction data (r_g structure).

Compound	Bond lengths, Å				Valence angles, °			φ_{NO_2}, °	Refs.
	C⩬C	C–N	N=O	C–X*	ONO	CC_NC	CC_XC		
$C_6H_5NO_2$	1.399(3)	1.486(4)	1.223(3)	—	125.3(2)	123.4(3)	—	13(1)	[92]
o-$ClC_6H_4NO_2$	1.387(2)	1.462(12)	1.226(2)	1.721(3)	123.6(10)	121.4(12)	121.7(7)	34(3)	[93]
m-$ClC_6H_4NO_2$	1.388(3)	1.442(10)	1.243(3)	1.746(6)	122.6(10)	123.0(15)	121.5(12)	13(6)	[94]
n-$ClC_6H_4NO_2$	1.388(4)	1.469(19)	1.233(4)	1.710(7)	123.2(16)	122.6(12)	120.4(10)	19(5)	[95]
2,6-$(NO_2)_2C_6H_3Cl$	1.395(3)	1.447(4)	1.229(2)	1.712(5)	123.0(3)	121.6(4)	118.9(6)	54(1)	[96]
1,3,5-Cl_3-2,6-$(NO_2)_2C_6H$	1.400(6)	1.469(15)	1.228(7)	1.705(6)	129.2(30)	120.9(14)	119.7(5)	65(1)	[97]
sym-$C_6Cl_3(NO_2)_3$	1.399(3)	1.464(6)	1.217(2)	1.699(4)	131.4(24)	120.6(5)	119.4(15)	79(1)	[98]
o-$BrC_6H_4NO_2$	1.386(3)	1.494(14)	1.218(3)	1.894(6)	128.6(15)	120.4(24)	119.6(12)	43(3)	[99]
m-$BrC_6H_4NO_2$	1.394(3)	1.448(14)	1.238(3)	1.865(8)	121.8(14)	121.4(15)	121.4(10)	25(5)	[99]
n-$BrC_6H_4NO_2$	1.399(3)	1.455(12)	1.240(4)	1.895(7)	125.0(7)	121.6(6)	122.6(6)	19(3)	[100]
2,6-$(NO_2)_2C_6H_3Br$	1.393(3)	1.468(9)	1.229(3)	1.899(9)	125.6(9)	122.7(9)	117.1(12)	58(3)	[99]
sym-$C_6Br_3(NO_2)_3$	1.402(7)	1.455(16)	1.242(5)	1.886(6)	133.8(20)	121.6(11)	118.4(11)	77(1)	[101]
o-$IC_6H_4HO_2$	1.398(3)	1.472(22)	1.238(4)	2.096(10)	122.4(9)	122.3(14)	118.6(11)	60(4)	[102]
m-$IC_6H_4NO_2$	1.392(2)	1.490(17)	1.227(3)	2.100(9)	124.0(5)	124.0(10)	121.9(7)	14(5)	[102]
n-$IC_6H_4NO_2$	1.397(2)	1.459(14)	1.229(2)	2.103(8)	122.4(6)	122.2(6)	122.2(4)	16(1)	[103]
sym-$C_6(CH_3)_3(NO_2)_3$	1.397(2)	1.487(8)	1.221(2)	1.482(11)	126.8(6)	123.5(8)	116.5(8)	72(1)	[104]
sym-$C_6(OH)_3(NO_2)_3$	(1.393)	1.491(7)	1.231(3)	1.371(7)	124.9(8)	120.0(11)	118.4(6)	12(7)	[105]
o-$NO_2C_6H_4SeBr$	1.396(6)	1.466(24)	1.229(8)	1.917(11)	124.8(6)	123.7(6)	—	0	[106]
o-$NO_2C_6H_4SCl$	1.397(3)	1.459(9)	1.229(3)	1.776(5)	125.1(40)	123.0(3)	—	0	[107]

*X is the substituent in addition to the NO_2 group (X = Cl, Br, I, CH_3, OH, SeBr, SCl).

review gives the results of the study of the structure of molecules of nitro-compounds of all three types, published in recent years. Among the C-nitro-compounds, most attention has been paid to aromatic halogeno- and polynitrobenzenes, and also nitrobiphenyls.

1. Aromatic C-nitro-compounds

The principal geometric parameters of a number of nitrobenzene derivatives in the gas phase are given in Table 8.

As noted earlier,[4,5,90] the geometry of aromatic nitro-compounds is determined by the mutual influences in the nitro-group – benzene ring – substituent system. Subsequent studies have confirmed this conclusion.

All compounds of this type show deformation of the benzene ring under the influence of the nitro-groups and other substituents (Cl, Br, I, CH_3). The addition of electron-acceptor groups to the benzene ring leads to an increase in the valence angle of the *ipso*-carbon atom.[90,91] This is shown most clearly in *para*- and *meta*-substituted nitrobenzenes. In the molecules of 1-chloro- and 1-bromo-2,6-dinitrobenzenes, the nitro-groups are responsible for the deformation of the benzene ring, and the influence of the chlorine and bromine atoms is slight. The competing influence of the nitro-groups and the chlorine (bromine) atoms is shown most clearly in the *sym*-trihalogenonitrobenzenes. Unfortunately, the experimental errors do not make possible a more detailed discussion of this question.

The greatest deformation of the benzene ring is observed in the *sym*-$C_6(CH_3)_3(NO_2)_3$ molecule, where the electron-acceptor NO_2 groups and the electron-donor CH_3 groups supplement one another. This can be seen by comparing the data in Table 9.

Table 9. Valence angles CC_XC (°) in the molecules of $C_6X_3(NO_2)_3$ and $C_6H_3X_3$.

X	$C_6X_3(NO_2)_3$		Refs.	$C_6H_3X_3$	Refs
Cl	119.4(5)	[120.6(5)]*	[98]	122.0(2)	[108]
Br	118.4(11)	[121.6(11)]	[101]	120.4(8)	[109]
CH_3	116.5(8)	[123.5(8)]	[104]	118.2(2)	[110]
NO_2	—	—	—	123.0(9)	[111]

*The values of the angles $CC_{NO_2}C$ are given in square brackets.

In the series of aromatic nitro-compounds given in Table 8, the C⩬C bond lengths in the benzene ring are shorter than in non-substituted benzene. This applies to *o*-chloro and *o*-bromonitrobenzenes (this feature was previously noted for *sym*-trinitro- and *p*-dinitrobenzenes[111]). In *sym*-$C_6Cl_3(NO_2)_3$, however, where the accuracy of the determination is fairly high, there is no decrease in the C⩬C bond length (in non-symmetrical nitro-derivatives, some non-equivalence of the C⩬C bonds may be assumed, but it is impossible to detect it experimentally by gas-phase electron diffraction). The average C⩬C bond length in nitrobenzenes is independent of the number of NO_2 groups.

Analysis of the parameters of the nitro-group shows that the scatter in the N=O bond lengths (average value 1.228 Å) does not exceed 0.015 Å. The average value of the angle ONO is 125°, but the values of this angle in nitrobenzene derivatives differ considerably.

The C–NO_2 bond lengths have been determined with fairly large errors. The average value of r(C–NO_2) is 1.47 Å. Because of the relatively large errors in the determintion of r(C–NO_2) and the small changes in this quantity, it is difficult to establish the influence of substituents on the length of this bond or the dependence of r(C–NO_2) on the angle of rotation of the nitro-group. The changes in r(C–N) and the angle φ_{NO_2} for halogenonitrobenzenes (Table 8) show no definite relationship between them.

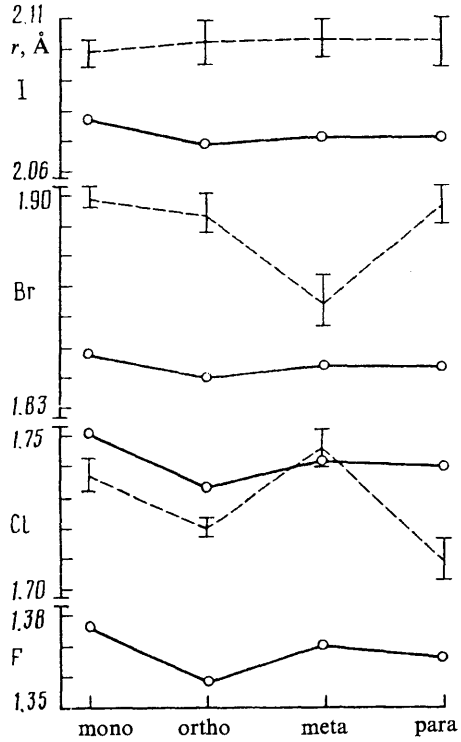


Figure 1. Dependence of the experimentally determined bond length r_g(C–X) (broken line) and the corresponding bond length r_e(C–X) (continuous line) obtained from non-empirical calculations on the position of X in halogenonitrobenzenes; the calculations were carried out using the basis sets 6-31GF for X = F, 3-21GF* for X = Cl, and STO-3GF* for X = Br and I respectively; the notation "mono" refers to the halogenobenzene, and "ortho", "meta", and "para" to the positions of the substituents X = F, Cl, Br, and I in the halogenonitrobenzenes.

Figure 1 gives the dependence of the C–X bond lengths (X = F, Cl, Br, I) on the positions of the substituents X in halogenonitrobenzenes.

Under the influence of the nitro-group in the molecules of chloronitrobenzenes there is a slight decrease in the length of the C–Cl bond in the *ortho*- and *para*-substituted nitro-derivatives compared with chlorobenzene [1.737(6) Å [112]]. This decrease in the C–Cl bond length is not observed in *m*-chloronitrobenzene.

The decrease in the C–Cl bond length in the *o*-chloronitro-derivatives is confirmed by the data for 1-chloro-2,6-dinitrobenzene, *sym*-trichloronitrobenzene, and 1,3,5-trichloro-2,6-dinitrobenzene.

The C–Br bond lengths in *o*- and *p*-bromonitrobenzenes are practically the same as that in bromobenzene [1.899(3) Å].[113] This is confirmed by the data for 1-bromo-2,6-dinitrobenzene. The shortest C–Br bond length was found experimentally in *m*-$BrC_6H_4NO_2$; this does not correspond to the trend detected for other molecules and by *ab initio* calculations.[102]

For iodonitrobenzenes, the changes in the C–I bond lengths are very small. As in the case of the C–Br bond, nitro-groups in the *ortho*- or *para*-positions have no influence on the C–I bond length.

Figure 1 also gives the results of *ab initio* calculations for the molecules of fluoro-, chloro-, bromo-, and iodonitrobenzenes. The largest changes in the C–X bond lengths were obtained for fluoronitrobenzenes, and the smallest for iodonitrobenzenes.

It is of interest to follow the influence of nitro-groups on the C–Cl, C–Br, and C–CH_3 bond lengths (in Å) by comparing the data obtained for the symmetrical 1,3,5-derivatives:

	C–Cl	C–Br	C–CH_3
1.3.5-$C_6H_3X_3$	1.734(2)	1.877(4)	1.509(2)
1.3.5-$C_6(NO_2)_3X_3$	1.699(4)	1.886(6)	1.482(11)

The C–Cl and C–CH_3 bond lengths decrease on going to the nitro-derivatives. Because of the relatively large experimental errors, the difference for the C–Br bond is statistically insignificant.

According to microwave data,[114] the potential of the internal rotation of the NO_2 group in the nitrobenzene molecule has a minimum at φ_{NO_2} = 0°, that is for the planar configuration of the molecule. The barrier to the rotation is 2.9 kcal mol^{-1}. Electron diffraction study makes it possible to determine the average value of the dihedral angle between the planes of the benzene ring and the nitro-group; for $C_6H_5NO_2$ the value does not coincide with the equilibrium value, and is equal to 13°.[92] The same situation apparently arises for the *meta*- and *para*-derivatives of nitrobenzene, where the minimum of the potential of the internal rotation of the NO_2 group corresponds to 0°, and the non-planar conformations, detected by electron diffraction, are related to the twisting vibrations of the nitro-groups. Allowance for these vibrations leads to planar equilibrium models with a barrier to rotation $V_2 \simeq 4-5$ kcal mol^{-1}.[115]

In the molecules of the *ortho*-derivatives of nitrobenzene there is considerable steric hindrance, and the equilibrium configurations are appreciably non-planar. Thus in the *ortho*-dinitro-derivatives and 1-halogeno-2,6-dinitro-derivatives the experimentally determined conformations are close to the equilibrium ones.

In the *sym*-trinitro-substituted benzenes $C_6(NO_2)_3X_3$ (C = Cl, Br, CH_3) the average dihedral angles are ~80°. If the equilibrium configuration corresponds to an angle φ_{NO_2} = 90°, it may be expected that vibrational effects will destroy the high symmetry of the equilibrium configuration, leading to a decrease in the dihedral angle φ_{NO_2}. Thus *ortho*-substituted nitrobenzenes are sterically "crowded" molecules, and the greatest steric strain is produced in the *sym*-tribsubstituted nitrobenzenes.

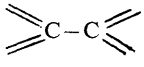
The decisive factor lowering the steric strain is the rotation of the nitro-group through the angle φ. Comparison of the shortest distances Cl...O, Br....O, CH_3...O and correspondingly Cl...N, Br...N, CH_3...N with the sums of the van der Waals radii for *sym*-hexasubstituted nitrobenzenes shows that the distances between the

non-bonded atoms X...O are close to the sums of the van der Waals radii, whereas the X...N distances are much smaller than the corresponding sums.

The molecules of *o*-$(NO_2)C_6H_4SCl$ and *o*-$(NO_2)C_6H_4SeBr$ are planar, with internuclear distances O...S (2.36 Å) and O...Se (2.39 Å) shorter than the sums of the van der Waals radii [3.13 Å (O...S) and 3.30 (O...Se)]. The planar conformations of these molecules, in which the S and Se atoms approach the NO_2 group, may be the result of conjugation of the lone pairs of S and Se with the electronic system of the nitro-group (donor–benzene ring–acceptor system), and also of intramolecular coordination of the oxygen of the nitro-group to these atoms.

The planar conformation has also been established for the $C_6(OH)_3(NO_2)_3$ molecule. This result is consistent with earlier data obtained for the molecules of *o*-nitrophenols in the crystalline phase, in which an intramolecular hydrogen bond is assumed. By analogy, the existence of a bond of this type may be expected for the molecules in the gas phase. The distance $r(O_{NO_2}...H_{OH})$ [1.55(5) Å] between neighbouring NO_2 and OH groups is much shorter than the sum of the van der Waals radii of the H and O atoms (2.45 Å), and the angle O–H...O is 116°.

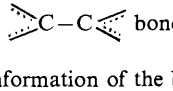
The very few structural data for nitro-derivatives of biphenyl relate mainly to the crystals. Until recently only one compound, 6,6′-dinitrobiphenyl-2,2′-dicarboxylic acid, had been studied in the gas phase.[116]

As in the case of non-substituted biphenyl,[117] a characteristic feature of the molecules of nitro-derivatives of biphenyl is the rotation of one benzene ring relative to the other round the central  bond. Thus in the "free" molecule of 6,6′-dinitro-biphenyl-2,2′-dicarboxylic acid the angle of rotation of the rings φ_{C-C} is 71°, and the angle of rotation of the nitro-group φ_{NO_2} is 30°.

Among the nitro-derivatives of biphenyl studied in the crystalline state, 2-nitrononafluorobiphenyl[118] shows the largest angle of rotation of the rings (86°). In this compound there is also appreciable rotation of the nitro-group (56°). Compounds with nitro-groups in the *para*-positions (4-nitrobiphenyl[119] and 4,4′-dinitrobiphenyl[120]) show an almost coplanar arrangement of these groups and the benzene ring, that is their conformation is analogous to that of *para*-derivatives of benzene. Within the experimental error, the length of the central C–C bond in the nitro-derivatives of biphenyl is close to that in non-substituted biphenyl (1.49 Å).

A series of electron diffraction studies of the biphenyl derivatives 4,4′-dinitrobiphenyl, 2-nitrobiphenyl, and 2,2′-dinitro-4,4′-dichloro-biphenyl has now been carried out.[121–123]

The results are compared with data for biphenyl and nitrobenzene in Table 10. For 4,4′-dinitrobiphenyl, the electron diffraction data are also compared with X-ray diffraction data.

The results supplement and confirm the previously noted geometric characteristics of the structure of nitrobiphenyls. In particular, comparison of the angles of rotation φ_{C-C} indicates that the introduction of nitro-substituents in the *para*-position to the central  bond has no statistically significant influence on the conformation of the biphenyl fragment.

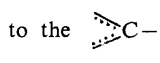
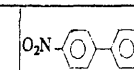
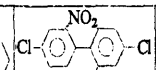
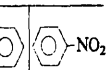
At the same time the introduction of an NO_2 group in the *ortho*-position to the  bond increases by 20° the angle of rotation of the benzene rings relative to one another (~65°), compared with non-substituted biphenyl. The highest value of the angle φ_{C-C} is observed in 2,2′-dinitro-4,4′-dichlorobiphenyl (87°), that is in the molecule with the greatest steric strain.

Table 10. Geometric parameters of the molecules of biphenyl, nitrobenzene, and nitro-derivatives of biphenyl.

Parameters						
	GE (Ref.122)	XRD (Ref.120)	GE (Ref.121)	GE (Ref.123)	GE (Ref.117)	GE (Ref.92)
Bond lengths, Å						
C–C	1.499(27)	1.499(16)	1.481(36)	1.507(39)	1.509(4)	—
C⋯C	1.402(2)	1.393(20)	1.395(3)	1.394(2)	1.400(5)	1.399(2)
C–N	1.479(8)	1.532(22)	1.466*	1.482(17)	—	1.486(2)
N=O	1.223(6)	1.201(18)	1.207(13)	1.220(5)	—	1.223(2)
Angles, °						
ONO	125.4(6)	128.6(24)	123.8(15)	127.8(9)	—	125.4(2)
CCNC	123.6(15)	126.9(16)	123.8*	124.8(6)	—	123.4(2)
φ_{C-C}	50.3(51)	32.7	64.8(51)	87.2(83)	44.4(12)	—
φ_{NO_2}	-25.0(48)	10.0(13)	-64.1(70)	-24.8(75)	—	13.3(10)

*Determined in agreement with experiment.

The principal difference between the structural parameters of 4,4′-$NO_2C_6H_4C_6H_4NO_2$ in the free molecule and in the crystal is observed for the central torsional angle φ_{C-C}. The other structural parameters are comparable, within the experimental error. The same conclusion was previously reached by comparing the geometries of non-substituted biphenyl in the gas phase and in the crystal.

As in the case of mono-substituted benzene derivatives, the addition of a nitro-group to the biphenyl ring leads to an increase in the endocyclic angle at the carbon atom joined to the nitro-group, compared with the trigonal value.

2. N-Nitramines (N-nitro-compounds)

In N-nitramines there is a direct interaction between the electron-donor amino-group and the electron-acceptor nitro-group. The geometry of the molecules of these compounds depends significantly on the substituents on the amine nitrogen atom.[89] We are speaking primarily of the changes in the N–N bond lengths and the pyramidal nature of the amine nitrogen atom.

Despite the fairly large number of published experimental studies of N-nitramines,[89] however, there is still no clear picture of the regularities in their structures and the energy parameters of the intramolecular motions involving inversion of the amine nitrogen atom and internal rotation about the N–N bond. The answers to many problems are not obtained by structural methods, and the unambiguous interpretation of the results is often difficult.

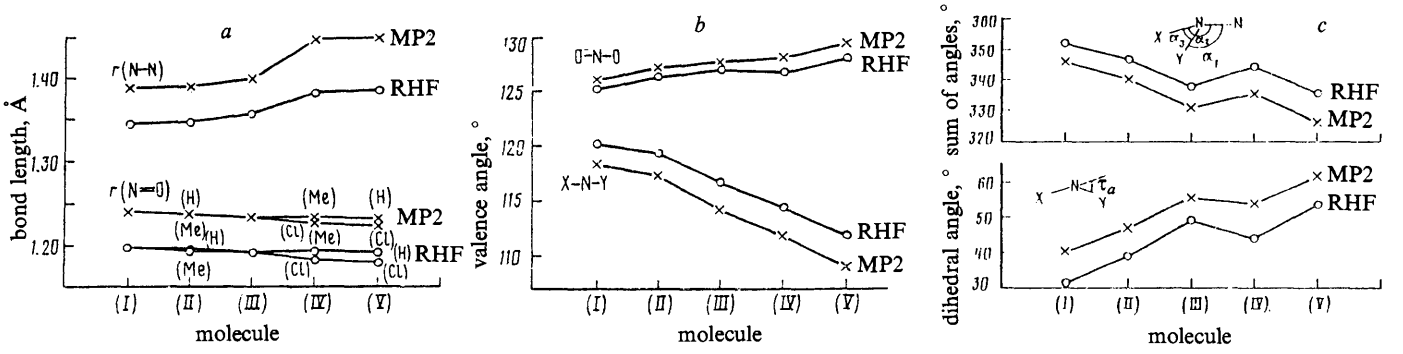


Figure 2. Influence of change in the electronegativity of the substituents on the amine nitrogen atom on the N–N and N=O bond lengths (*a*), the valence angles ONO and XNY (*b*), and the pyramidal character of the configuration of the amine nitrogen atom [the change in the dihedral angle between the NNX and NNY planes (τ_a) and the sum of the valence angles at the nitrogen atom ($\Sigma\alpha_N$)] (*c*) in the N-nitramines (I)–(V), from the results of RHF/6-31GF* and MP2/6-31GF* calculations.

a. Non-empirical quantum-chemical calculations for N-nitramines

These compounds, which are important for theoretical and practical chemistry, can now be studied systematically using another powerful instrument, namely quantum-chemical calculations. The results of calculations for five N-nitramines, H_2NNO_2, $MeNHNO_2$, $ClNHNO_2$, $MeNClNO_2$, and Me_2NNO_2,[124,125] carried out by the restricted Hartree–Fock (RHF) method with allowance for electron correlation using second-order Möller–Plesset theory (MP2), are of interest. The standard basis set 6-31GF*, which has proved effective in similar studies,[8,126–128] was used.

Many structural parameters of amino-derivatives, including the valence angles at the nitrogen atom, are reproduced with this basis set within the experimental error of their determination, even at the RHF level. Allowance for electron correlation in the MP2 approximation largely removes the discrepancies between the calculated and experimental lengths of multiple bonds and neighbouring bonds. Simultaneously, however, the pyramidal nature of the amine nitrogen atom is overestimated slightly.

Analysis of the results reveals a trend towards a coordinated change in the geometric parameters with change in the effective electronegativity of the substituents on the amine nitrogen atom. With increase in the electronegativity of the substituents, that is with decrease in the electron-donor properties of the substituted amino-group, there is an increase in the N–N bond length, a decrease in the N=O bond length, an increase in the pyramidal character of the bond configuration of the amine nitrogen atom, and an increase in the non-planarity of the nitro-group. All this can be regarded as a consequence of a decrease in the $p-\pi$ conjugation between the lone pair of electrons of the amine N atom and the π-system of the NO_2 group.

This is clearly demonstrated by the graphs in Fig. 2 giving the changes in the geometric parameters, where the discrete points on the abscissa correspond to the positions of the compounds in order of increasing electronegativity of the substituents: Me_2NNO_2 (I), $MeNHNO_2$ (II), H_2NNO_2 (III), $MeNClNO_2$ (IV), and $ClNHNO_2$ (V). The greatest difference in the N–N bond lengths (up to 0.06 Å) is observed on going from molecule (I) to (V) (Table 11).

An interesting feature is that with increase in the electronegativity of the substituents X and Y on the amine nitrogen atom the valence angles ONO and XNY change synchronously, but in opposite directions away from the value 120°; the angle ONO increases with increase in the electronegativity of the substituents X and Y (this can be related to the change in the electron density distribution with decrease in the N=O bond length), whereas the angle XNY decreases.

Table 11. N–N bond lengths in N-nitramines, from experimental data and the results of non-empirical quantum-chemical calculations for the equilibrium structures (ES) and the transition states of the inversion (TS_{inv}) of the amino-group and internal rotation (TS_r) (in Å).

Molecule	Experiment				RHF/6-31GF* calculation (Refs. 124, 125)			MP2/6-31GF* calculation (Refs. 124, 125)		
	method	parameter	r(N–N)	Refs	ES	TS_{inv}	TS_r	ES	TS_{inv}	TS_r
Me_2NNO_2	GE	r_a	1.382(3)	[129]	1.344	1.326	1.424	1.387	1.359	1.463
$MeNHNO_2$	GE	r_a	1.381(6)	[130]	1.346	1.325	1.422	1.389	1.358	1.463
H_2NNO_2	MW	r_0	1.427(2)	[131]	1.356	1.327	1.421	1.399	1.361	1.462
	MW	r_0	1.381	[130]						
$MeNClNO_2$	GE	r_a	1.469(5)	[130]	1.381	1.343	1.442	1.447	1.379	1.506
$ClNHNO_2$	–	—	—	—	1.384	1.341	1.440	1.449	1.380	1.511
$MeN(NO_2)_2$	GE	r_a	1.480(5)	[132]						

The systematic increase in the dihedral angle τ_a between the planes NNX and NNY and the simultaneous decrease in the sum of the valence angles at the amine N atom, together with the changes in the angle XNY, indicate that the pyramidal nature of the amine nitrogen atom increases with increase in the electronegativity of the substituents.

Unlike the experimental data (Table 12), the results of the calculation give a pyramidal bond configuration for the amine nitrogen atom for all the molecules studied. Thus the interaction of

the amine nitrogen atom with the nitro-group, unlike that for other functional groups (the acyl group and the nitrosyl group[126–128]), does not lead to a planar bond configuration for the amine nitrogen atom in the equilibrium state of the molecule.

Table 12. Dihedral angle NNX/NNY in N-nitramines (τ_a, °), from experimental data and the results of non-empirical quantum-chemical calculations of the equilibrium structures (ES) and the transition states of internal rotation (TS_r).

Molecule	Experiment			RHF/6-31GF* calculation (Refs. 124, 125)		MP2/6-31GF* calculation (Refs 124, 125)	
	method	τ_a	Refs.	ES	TS_r	ES	TS_r
Me_2NNO_2	GE	0	[129]	31.2	56.1	40.4	60.7
$MeNHNO_2$	GE	not determined	[130]	39.1	62.5	47.0	66.0
H_2NNO_2	MW	53.0	[131]	49.1	67.2	55.5	71.9
	MW	45.0	[130]				
$MeNClNO_2$	GE	51.4	[130]	44.1	59.2	53.8	64.4
$ClNHNO_2$	–	—	—	53.6	67.2	61.7	72.3

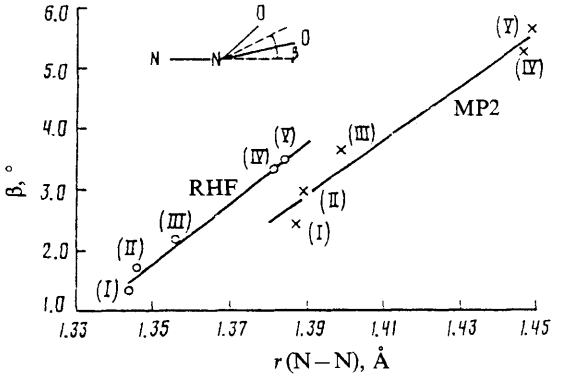


Figure 3. Relationship between the N–N bond length and the angle of displacement of the N–N bond from the ONO plane (β) in the N-nitramines (I)–(V), from the results of RHF/6-31GF* and MP2/6-31GF* calculations.

The deviation from the planar configuration of the nitrogen atom of the nitro-group is defined by the angle of displacement of the N–N bond from the ONO plane (β), the change in which is practically proportional to the change in the N–N bond length. Figure 3 give the dependence of the angle β on r(N–N) for the N-nitramines studied. It is consistent with the concept of $p-\pi$-conjugation: the greater the conjugation and the shorter the N–N bond becomes, the greater the flattening of the bond configuration of the nitrogen atom of the nitro-group. An equally simple relationship is not obtained for the angle of displacement of the N–N bond from the plane of the amine nitrogen atom XNY. This may indicate that change in the steric factors has a significant influence on the configuration of the amine group.

To characterise the potential function of the displacement of the N–N bond from the plane of the nitro-group, the geometry of the molecules Me_2NNO_2, $MeNHNO_2$, and $ClNHNO_2$ was optimised for a fixed planar configuration of the NNO_2 fragment. The total energies of the optimised models were greater than that of the equilibrium form. It is significant that in all cases there were no imaginary normal-vibration frequencies. This indicates that the planar form of the nitro-group in the N-nitramines studied does not correspond to transition states. Cordell[133] obtained for the Me_2NNO_2 molecule the potential curve for the displacement of the N–N bond from the ONO plane, which has a single minimum at an angle of displacement of the N–N bond from the plane of the nitro-group equal to 1.2°, and which can be approximated by a function close to harmonic. Thus the motion being considered is the wagging vibration.

Analysis of the results of the calculation of the transition states for the inversion of the amino-group (TS_{inv}) and internal rotation about the N–N bond (TS_r) leads to the following important conclusion. The flattening of the bond configuration of the amine nitrogen atom during inversion, and the deviation of the structure of the molecule from the equilibrium form during internal rotation, are accompanied by a significant change in the other geometric parameters. Particularly marked changes are undergone by the N–N bond lengths, which are 0.06–0.08 Å longer in TS_r than in the equilibrium forms (see Table 11).

In addition, the transition state of the inversion shows a decrease in the N–N bond length, an increase in the valence angle XNY, and a slight increase in the N–O bond lengths, and the transition state of the internal rotation shows a significant increase in the pyramidal nature of the configuration of the amine nitrogen atom (see Table 12) and a decrease in the N–O bond lengths.

Roughly speaking, the planar transition state of the inversion of the amino-group should promote an increase in $p-\pi$-conjugation, whereas the perpendicular form of the transition state of the internal rotation is unfavourable for this interaction. In this connection it is of interest that the observed relaxational changes in the N–N bond lengths and other parameters during inversion or internal rotation take place in coordinated fashion and in accordance with the concept of $p-\pi$-conjugation. Moreover, the coordinated nature of the changes in the parameters in the intra-molecular motions observed in this case apparently has the same basis as the changes examined above in the parameters of the same structures as a result of the influence of the electronegativity of the substituents on the electron density distribution.

In contrast to the equilibrium forms of molecules (I)–(V), where the N–N bond lengths change regularly with change in the extent of the conugation, in TS_{inv} and TS_r the lengths of these bonds are determined almost entirely by the presence or absence of the Cl-substituent.

The graphs in Fig. 4 give the dependence of the heights of the barriers to inversion (V_i) and rotation (V_r) in the N-nitramines (I)–(V) on the electronegativity of the substituents on the amine nitrogen atom. Both methods of calculation (RHF and MP2) reveal the same trend in the changes in V_i and in V_r; the RHF calculation gives higher values than MP2 for V_r, and lower values for V_i. The height of the barrier to inversion in the H_2NNO_2 molecule, obtained by the MP2 calculation (3.1 kcal mol^{-1}), effectively reproduces the

experimental value of 2.7 kcal mol^{-1}.[135] The last value is at present the only experimentally determined energy characteristic of intramolecular motion in N-nitramine molecules.

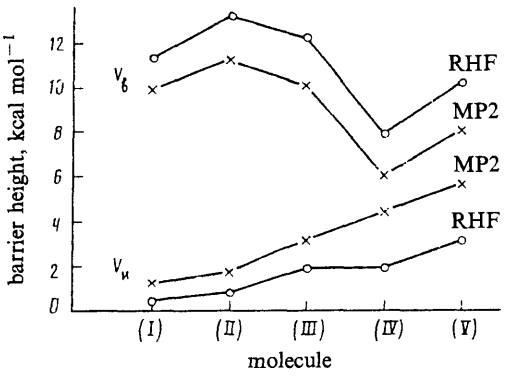


Figure 4. Changes in the heights of the barriers to inversion of the amine nitrogen atom (V_i) and internal rotation about the N–N bond (V_r) in the nitramines (I)–(V), from the results of RHF/6-31GF* and MP2/6-31GF* calculations.

The results show that the greater the pyramidal nature of the amino-group in the equilibrium state of the molecule, the higher the barrier to pyramidal inversion and in general the lower the barrier to internal rotation about the N–N bond.[8] The relationship is more complex for the barrier to rotation, however. This may reflect changes in the contributions of steric factors to the rotation potential. All estimates of the barriers to inversion of the amine nitrogen atom lie in the range 0.4–6.0 kcal mol^{-1} (for comparison, the barrier to inversion has the values 5.8 for ammonia, 2.0 for cyanamide, and 10.3 kcal mol^{-1} for diethylochloroamine[134–136]). The barriers to internal rotation in N-nitramines are 6–13 kcal mol^{-1}, that is they are 1.5–2 times lower than those for amides and N-nitrosamines.[127,128,137–140]

The existence of conjugation in the equilibrium forms of nitramines, as in other amino-derivatives with unsaturated substituents, may be indicated by the flattening of the pyramid of the bonds of the amino-group and the decrease in the N–N bond length. This is accompanied by a lowering of the barrier to inversion of the amine nitrogen atom and a raising of the barrier to internal rotation about the N–N bond. The effect of conjugation in nitramines, however, is less marked than that in amides and nitrosamines.[8] The appreciable change in the geometric parameters in the transition states compared with the equilibrium state may indicate an increase in conjugation during inversion, and breakdown of the $p-\pi$-conjugation on rotation about the N–N bond.

Finally, another interesting result of the calculation may be noted. The inversion of the amine nitrogen atom is coordinated with the flattening of the nitro-group. For a fixed planar configuration of the amino-group, optimisation of the other geometric parameters invariably leads to a planar configuration of the bonds formed by the nitrogen atom in the nitro-group. In the equilibrium states, however, as already noted, the configuration of the bonds formed by the nitrogen atom of the nitro-group is slightly pyramidal, and the degree of pyramidal character correlates well with the change in the N–N bond length.

Table 13. Structural parameters of some of the simplest N-nitramines.

Parameter	$CH_3(CH_2=CH)NNO_2$ (Ref.141)	$(CH_2Cl)_2NNO_2$ (Ref.142)	$(CH_2Cl)CH_3NNO_2$ (Ref.143)	$(CH_3)_2NNO_2$ (Ref.129)
Bond lengths, Å				
N=O	1.213(3)	1.216(3)	1.212(2)	1.223(2)
N–N	1.385(8)	1.422(5)	1.424(5)	1.382(3)
C–N	1.432(15) (vinyl) 1.459(15) (methyl)	1.443(4)	1.476(9)	1.460(3)
C–Cl	—	1.803(4)	1.809(4)	—
Angles, °				
ONO	128.0(21)	128.0(14)	127.5(10)	130.4(13)
NNC_{CH_3}	113.5(12)	116.3(4)	116.6(6)	116.2(3)
CNC	124.1(10)	124.8(9)	127.0(9)	127.6(6)
NCCl	—	111.6(5)	107.7(9)	—
φ_{NO_2}	2(18)	2.6(15)	32.9(29)	0
φ_{CH_2}	—	10.8(17)	–4.3(18)	—

b. Electron diffraction data

Work on the determination of the structure of the simplest N-nitramines in the gas phase includes gas-phase electron diffraction studies of the molecules of $(CH_2Cl)_2NNO_2$ and $CH_3(CH_2=CH)$. $.NNO_2$ (Table 13). For comparison, Table 13 also gives the parameters of the $(CH_3)_2NNO_2$ and $(CH_2Cl)CH_3NNO_2$ molecules.

In all these molecules the effective configuration of the amine nitrogen atom is planar. The CNC angle in these molecules is much larger than that in alkylamines. The influence of the Cl atom of the chloromethyl groups in $(CH_2Cl)_2NNO_2$ and $(CH_2Cl)CH_3NNO_2$ on the nitroamine fragment is slight.

In the examination of the conformation of these molecules, the following should be noted. In the $(CH_2Cl)CH_3NNO_2$ molecule, the chloromethyl group is oriented in such a way that the ClCN plane is approximately perpendicular to the CNC plane. The same orientation of the CH_2Cl group is observed in the $(CH_2Cl)_2NNO_2$ molecule, and the C–Cl bonds are on different sides of the C_2NNO_2 plane. For the $CH_3(CH_2=CH)NNO_2$ molecule, the most probable conformation is that with the *trans*-arrangement of the NO_2 and $CH=CH_2$ groups. In this molecule, conjugation between the vinyl and nitroamine fragments apparently does not influence the geometric parameters.

Until recently there were no published data on the structure of cyclic nitramines in the gas phase. Electron diffraction data have now been obtained on the structure of 1,3,5-trinitro-1,3,5-triazacyclohexane [$(CH_2NNO_2)_3$, RDX], 1,3-dinitro-1,3-diazacyclopentane [$CH_2(CH_2NNO_2)_2$, DDCP], and N-nitropyrrolidine [$(CH_2)_4NNO_2$, NP].[144] These molecules are of interest since in their five- and six-membered rings the possibilities for change in the endocyclic angles are limited, and this may lead to appreciable deviation from the planar bond configuration of the amine nitrogen atom. The actual conformation of the rings is also of interest.

The results (Table 14) show that the six-membered ring in the RDX molecule has the "chair" conformation with the nitro-groups in the axial position. The assumed C_3 symmetry is consistent with the experimental data.

Table 14. Structural parameters of cyclic N-nitramines.[144]

Parameters	RDX	DDCP	NP
Bond lengths, r_g, Å			
C–N	1.464(6)	1.483(8)	1.477(8)
N–N	1.413(5)	1.393(8)	1.363(4)
N=O	1.213(2)	1.226(2)	1.225(2)
Angles, °			
CNC	123.7(6)	109.7(17)	110.3(14)
NNC	116.3(5)	114.8(8)	116.0(11)
Σ_N^*	356(3)	339.3	342.3
NCN	109.4(6)	109.7(17)	—
NCC	—	100.2(24)	99.6(4)
ONO	125.5(10)	128.2(18)	126.3(19)

*Sum of the valence angles at the nitrogen atom.

The five-membered ring in DDCP has the "half-chair" conformation (assuming C_2 symmetry for the molecule), and that in NP has the "envelope" conformation. In both molecules (DDCP and NP) the nitro-groups are in the equatorial positions. The angles of displacement of the N–N bond from the CNC plane vary from ~20° in RDX to ~40° in DDCP and NP.

Comparison of the principal geometric parameters of the cyclic nitramines studied and of dimethylnitramine shows that the CNN angles in all four molecules are the same within the experimental error. At the same time the CNC angle in RDX is slightly smaller than the corresponding angle in $(CH_3)_2NNO_2$, and those in DDCP and NP show an even sharper decrease. This leads to a change in the bond configuration of the amine nitrogen atom from almost planar in dimethylnitramine to pyramidal in the five-membered cyclic molecules of DDCP and NP. The RDX molecule occupies an intermediate position in this series.

In the cyclic nitramines studied, no increase in the N–N bond length with increase in the pyramidal nature of the bond configuration of the nitrogen atom is observed.

3. O-Nitrates (O-nitro-compounds)

The molecular structures of O-nitro-compounds in the gas phase have been less extensively studied than those of C- and N-nitro-compounds. The geometric parameters of the $HONO_2$, O_2NONO_2, CH_3ONO_2, and $C_2H_5ONO_2$ molecules are given in Table 15.

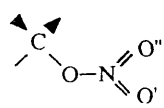
A difference in the parameters is observed only for the N_2O_5 molecule. In this molecule, the two NO_2 groups joined through the central oxygen atom undergo twisting vibrations of large amplitude. The potential energy minimum corresponds to equal torsional angles $\tau_1 = \tau_2 = 30°$ (measured from the planar conformation). The torsional movements are correlated so that an increase in one of the angles τ is accompanied by a decrease in the other.

Table 15. Geometric parameters of the O-nitro-compounds $XONO_2$ (X = H, NO_2, CH_3, C_2H_5).

Parameter	$HONO_2$	O_2NONO_2	CH_3ONO_2	$CH_3CH_2ONO_2$		
	MW, r_0 (Ref.145)	GE, r_α (Ref.146)	MW, r_s (Ref.147)	GE, r_g (Ref.148)	NC (Ref.148)*	MB (Ref.149)**
Bond lengths,						
C–O	–	–	1.437(5)	1.444(4)	1.447	1.430
N–C	–	–	–	1.520(4)	1.512	1.528
N–O	1.406(3)	1.492(4)***	1.402(1)	1.406(4)	1.412	1.407
N=O′	1.203(3)	1.183(2)***	1.208(5)	1.208(3)***	1.219	
N=O″	1.210(3)		1.205(5)		1.224	1.215
Valence angles, °						
XON (X=H, N, C)	101.9(10)	111.8(6)	112.7(3)	113.0(6)	113.2	111.0
O=N=O	130.0	133.3(6)***	129.5(5)	129.6(17)	129.9	131.0
O–N=O′	113.9(3)	113.4(4)***	112.4(3)	112.2(10)	112.6	111.0
O–N=O″	116.1(3)		118.1(3)	118.2(7)	117.5	118.0
CCO	–	–	–	106.0(10)	104.7	109.5

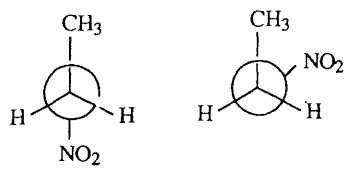
**Ab initio* calculation, MP2/6-31GF*.
**Assumed structure.
***The average value is given.

The nitric acid molecule is planar. In methyl and ethyl nitrates, the core also has a planar structure:



In $HONO_2$, CH_3ONO_2, and $C_2H_5ONO_2$ the valence angles O–N=O are different; the angle O–N=O″ is larger than the angle O–N=O′. In methyl and ethyl nitrates the difference between these angles is 6°.

The structure of ethyl nitrate in the gas phase has been studied by gas-phase electron diffraction and microwave, infrared, and Raman spectroscopy. The data obtained by all these methods show that ethyl nitrate is a mixture of two rotational forms (*trans* and *gauche*), if rotation about the C–O bond is considered; the *trans*-form is more stable, by ~0.6 kcal mol^{-1}.



According to GE data, the concentration of the *gauche*-form is about 20%. The angle of rotation about the C–O bond in this form is about 100° (if the angle of rotation for the *trans*-form is taken as 0°).[148]

A separate group of O-nitro-compounds is formed by the metal nitrates. The monovalent metal nitrates MNO_3 (M = Cs, Rb, Tl) (Table 16) in the gas phase contain a planar bidentate NO_3 group, and the metal atom lies on the bisector of the angle O(1)NO(1′):

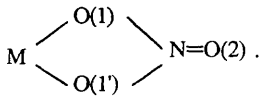


Table 16. Geometric parameters of metal nitrates.

Compound	N–O(1), Å	N=O(2), Å	O(1)NO(1′), °	Refs.
$RbNO_3$	1.252(3)*		115(6)	[150a]
$CsNO_3$	1.252(5)*		117(5)	[150b]
$TlNO_3$	1.254(8)*		114.(5)	[150c]
$Cu(NO_3)_2$	1.298(3)	1.205(5)	113.5(6)	[151]
$Zr(NO_3)_4$	1.284(7)	1.184(10)	—	[152]
$Sn(NO_3)_4$	1.281(5)	1.179(8)	—	[152]
$CrO_2(NO_3)_2$	1.254(4)	1.193(4)	112.2(4)	[153]
$Be_4O(NO_3)_6$	1.298(4)	1.185(5)	117.0(9)	[154]

*The average of the N–O(1) and N=O(2) bond lengths is given.

The $MONO_2$ fragment is also planar in the nitrates of copper $Cu(NO_3)_2$, zirconium $Zr(NO_3)_4$, and tin $Sn(NO_3)_4$. In $Cu(NO_3)_2$ the copper atom lies in the plane of the square formed by the oxygen atoms of two bidentate NO_3 groups. The ligand atoms round the central atom in Zr and Sn tetranitrates give a distorted tetrahedral configuration.

In the $CrO_2(NO_3)_2$ molecule (C_2 symmetry) the coordination of the Cr atom is best described as a distorted octahedron, since the bidentate nitrate groups are joined asymmetrically to the Cr atom. The Cr–O–NO_2 group is slightly non-planar, with a dihedral angle between the CrON and NO_2 planes of ~16(3)°. There is apparently weak torsional motion round any of the single bonds in the –O–NO_2 groups.

The structure of $Be_4O(NO_3)_6$ deviates slightly from T_d symmetry, probably as a result of a complex intramolecular motion.

In the molecules of $Cu(NO_3)_2$, $Zr(NO_3)_4$, $Sn(NO_3)_4$, $CrO_2(NO_3)_2$, and $Be_4O(NO_3)_6$, the N–O bonds are non-equivalent; the N=O(2) bond is ~0.1 Å shorter than N–O(1). For the monovalent metal nitrates, only the average N–O bond length has been obtained. The O(1)NO(1′) valence angles in the ring are smaller than 120°.

V. Complex compounds of nitrogen

A large amount of interesting material has now been accumulated on the structure of donor–acceptor compounds of nitrogen in the gas phase. A large proportion of the structural data relates to adducts of the type $Y_3E{\leftarrow}NX_3$, where E is a group III element (B, Al, Ga). The experimental data for pyridine-containing complexes in the gas phase are fundamentally new, particularly in view of their low stability. Dimeric and trimeric amino-compounds of group III elements, lithium, and tin(II), and various derivatives of the anthrane type with an intramolecular donor–acceptor bond, have also been examined.

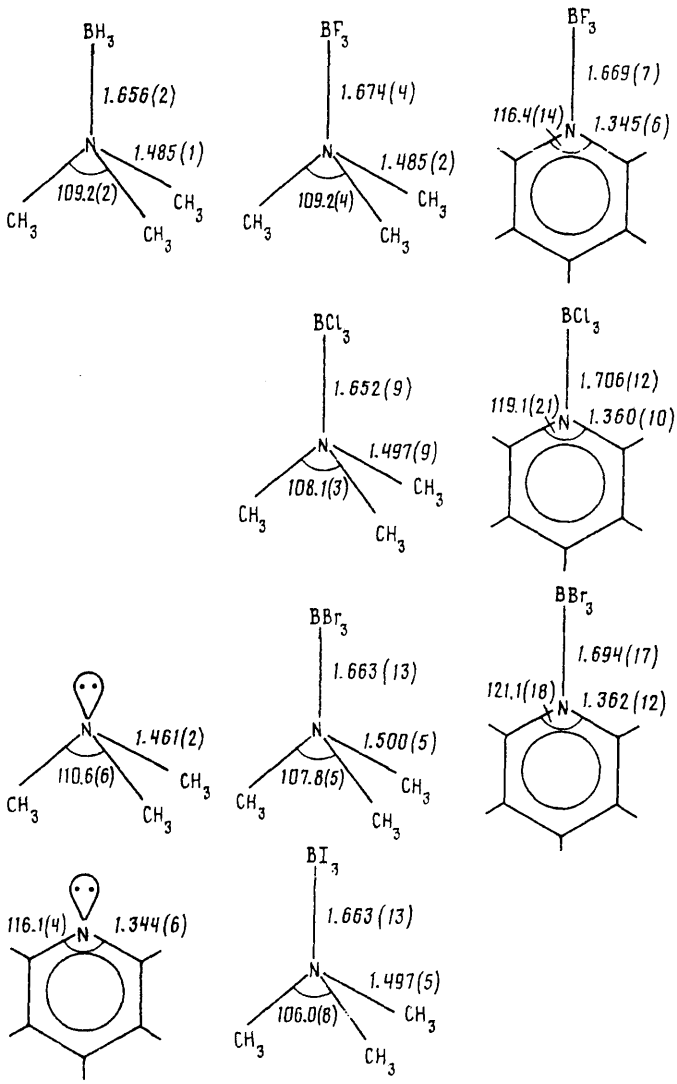


Figure 5. Comparison of the parameters of the r_g-structure of the free molecules of trimethylamine[13] and pyridine[169] and their boron adducts (see Table 17).

A new approach to the classification of the donor–acceptor bond as a unique type of bond has been proposed by Haaland,[7] who showed from an analysis of various physicochemical properties (including the geometric structure) that the donor–acceptor bond differs from a simple covalent bond.

Table 17. Adducts containing a nitrogen–boron bond.

Molecule	Parameters	Bond lengths, Å		Valence angles, °				Method	Refs.
		B–N	N–X	BNX	XNX	NBY	YBY		
$H_3B{\cdot}NH_3$	r_s	1.6576(16)	1.014(2)	110.28(14)	108.65(14)	104.69(11)	113.80(11)	MW	[155]
	r_0	1.6722(5)	1.0136(36)	109.85(23)	109.09(23)	104.53(15)	113.93(15)	MW	[155]
$H_3B{\cdot}NMe_3$	r_s	1.638(10)	1.483(10)	107.9(10)		105.32(16)		MW	[156, 157]
	r_α^0	1.651(2)	1.482(1)		109.4(2)		113.4(4)		
	r_g	1.656(2)	1.485(1)		109.2(2)		112.8(4)	GE+MW	[158]
$Me_3B{\cdot}NMe_3$	r_0	1.698*	1.470(1)	111.6(5)		108.0(15)		MW	[159]
$FH_2B{\cdot}NMe_3$	r_0	1.633(6)	1.492(9)	109.5(10)		105.3(5)		MW	[160]
			1.494(16)	(for CH_3 in the NBF plane)					
				110.1(5)		104.7(7)			
$F_3B{\cdot}NMe_3$	r_0	1.636(4)	1.476(5)	110.4(3)	108.6(2)	106.3(2)	112.4(2)	MW	[161]
	r_α^0	1.669(4)	1.481(2)		109.4(4)		113.1(3)	GE+MW	[162]
	r_g	1.674(4)	1.485(2)		109.2(4)		112.6(3)	GE+MW	[162]
	r_a	1.664(11)	1.468(10)		108.5(7)		113.1(9)	GE	[163,164]
$Cl_3B{\cdot}NMe_3$	r_α	1.650(9)	1.491(3)		108.3(3)		111.1(2)	GE	[165]
	r_g	1.652(9)	1.497(3)		108.1(3)		110.9(2)	GE	[165]
	r_a	1.659(6)	1.495(4)		108.7(5)		110.8(3)	GE	[163, 164]
$Br_3B{\cdot}NMe_3$	r_α	1.656(13)	1.483(5)		107.9(5)		110.4(3)	GE	[165]
	r_g	1.663(13)	1.500(5)		107.8(5)		110.3(3)	GE	[165]
$I_3B{\cdot}NMe_3$	r_α	1.658(13)	1.488(5)		106.2(8)		108.9(4)	GE	[166]
	r_g	1.663(13)	1.497(5)		106.0(8)		108.6(4)	GE	[166]
$F_3B{\cdot}$	r_g	1.669(7)	1.345(6)	r_a 116.4(14)			113.3(4)	GE	[167,168]
$Cl_3B{\cdot}$	r_g	1.706(12)	1.360(10)	r_a 119.1(21)			112.5(3)	GE	[168]
$Br_3B{\cdot}$	r_g	1.694(17)	1.362(12)	r_a 121.1(18)			111.9(3)	GE	[168]

1. Adducts containing a nitrogen–boron bond

Table 17 gives the parameters of complexes $Y_3B.NX_3$ studied in the gas phase by microwave spectroscopy (r_s, r_0) and electron diffraction (r_α^0, r_α, r_g, r_a) and by both methods. The differences between the data obtained by these two methods may be extremely large, because of the difference in the physical significance of the parameters obtained. Thus for one of the most interesting parameters, namely the NB bond length, the differences reach 0.03 Å, corresponding to the level of structural effects. In the subsequent analysis, therefore, we shall try to use comparable quantities.

When an adduct is formed, the lone pair of electrons of the nitrogen atom is partly transferred to the unoccupied orbital of the boron atom. This is accompanied by changes in the geometry of the original monomers, and the changes in the molecular parameters of the acceptor BY_3 are much greater than those for the donor NX_3.[6] We are interested primarily in the structural characteristics of the NX_3 fragment. The comparison in Fig. 5 shows that the participation of the trimethylamine molecule in complex formation as a donor leads to a significant increase in the length of the N–C bonds and a decrease in the CNC valence angles. In the adducts with boron trihalides these changes increase in the order

$$F_3B \cdot NMe_3 < Cl_3B \cdot NMe_3 < Br_3B \cdot NMe_3 < I_3B \cdot NMe_3.$$

A similar trend is observed in the change in the parameters of the nitrogen fragment of the pyridine ring on complex formation, the only but extremely significant difference being that the intra-cyclic CNC valence angle does not decrease, but increases.

The replacement of some substituents on the boron atom by others, however, does not have such a clear and systematic influence on the N–B bond length (Figs. 5 and 6). The N–B bond in the adduct $F_3B.NMe_3$ is slightly longer, whereas that in the corresponding adduct with pyridine is shorter, than those in the other members of the corresponding series of derivatives.

Although microwave studies have not given an accurate value for the N–B bond length in the adduct $Me_3B.NMe_3$ (indirect estimates give the value 1.70–1.80 Å [6]), the available data suggest that the methyl substituents in the amino-group lead to a decrease in the N–B bond length, whereas the same substituents in the acceptor fragment lead to an increase (Table 17).

The geometric parameters of adducts of the type $Y_3.B.NMe_3$ in the crystalline phase differ considerably from those in the gas phase. The B–Y and N–C bond lengths become larger, and the YBY angles and, which is most important, the N–B bond lengths are smaller than those in the gas phase. For the N–B bond the difference reaches 0.05–0.10 Å.[6] This shows that in the crystal the degree of charge transfer increases considerably, and the N–B donor–acceptor bond becomes stronger. The molecules of the adducts $Y_3B.NX_3$ have the staggered conformation (C_{3v} symmetry) in both phases.

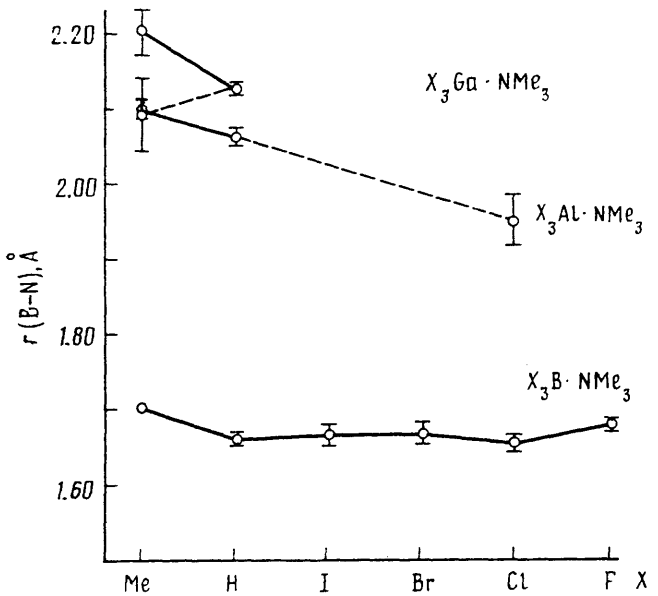


Figure 6. Influence of substitution in the acceptor group of the adducts $X_3E.NMe_3$ on the E–N bond lengths (E = B, Al, Ga; X = Me, H, I, Br, Cl, F).

The determination of the heights of the potential barriers is of considerable interest in relation to possible internal rotation about the N–B bond. Apart from anything else, these parameters are important for characterising the strength of the dative bond. The heights of the potential barriers in $Y_3B.NX_3$ cannot be estimated from the infrared and Raman spectra, however, since the twisting vibrations are not active in these spectra. The possibility of obtaining the heights of the potential barriers from an analysis of electron diffraction data using available spectral information is therefore of interest. The results of this analysis, and some microwave data, are given in Table 18.

Table 18 shows that the barriers to rotation are apparently higher in the $Cl_3B.NMe_3$ and $Br_3B.NMe_3$ molecules than in the other molecules, although the accuracy of the determination is low. The change in the height of the barriers, and also the change in the N–B bond length, most probably depend not only on the electronegativity of the substituents but also on steric factors.

2. Adducts containing nitrogen–aluminium, nitrogen–gallium, and nitrogen–halogen bonds

The structural parameters of donor–acceptor complexes containing N–Al and N–Ga bonds (mainly from electron diffraction data) are given in Table 19. They reflect more clearly the regularities established above from the analysis of the parameters of their boron analogues.

Table 18. Barriers to rotation about the dative bond N→B in the adducts $Y_3B.NX_3$.

Molecule	Height of the barrier to rotation, kcal mol^{-1}	Method	Refs.
$H_3B.NH_3$	2.03	MW	[155]
$H_3B.NMe_3$	3.4	MW	[157]
	>5	GE	[158]
$F_3B.NMe_3$	4.3(3)	GE	[162]
	6.2	GE	[164]
$Cl_3B.NMe_3$	18	GE	[165]
	13.7	GE	[164]
$Br_3B.NMe_3$	12	GE	[165]
$I_3B.NMe_3$	3.5	GE	[166]

Table 19 clearly shows the tendency for the N–Al bond length to decrease with increase in the electronegativity of the ligands on the Al atom in the order Me < H < Cl (see Fig. 6). Increase in the acceptor power of the aluminium fragment also leads to an increase in the N–C bond lengths in the donor fragment NMe_3. In turn, increase in the electronegativity of the substituent on the N atom (Me < H) is accompanied by an increase in the N–Al bond length, that is by a decrease in its strength as a result of the decrease in the donor power of the nitrogen fragment.

A characteristic feature of adducts containing N–Al and N–Ga bonds, distinguishing them from the corresponding adducts containing an N–B bond, is that complex formation leads to an increase in the CNC valence angles of the donor fragment NMe_3 (see Fig. 5). The reason apparently is that the overall increase in the N–Al and N–Ga bond lengths compared with the N–B bond lengths (by ~0.3–0.5 Å) leads firstly to a decrease in the strength of the repulsion between the bonding electron pairs of the donor and the electrons involved in the formation of the coordinate bond, and secondly to a decrease in the steric interactions between the ligands of the donor and the acceptor. In the boron complexes these factors have a more significant influence not only on the N–B bond lengths and the CNC valence angles but also on the parameters of the potential functions of the internal rotation. These interactions may determine the differences in the structural regularities examined above for the boron–nitrogen adducts with trimethylamine and pyridine (see Fig. 5).

The only results not agreeing with the other data examined in this section are those obtained in the study of the $Me_3Ga.NMe_3$ molecule.[180,181] In this compound the two key parameters characterising the structure of the adduct {the N–Ga bond length

Table 19. Adducts containing nitrogen–aluminium, nitrogen–gallium, and nitrogen–halogen bonds.

Molecule	Parameter	Bond lengths, Å		Valence angles, °				Method	Refs.
		E–N	N–X	ENX	XNX	NEY	YEY		
$Cl_3Al{\cdot}NH_3$	r_a	1.996(19)				101.2	116.35(40)	GE	[170, 171]
$Br_3Al{\cdot}NH_3$	r_a	1.997(19)	1.057(33)		114.5(40)	101.5	115.7(3)	GE	[171, 172]
$H_3Al{\cdot}NMe_3$	r_a	2.063(8)	1.476(3)	109.0(3)		104.3(11)	114.1	GE	[173]
$Me_3Al{\cdot}NMe_3$	r_a	2.099(10)	1.474(3)	109.3(4)		102.3(3)	115.6	GE	[174]
$Cl_3Al{\cdot}NMe_3$	r_a	1.945(35)	1.516(12)	112.6(15)		104.9(7)	113.6	GE	[175]
$H_3Al{\cdot}2NMe_3$	r_a	2.19(2)	1.483(5)	106.5(8)	112.6(8)			GE	[176]
$Cl_3Ga{\cdot}NH_3$	r_a	2.057(11)	1.024(12)		114.3(12)	101.1	116.4(3)	GE	[171, 177]
$Br_3Ga{\cdot}NH_3$	r_a	2.081(23)	1.061(33)		115.6(41)	100.8	116.1(3)	GE	[171, 172]
$H_3Ga{\cdot}NMe_3$	r_0	2.111(2)	1.476(20)	110(1)		102*		MW	[178]
	r_a	2.124(7)	1.482(5)	109.9(5)		102*		GE	[179]
$Me_3Ga{\cdot}NMe_3$	r_a	2.09(5)	1.484(8)	114.5(31)	104.0	99.3(22)	117.4	GE	[180]
	r_a	2.20(3)	1.485(4)		109.6	101	116.7	GE	[181]
$Br_2{\cdot}NMe_3$	r_a	1.98(3)	1.67(2)		104(2)	112(3)	—	GE	[182]
$CF_3I{\cdot}NMe_3$	r_0	2.93(2)						MW	[183]

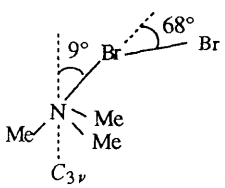
*Accepted value.

[2.09(5) Å] and the CNC valence angle (104.0°)} clearly do not correspond to the regularities examined above. Without going into details of the electron diffraction analysis, we may note that the deviation in this case is due to the unreliability of the determinaiton of the N–Ga bond length. The complexities of its determination were related to two factors: 1, the large amplitude of the vibrations for this distance, characteristic of a donor–acceptor bond, and 2, the possible decomposition of the substance on heating during the electron diffraction experiment, since dative bonds become weaker on going to the elements of the lower part of group III.[6]

An interesting feature is that the summary of the preliminary results of the structural analysis[181] gave what are apparently better justified values of these parameters, namely r(N–Ga) = 2.20(3) Å and angle CNC = 109.6°. In the crysalaline Al and Ga adducts, the molecular core also has C_{3v} symmetry, and the N–Al and N–Ga bonds, like the N–B bonds, are ~0.1 Å shorter than those in the molecules in the gas phase,[6] corresponding to an increase in the extent of charge transfer.

In the study of the structure of the double adduct $H_3Al.2NMe_3$ in the gas phase it was not possible to obtain information on the form of the molecule, apparently because of its partial dissociation. The value found for the N–Al bond length is more than 0.1 Å greater than that for the 1 : 1 adduct.

There are as yet only isolated data on adducts of trimethylamine containing a halogen atom as acceptor. The conformation of the Br_2NMe_3 molecule in the gas phase differs considerably from that found in the crystal for I_2NMe_3 (C_{3v} symmetry). The Br atom closest to the nitrogen atom deviates by 9(2)° from the three-fold axis of the NMe_3 fragment. The second Br atom deviates from the N–Br bond by a further 68(3)°.



3. Dimers and trimers of amino-compounds of various non-transition elements.

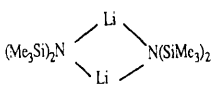
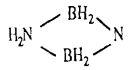
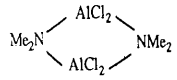
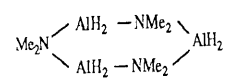
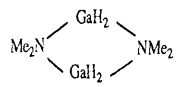
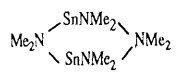
Anthrane compounds

Dative bonds involving the nitrogen atom as donor stabilise the molecular structure of the derivatives of various non-transition elements.

These structures include *n*-meric amine systems. The structures of some of the compounds have been studied in the gas phase (Table 20).

Monomeric lithium amines $LiNR_2$ with a three-coordinate nitrogen atom are extremely rare. Most lithium amines form *n*-meric cyclic systems in which the nearest lithium atoms are joined by amide bridges with four-coordinate nitrogen. Crystallographic data indicate that the $(LiN)_2$, $(LiN)_3$, and $(LiN)_4$ rings are invariably planar.[184,185]

Table 20. Dimers and trimers of the amino-derivatives of various non-transition elements.

Molecule	Conformation of the ring	Parameter	Bond lengths, Å		Valence angles, °			Method	Refs.
			E–N	N–X	ENE	NEN	XNX		
	planar	r_a	1.99(3)	1.712(7)	80(3)	100(3)	129.8(17)	GE	[184,185]
	ditto	r_s	1.558(1)	1.005(6) (r_0)	75.9(1)	97.1(6)	111.0(12) (r_0)	MW	[186]
	" "	r_a	1.961(6)	1.479(4)	92.5(4)	87.5(4)	101.3(18)	GE	[187]
	"chair"	r_a	1.970(6)	1.486(9)	113.5(27)	95(2)	112.0(21)	GE	[188]
	planar	r_a	2.027(4)	1.463(13)	90.6(8)	89.4(8)	109.6(16)	GE	[189]
	»	r_g	2.293(5)	1.483(3)	96.1(5)	83.9		GE	[60]

The only electron diffraction data for dimeric $[LiN(SiMe_3)_2]_2$ in the gas phase also indicate a planar cyclic system. The molecule as a whole has D_2 symmetry. The cores of the bridging ligands $N(SiMe_3)_2$ lie in a plane perpendicular to the plane of the ring, and the $SiMe_3$ groups of each of the ligands are arranged in a staggered conformation relative to one another. An interesting feature is that the Li–N bond length found in this case is indistinguishable from the corresponding distances in the crystalline trimeric and tetrameric lithium amines (1.97–2.00 Å [184,185]), whereas the Li–N bonds in the crystalline dimers studied show a tendency to increase, apparently as a result of the presence of the additional ligands on the Li atom.

Comparison of the electron diffraction data with the X-ray diffraction also shows that the intra-ring valence angles at the Li atom are influenced more strongly than the angles at the N atom by the dimensions of the ring. Thus the LiNLi angles change from 80° to 100° on going from the dimers to the trimers, whereas the NLiN angles change from 100° to ~170°.[184,185]

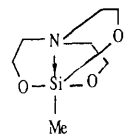
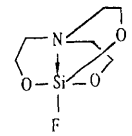
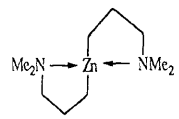
A consequence of the tetrahedral coordination of the N atom in the dimer $[LiN(SiMe_3)_2]_2$ is the slight decrease in the N–Si bond length compared with that in the $HN(SiMe_3)_2$ molecule [r_a 1.738(5) Å [64]]. The SiNSi angle in the dimeric Li amine is practically the same as the corresponding valence angle in $HN(SiMe_3)_2$ [131.3(15)° [64]].

For all the elments of the boron sub-group, the cyclic dimers $(Me_2NEH_2)_2$ are more characteristic than the monomeric structures $Me_2N{=}EH_2$ containing a multiple bond. This is due to the greater stability of the dimeric form. Experimental data obtained by various methods show that structures in which the NMe_2 groups form bridges producing a four-membered N_2E_2 ring exist in the gas phase, in solution, and in the crystalline phase.

The electron diffraction data for the Al and Ga derivatives (Table 20) are consistent with a molecular model having a planar ring and effective D_{2h} symmetry of the core $(C_2NEH_2)_2$. Since the nitrogen atoms in these compounds become four-coordinate by using their lone pair of electrons for bond formation, it is of interest to compare the E–N bond lengths in the four-membered rings and in the adducts $Y_3E.NX_3$ (see above). The comparison shows that the change to the cyclic system and the changes in the coordination spheres of the atoms lead to an appreciable decrease in the E–N bond lengths. Thus the B–N bond in aminodiborane $H_2N{\rightarrow}BH_2{-}H{\ldots}BH_2$ is ~0.1 Å shorter than in any of the adducts $Y_3B.NX_3$ studied. The Ga–N bond in the dimer $(Me_2NGaH_2)_2$ is ~0.1 Å shorter than that in the $H_3Ga.NMe_3$ molecule. The Al–N bond length in the four-membered ring of $(Me_2NAlCl_2)_2$ coincides (within the large error of the determination) with that found in the $Cl_3Al.NMe_3$ molecule, but is shorter than the dative bonds in other acyclic aminoalanes. The available X-ray diffraction data also indicate a decrease in the E–N bond lengths in the rings on going from the gas to the crystalline phase.[187,189]

The intra-ring valence angles at the Al and Ga atoms in the dimers $(Me_2NAlCl_2)_2$ and $(Me_2NGaH_2)_2$ being considered are only slightly smaller than the angles at the N atoms, so that the four-membered rings are practically square. In the six-membered ring of the aminoalane $(Me_2NAlH_2)_3$ the valence angles at the N atoms are

Table 21. Electron diffraction data for compounds of the anthrane type.

Molecule	Parameter	Bond lengths, Å			Valence angles, °		Refs.
		E–N	E–R	N–C	ENC	NSiO NZnC	
	r_g	2.453(17)	1.853(15)	1.458(6)	103.4(16)	79.0(15)	[190]
	r_g	2.324(14)	1.568(6)	1.481(8)	103.2(4)	81.3(3)	[191]
	r_a	2.392(15)	1.991(6)	1.467(3)	101(2)	82(2)	[192]

increased to a much greater extent than the angles at the Al atoms. In these rings the steric repulsion between the Al or Ga atoms is apparently greater than the interaction between the N atoms. The valence angles at the latter are greater than those found in the dimeric Li amine or aminodiborane.

Studies of trimeric aminoalanes in the gas phase (Table 19) and in the crystals[188] indicate that the valence angles at the nitrogen atoms are more easily altered parameters of the ring than the angles at the Al atom. Electron diffraction data for the $(Me_2NAlH_2)_3$ molecule show that the six-membered $(AlN)_3$ ring in it is non-planar and has the "chair" conformation (C_{3v} symmetry). Although the Al–N bond lengths found are only slightly longer than those in the chloro-substituted dimer $(Me_2NAlCl_2)_2$, the direction of the change corresponds to the influence of substituents on the E–N bond lengths observed for adducts of the type $Y_3E.NX_3$. As in the case of the dimers examined above, the Al–N bond in $(Me_2NAlH_2)_3$ is ~0.1 Å shorter than that in the adduct $H_3Al.NMe_3$. Moreover, the value obtained is 0.03–0.05 Å larger than that in various crystalline trimeric aminoalanes.[188]

The bis(dimethylamino)tin(II) dimer is less stable than the corresponding monomer (see section II). A study of this compound in the gas phase showed that its concentration in the mixture is 24 ± 1%. The Sn–N bond length in the cyclic dimer is 0.3 Å larger than that in the monomer. The four-membered $(Sn-N)_2$ ring is planar, and, as in the case of the dimeric amines of the boron sub-group, the intra-ring valence angles at the nitrogen atom are slightly greater than the angles at the tin atoms. An X-ray diffraction study, carried out in parallel with the electron diffraction study, showed that the structures of the dimer in the gas phase and in the crystal differ considerably.

The study of the structure of compounds of the anthrane type in the gas phase is also of considerable interest. At the present time, data of this kind are available for Me- and F-substituted silatranes and a chelate spiro-structure with two dative N→Zn bonds (Table 21).

Silatranes are biologically active molecules in which the properties of the substituent on the Si atom have a marked influence on the strength of the dative bond. This is confirmed by electron diffraction data. Thus electronegative substituents (for example the F atom) lead to a decrease in the N→Si bond length of more than 0.1 Å, compared with the Me-derivative. The N–C bonds in the ring systems of the F-silatrane become longer by more than 0.02 Å, as in the adducts $Y_3E.NMe_3$. The identical donor–acceptor nature of the interaction of the nitrogen atom in the silatranes and in the other classes of compound examined in this section is also revealed by the decrease in the N→Si bond length on going from the gas to the crystalline phase,[193] which is more clearly defined in the silatranes (~0.3 Å). Simultaneously, the length of the bond formed by the Si atom with the ring substituent increases by 0.02–0.05 Å.

The donor–acceptor interaction of the Zn atom with the amine nitrogen atom in its diorgano-derivatives is much weaker than that in the adducts of boron, aluminium, or gallium. Thus according to electron diffraction data, the monoligand complex $Me_2Zn.NMe_3$, which exists in the liquid phase, is completely dissociated in the gas phase even at 30 °C to $ZnMe_2$ and NMe_3,[192] and the diligand complex $Me_2Zn(NMe_3)_2$ is not known.

Nevertheless, N→Zn dative bonds are fairly stable in diorgano-derivatives of Zn with N donor atoms in the δ- or ε-positions of the substituent chain, in particular in the $Zn[(CH_2)_3NMe_2]_2$ molecule. The $(CH_2)_3NMe_2$ substituents bend to form rings, bringing the N atoms closer to the Zn atom, to give additional intramolecular coordination of the N atoms to the Zn atom with the production of a chelate structure.

A possible explanation for the instablity of the simplest adducts of Zn examined above may be that the increase in entropy associated with their dissociation plays a more significant role than the energy effect of complex formation. In contrast to this, on intramolecular coordination the entropy changes are minimal, and even a relatively low energy of complex formation is sufficient to stabilise the donor–acceptor bonds.

The weakness of the dative interaction of the N and Zn atoms is revealed by the increase in the N→Zn bond length by 0.6 Å compared with the length of the Zn—N covalent bond in the monomeric amine $Zn[N(SiMe_3)_2]_2$ (see Table 3). This is also indicated by the high value of the mean amplitude of the vibrations of the N→Zn bond [0.17(3) Å]; the amplitude of the vibrations of the Zn—C bond in the chelate ring system is only 0.073(6) Å. The transfer of the Zn-derivative from the gas to the crystalline phase is accompanied by a decrease in the N→Zn bond length (by 0.085 Å)[192] which although not so great as that in silatranes is nevertheless considerable. The bond lengths and valence angles in the five-membered rings of the chelate system of $Zn[(CH_2)_3NMe_2]_2$ are very close to those found in silatranes (Table 21).

VI. Summary

Systematic experimental studies of series of compounds are required to determine the relationships between the geometry of molecules and their chemical properties. Unfortunately, complete systems of data often are not available. This is due both to problems of synthesis and to the limited possibilities provided by the methods of studying structure. In these cases the use of non-empirical quantum-chemical calculations at a high level becomes extremely effective.

The structural data given and the regularities found reveal the important role of steric repulsion in compounds with bulky substituents. This conclusion is naturally very simple. In some cases, however, it is difficult to distinguish an interaction having a decisive influence on the configuration of a molecule. Thus the CNC valence angle at the amine nitrogen atom in methyl- and chloro-substituted N-nitramines is appreciably greater (by ~15°) than that in $(CH_3)_3N$ (~110°). At the same time, in metal amines this angle is not increased (~111°), although the configuration of the bonds formed by the nitrogen atom in these compounds, as in the Me-derivatives of N-nitramine, is planar or close to planar.

In di-imides with the cumulene bond system $\diagdown N=C=N\diagup$ the expected orthogonal configuration of the bonds formed by the nitrogen atom with substituents is not observed. This emphasises the important role of the interaction of non-bonded atoms (even at appreciable distances).

Data on nitro-aromatic derivatives and N-nitramines indicate that conjugation has an extremely limited influence on the configuration of the molecule, since the $C-NO_2$ bond length is practically independent of the angle of rotation of the NO_2 group about the C—N bond. The same appreciable pyramidal character of the bonds formed by the amine nitrogen atom in pyrroles does not change in the N—N bond length.

In complex compounds containing a "pure" donor—acceptor bond involving the nitrogen atom, the stereochemistry of the donor and acceptor fragments is consistent with Gillespie's ideas. The almost square structure of the planar four-membered rings in the dimeric complexes of metal amino-derivatives is difficult to explain, however, because of the differences in the elastic constants of the valence angles at the atoms of nitrogen and the acceptor metal.

References

1. L V Vilkov, L S Khaikin, I I Nazarenko, et al. *Sovremennye Problemy Fizicheskoi Khimii* (Present-Day Problems in Phsyical Chemistry) (Edited by Ya I Gerasimov, M I Shakhparonov) Vol. 7, Izd. Mosk. Gos. Univ., Moscow, 1973, p. 377
2. L V Vilkov, V S Mastryukov, N I Sadova *Opredelenie Geometricheskogo Stroeniya Svobodnykh Molekul* (The Determination of the Geometric Structure of Free Molecules), Khimiya, Leningrad, 1978, 224 pp
3. L V Vilkov, L S Khaikin *Topics in Current Chemistry. Vol. 53. Gas-Phase Electron Diffraction*, Springer-Verlag, Berlin, Heidelberg, New York, 1975, pp 25—70
4. L V Vilkov, V S Mastryukov, N I Sadova *Determination of the Geometrical Structure of Free Molecules*, Mir, Moscow, 1983, 280 pp
5. L V Vilkov, N I Sadova *Stereochemical Applications of Gas-Phase Electron Diffraction. Pt. B* (Edited by I Hargittai, M Hargittai), VCH Publishing, New York, 1988, pp 35—92
6. M Hargittai, I Hargittai *Vapour-Phase Molecular Geometry of Coordination Compounds* (Translated into Russian), Mir, Moscow, 1976, 248 pp
7. A Haaland *Angew. Chem. Int. Ed. Engl.*, 1989, **28** 992—1007
8. J E Boggs, L S Khaikin, V I Perevozchikov, et al. *Molecules in Natural Science and Medicine. An Encomium for Linus Pauling. Pt. 1. Molecular Structure* (Edited by Z B Maksic, M Eckert-Maksic), Ellis Harwood Ltd., New York, etc., 1991, p. 83
9. Landolt-Bornstein *Numerical Data and Function Relationships in Science and Technology. New Series. Group II. Vol. 15/7). Structure Data of Free Polyatomic Molecules* (Edited by K-H Hellwege, A M Hellwege), Springer-Verlag, Berlin, etc., 1987, 608 pp
10. T Iijima, H Jimbo, M Taguchi *J. Mol. Struct.*, 1986, **144**(3/4) 381
11. B Beagley, T G Hewitt *Trans. Faraday Soc.*, 1968, **64**(10) 2561
12. J E Wollrab, V W Laurie *J. Chem. Phys.*, 1968, **48** 5058
13. B Beagley, A R Medwid *J. Mol. Struct.*, 1977, **38** 229
14. H Bürger, H Niepel, G Pawelke, et al. *J. Mol. Struct.*, 1979, **54** 159
15. Y Hamada, M Tsuboi, K Yamanouchi, et al. *J. Mol. Struct.*, 1986, **146** 253
16. S Konaka, N Yanagihara *J. Mol. Struct.*, 1989, **196** 375; 1990, **222** 503
17. M Rall, M D Harmony, D A Cassada, et al. *J. Am. Chem. Soc.*, 1986, **108**(20) 6184
18. J H M Ter Brake, V Mom, F C Mijlhoff *J. Mol. Struct.*, 1980, **65** 303
19. H Van der Does, F C Mijlhoff, G A Rene *J. Mol. Struct.*, 1981, **74** 153
20. H Takeuchi, S Konaka, M Kimura *J. Mol. Struct.*, 1986, **146** 361
21. T Fjeldberg, M F Lappert, S J Smith *J. Mol. Struct.*, 1986, **140** 209
22. S Konaka, J Hirose, A Suwa, et al. *J. Mol. Struct.*, 1991, **244** 1
23. H G Mack, H Oberhammer *J. Mol. Struct.*, 1989, **197** 329
24. S C Mehrotra, L L Griffin, C O Britt, et al. *J. Mol. Spectrosc.*, 1977 **64**(2) 244
25. M Otake, C Matsumura, Y Morino *J. Mol. Spectrosc.*, 1968, **38**(3) 316
26. D Christen, R Minkwitz R Nass *J. Am. Chem. Soc.*, 1987, **109**(23) 7020

27. L V Vilkov, I I Nazarenko *Zh. Strukt. Khim.*, 1967, **8**(2) 346
28. H Oberhammer, H Guenther, H Bürger, et al. *J. Chem. Phys.*, 1982, **86**(5) 664
29. G Cazzoli, P G Favero, A Dal Borgo *J. Mol. Spectrosc.*, 1974, **50**(1–2) 82
30. H B Bürgi, D Stedman, L S Bartell *J. Mol. Struct.*, 1971, **10** 31
31. J R Durig, K K Chatterjee, N E Lindsay *J. Am. Chem. Soc.*, 1986, **108** 6903
32. W Caminati, R Cervellati, A M Mirri *J. Mol. Spectrosc.*, 1974, **51** 288
33. G Cazzoli, D G Lister, P G Favero *J. Mol. Spectrosc.*, 1972, **42**(2) 286
34. D G Lister, J K Tyler, J H Hoeg, et al. *J. Mol. Struct.*, 1974, **23**(2) 253
35. M Colapietro, A Domenicano, G Portalone, et al. *J. Phys. Chem.*, 1987, **91**(7) 1728
36. D Christen, D Damiani, D G Lister *J. Mol. Struct.*, 1977, **41**(2) 315
37. G Cazzoli, D Damiani, D G Lister *J. Chem. Soc. Faraday Trans., 1*, 1973, **69** 119
38. A Hastie, D G Lister, R L McNeil, et al. *J. Chem. Soc., Chem. Commun.*, 1970, 108
39. A Bouchy, G Roussy *J. Mol. Spectrosc.*, 1984, **108** 230
40. A Nonat, A Bouchy, G Roussy *J. Mol. Struct.*, 1983, **97** 83
41. A Nonat, A Bouchy, G Roussy *J. Mol. Struct.*, 1987, **116**(3/4) 227
42. R Cervellati, A Dal Borgo, F Scappini *J. Mol. Struct.*, 1979, **56**(1) 69
43. R Cervellati, G Corbelli, A Dal Borgo *J. Mol. Struct.*, 1981, **73** 31
44. R A Kydd, A R C Dunham *J. Mol. Struct.*, 1983, **98**(1/2) 39
45. R Cervellati, A Dal Borgo, D G Lister *J. Mol. Struct.*, 1982, **78**(3/4), 161; 1985, **122** 173
46. L V Vilkov, T P Timasheva *Dokl. Akad. Nauk SSSR*, 1965, **161**(2) 351
47. Y Sasaki, K Kimura, M Kubo *J. Chem. Phys.*, 1959, **31**(2) 477
48. V A Naumov *Dokl. Akad. Nauk SSSR*, 1966, **169**(4) 839
49. W Den Brinker, P A G Huisman, F C Mijlhoff *J. Mol. Struct.*, 1979, **54** 293
50. F J Lovas, F O Clark, E Tiemann *J. Chem. Phys.*, 1975, **62** 1925
51. V A Naumov, O N Kitaeva *Molekulyarnoe Stroenie Organicheskikh Soedinenii Kisloroda i Sery v Gazovoi Faze* (The Molecular Structure of Organic Compounds of Oxygen and Sulphur in the Gas Phase), Nauka, Moscow, 1990, 160 pp
52. A H Clark, A Haaland *Acta Chem. Scand.*, 1970, **24** 3024
53. T Fjeldberg, R A Andersen *J. Mol. Struct.*, 1984, **125** 287
54. A Haaland, K Hedberg, P P Power *Inorg. Chem.*, 1984, **23** 1972
55. E C Alyea, K J Fisher, T Fjeldberg *J. Mol. Struct.*, 1985, **127** 325
56. E C Alyea, K J Fisher, T Fjeldberg *J. Mol. Struct.*, 1985, **130** 263
57. R A Andersen, K Faegri, J C Green, et al. *Inorg. Chem.*, 1988, **27** 1782
58. T Fjeldberg, H Hope, M F Lappert, et al. *J. Chem. Soc., Chem. Commun.*, 1983, 639
59. M F Lappert, P P Power, M J Slade *J. Chem. Soc., Chem. Commun.*, 1979, 369
60. B Beagley, N G Scott, D Schmidling *J. Mol. Struct.*, 1990, **221** 15
61. R S Drage, K J Fisher *Inorg. Chem.*, 1975, **14** 2804
62. H Bürger, W Sawodny, U Wannagat *J. Organomet. Chem.*, 1965, **3** 113
63. D H Harris, M F Lappert, J B Pedley, G J Sharp *J. Chem. Soc., Dalton Trans*, 1976, 945
64. T Fjeldberg *J. Mol. Struct.*, 1984, **112** 159
65. T Fjeldberg, R A Andersen *J. Mol. Struct.*, 1985, **128** 49
66. R A Andersen, T Fjeldberg, H V Volden *The Norwegian Electron Diffraction Group Annual Report*, Oslo University, 1985, p. 12 (3B2)
67. T Fjeldberg, R A Andersen *J. Mol. Struct.*, 1985, **129** 93
68. A Haaland, K Rypdal, H V Volden, R A Andersen *J. Chem. Soc., Dalton Trans*, 1992 (in the press)
69. K Hagen, C J Holwill, D A Rice, J D Runnacles *Inorg. Chem.*, 1988, **27** 2032
70. C J Holwill, G A Forsyth, D A Rice, K Hagen *The Norwegian Electron Diffraction Group Annual Report*, Oslo University, 1990, p. 14 (3.2)
71. K Hagen, C J Holwill, D A Rice, J D Runnacles *Acta Chem. Scand. A*, 1988, **42** 578
72. P G Eller, D C Bradley, M B Hursthouse, D W Meek *Coord. Chem. Rev.*, 1977, **24** 1
73. R A Andersen *Am. Chem. Soc. Symp. Ser.*, 1980, **131** 31
74. D C Bradley, M H Gitlitz *J. Chem. Soc., A*, 1969, 980, 2330
75. M H Chisholm, F A Cotton, M W Extine *Inorg. Chem.*, 1978, **17** 1329
76. R Pearson, F J Lovas *J. Chem. Phys.*, 1977, **66** 4149
77. D Christen, H Oberhammer, R M Hammaker, et al. *J. Am. Chem. Soc.*, 1982, **104** 6186
78. D Christen, K Kalcher *J. Mol. Struct.*, 1983, **97** 143
79. I Hargittai, H M Seip *Acta Chem. Scand, Ser. A*, 1976, **30** 540
80. C Glidewell, A G Robiette *Chem. Phys. Lett.*, 1974, **28** 290
81. A Hammel, H V Volden, A Haaland, et al. *J. Organomet. Chem.*, 1991, **408** 35
82. J D Murdoch, D W H Rankin, B Beagley *J. Mol. Struct.*, 1976, **31** 291
83. D W H Rankin *J. Chem. Soc., Dalton Trans.*, 1972, (7) 869

84a. K Hagen, K Hedberg, P Rademacher, M Kindermann *J. Phys. Chem.*, 1992 (in the press)

84b. K Hagen, K Hedberg *J. Phys. Chem.*, 1992 (in the press)

85. H Oberhammer, C W Bauknight, Jr., D D Des Marteau *Inorg. Chem.*, 1989, **28** 4340
86. I Hargittai, D Schultz, V A Naumov, Yu P Kitaev *Dokl. Akad. Nauk SSSR*, 1976, **227** 1131
87. B Beagley, R G Pritchard *J. Mol. Struct.*, 1985, **130** 55
88. K Kohata, T Fukuyama, K Kuchitsu *J. Chem. Phys.*, 1982, **86** 602
89. N I Sadova, L V Vilkov *Usp. Khim.*, 1982, **51**(1) 153 [English translation in *Russ. Chem. Rev.*, 1982,(1)]
90. L V Vilkov, V S Mastryukov, M V Popik, et al. *Molekulyarnaya Struktura: Mezhvuzovskii Sbornik Nauchnykh Trudov* (Molecular Structure: Collected Scientific Papers from Higher Educational Establishments), Izd. Ivanov. Khim.-Tekhnol. Inst., Ivanovo, 1990, p. 95
91. A Domenicano *Stereochemical Applications of Gas-Phase Electron Diffraction. Pt. B* (Edited by I Hargittai, M Hargittai), VCH Publishing, New York, 1988, pp 281–324
92. A Domenicano, M Colapietro, G Portalone, et al. *Struct. Chem.*, 1989, **1** 107
93. O G Batyukhova, N I Sadova, L V Vilkov, et al. *Zh. Strukt. Khim.*, 1985, **26**(5) 175

94. O G Batyukhnova, N I Sadova, L V Vilkov, et al. *J. Mol. Struct.*, 1983, **97** 153
95. N I Sadova, N P Penionzhkevich, L V Vilkov *Zh. Strukt. Khim.*, 1976, **17**(4) 753
96. O G Batyukhnova, L V Vilkov, N I Sadova, et al. *Zh. Strukt. Khim.*, 1984, **25**(3) 166
97. E I Kulikova, N I Sadova, A A Ivanov, et al. *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1990, **31**(3) 221
98. E I Kulikova, N I Sadova, M V Popik, et al. *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1989, **30**(4) 338
99. O G Batyukhnova, N I Sadova, Yu N Syshchikov *Zh. Strukt. Khim.*, 1988, **29**(4) 53
100. A Almenningen, J Brunvoll, M V Popik, et al. *J. Mol. Struct.*, 1984, **118** 37
101. E I Kulikova, N I Sadova, L V Vilkov, et al. *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1990, **31**(4) 340
102. S Samdal, L V Vilkov, H V Volden *Acta Chem. Scand.*, 1992 (in the press)
103. J Brunvoll, S Samdal, H G Thomassen *Acta Chem. Scand.*, 1990, **44** 23
104. E I Kulikov, N I Sadova, M V Popik, et al. *Dep. in VINITI*, 23rd June 1988, No. 4941-V, 1988, 16 pp
105. E I Kulikova, N I Sadova, M V Popik, et al. *13-th Austin Symposium on Molecular Structure, Austin Texas*, 1990, Vol. 22, p. 109
106. N M Zaripov, A V Golubinskii, S V Sokolkov, et al. *Dokl. Akad. Nauk SSSR*, 1984, **278**(3) 664
107. G Schultz, I Hargittai, I Karpovits, et al. *J. Chem. Soc., Faraday Trans., 2*, 1984, **80** 1273
108. A Almenningen, I Hargittai, J Brunvoll, et al. *J. Mol. Struct.*, 1984, **116**(1/2) 199
109. V P Nivikov, S V Sokolkov, A V Golubinskii, et al. *Zh. Strukt. Khim.*, 1986, **27**(1) 50
110. A Almenningen, I Hargittai, S Samdal, et al. *J. Mol. Struct.*, 1983, **96** 373
111. N P Penionzhkevich, N P Sadova, M V Popik, et al. *Zh. Strukt. Khim.*, 1979, **20**(4) 603
112. N P Penionzhkevich, N I Sadova, L V Vilkov *Zh. Strukt. Khim.*, 1979, **20**(3) 527
113. A Almenningen, J Brunvoll, M V Popik, et al. *J. Mol. Struct.*, 1985, **127** 85
114. J H Hoeg, L Nygaard, G O Soerensen *J. Mol. Struct.*, 1971, **7** 111
115. Yu N Syshchikov, O G Batyukhnova, L V Vilkov, et al. *Issledovaniya Struktury i Energetiki Molekul: Mezhvuzovskii Sbornik Nauchnykh Trudov* (Studies of the Structure and Energetics of Molecules: Collected Scientific Papers from Higher Educational Establishments), Izd. Ivanov. Khim.-Tekhnol. Inst., Ivanovo, 1986, p. 64
116. V P Novikov, M V Popik, L V Vilkov *J. Mol.. Struct.*, 1979, **53**(2) 211
117. O Bastiansen, S Gundersen, S Samdal *Acta Chem. Scand.*, 1989, **43** 6
118. M J Hamor, T A Hamor *Acta Crystallogr., Sect. B*, 1978, **34** 2994
119. G Casalone, A Gavezzotti, M Simonetta *J. Chem. Soc., Perkin Trans. 2*, 1973, (4) 342
120. E G Boonstra *Acta Crystallogr.*, 1963, **16** 816
121. P B Levit, A V Belyakov, I V Tselinskii, et al. *J. Mol. Struct.*, 1992, **265** 337
122. P B Levit, A V Belyakov, I V Tselinskii, et al. *Zh. Fiz. Khim.*, 1991, **65**(7) 1946 [English translation in *Russ. J. Phys. Chem.*, 1991(7)]
123. P B Levit, Candidate's Thesis, Technological Institute, St. Petersburg, 1991
124. L S Khaikin, O E Grikina, L V Vilkov, et al. *Zh. Strukt. Khim.*, 1993 (in the press)
125. L S Khaikin, O E Grikina, L V Vilkov, J E Boggs *Zh. Strukt. Khim.*, 1993 (in the press)
126. J E Boggs, Z Niu *J. Comput. Chem.*, 1985, **6** 46
127. L S Khaikin, V I Perevozchikov, J E Boggs, L V Vilkov *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1991, **32**(5) 441
128. L S Khaikin, V I Perevozchikov, J E Boggs, L V Vilkov *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1992, **33**(1) 24
129. R Stoelevik, P Rademacher *Acta Chem. Scand.*, 1969, **23** 672
130. N I Sadova, G E Slepnev, N A Tarasenko, et al. *Zh. Strukt. Khim.*, 1977, **18** 865
131. J K Tyler *J. Mol. Spectrosc.*, 1963, **11** 39
132. N A Tarasenko, L V Vilkov, G E Slepnev, Yu A Pankrushev *Zh. Strukt. Khim.*, 1977, **18** 953
133. F R Cordell, Thesis, The University of Texas at Austin (USA), 1987, 101 pp
134. J D Swalen, J A Ibers *Chem. Phys.*, 1962, **36** 1914
135. D G Lister, J K Tyler *J. Chem. Soc., Chem. Commun.*, 1966, 152
136. W B Jennings, R Spratt *J. Chem. Soc., Chem. Commun.*, 1971, 54
137. B Sunners, L H Piette, W G Schneider *Can. J. Chem.*, 1960, **38** 681
138. H Kamei *Bull. Chem. Soc. Jpn.*, 1968, **41** 2269
139. T Drakenberg, S Forsen *J. Phys. Chem.*, 1970, **74** 1
140. R K Harris, R A Spragg *J. Chem. Soc. Chem. Commun.*, 1967, 362
141. O G Batyukhnova, N I Sadova, L V Vilkov *Zh. Strukt. Khim.*, 1984, **25**(6) 47
142. I F Shishkov, L V Vilkov, I Hargittai *J. Mol. Struct.*, 1991, **248** 125
143. I F Shishkov, N I Sadova, L V Vilkov, et al. *Zh. Strukt. Khim.*, 1982, **23**(4) 73
144. I F Shishkov, L V Vilkov, M Kolonits, et al. *Struct. Chem.*, 1991, **2** 57
145. P N Ghosh, C E Blom, A Bauder *J. Mol. Spectrosc.*, 1981, **89** 159
146. B W McClelland, L Hedberg, K Hedberg, et al. *J. Am. Chem. Soc.*, 1983, **105** 3789
147. A P Cox, S Waring *Trans. Faraday Soc.*, 1971, **67** 3441
148. I F Shishkov, L V Vilkov, I Hargittai, et al. *Chem. Phys. Lett.*, 1993 (in the press)
149. D G Scroggin, J M Riveros, E B Wilson *J. Chem. Phys.*, 1974, **60** 1376
150. B A Kulikov, V V Ugarov, N G Rambidi *Zh. Strukt. Khim.*, 1981, **22**(2) 196; 1981, **22**(3) 168; 1981, **22**(3) 166
151. S Shibata, K Iijima *J. Mol. Struct.*, 1984, **117** 45
152. N I Tuseev, A V Golubinskii, E Z Zasorin *6th Austin Symposium on Molecular Structure, Austin, Texas*, 1976, No. A34
153. C J Marsden, K Hedberg, M M Ludwig, et al. *Inorg. Chem.*, 1991, **30** 4761
154. N I Tuseev, V A Sipachev, R F Galimzyanov, et al. *J. Mol. Struct.*, 1984, **125** 277

155. L R Thorne, R D Suenram, F J Lovas *J. Chem. Phys.*, 1983, **78** 167
156. P Cassoux, R L Kuczkowski, P S Bryan, R C Taylor *Inorg. Chem.*, 1975, **14** 126
157. J R Durig, Y Li, J D Odom *J. Mol. Struct.*, 1973, **16** 443
158. K Iijima, N Adachi, S Shibata *Bull. Chem. Soc. Jpn.*, 1984, **57** 3269
159. P M Kuznesof, R L Kuczkowski *Inorg. Chem.*, 1978, **17** 2308
160. P Cassoux, R L Kuczkowski, G D Fong, R A Geanangel *J. Mol. Struct.*, 1978, **48** 25
161. P Cassoux, R L Kuczkowski, A Serafini *Inorg. Chem.*, 1977, **16** 3005
162. K Iijima, S Shibata *Bull. Chem. Soc. Jpn.*, 1979, **52** 711
163. M Hargittai, I Hargittai *J. Mol. Struct.*, 1977, **39** 79
164. M Hargittai, J Brunvoll *Inorg. Chim. Acta*, 1978, **31** L379
165. K Iijima, S Shibata *Bull. Chem. Soc. Jpn.*, 1980, **53** 1908
166. K Iijima, S Shibata *Bull. Chem. Soc. Jpn.*, 1983, **56** 1891
167. K Iijima, I Oonishi, S Shibata *Chem. Lett.*, 1983, 251
168. K Iijima, T Noda, M Maki, T Sasase, S Shibata *J. Mol. Struct.*, 1986, **144** 169
169. W Pyckhout, N Horemans, C V Alsenoy, et al. *J. Mol. Struct.*, 1987, **156** 315
170. M Hargittai, I Hargittai, V P Spiridonov *J. Mol. Struct.*, 1975, **24** 27
171. M Hargittai, J Tamas, M Bihari, I Hargittai *Acta Chim. Acad. Sci. Hung.*, 1979, **99** 127
172. M Hargittai, I Hargittai, V P Spiridonov, A A Ivanov *J. Mol. Struct.*, 1977, **39** 225
173. A Almenningen, G Gundersen, T Haugen, A Hasland *Acta Chem. Scand.*, 1972, **26** 3928
174. G A Anderson, F R Forgaard, A Haaland *Acta Chem. Scand.*, 1972, **26** 1947
175. A Almenningen, A Haaland, T Haugen, D P Novak *Acta Chem. Scand.*, 1973, **27** 1821
176. V S Mastryukov, A V Golubinskii, L V Vilkov *Zh. Strukt. Khim.*, 1979, **20** 921
177. M Hargittai, I Hargittai, V P Spiridonov *J. Mol. Struct.*, 1976, **30** 31
178. J R Durig, K K Chatterjee, Y Li, et al. *J. Chem. Phys.*, 1980, **73** 21
179. P L Baxter, A J Downs, D W H Rankin *J. Chem. Soc., Dalton Trans.*, 1984, 1755
180. V S Mastryukov, V P Novikov, L V Vilkov, et al. *Zh. Strukt. Khim.*, 1987, **28** 143
181. L M Golubinskaya, A V Golubinskii, V S Mastryukov, et al. *J. Organomet. Chem.*, 1976, **117** 4
182. S Shibata, J Iwata *J. Chem. Soc., Perkin Trans. 2*, 1985, 9
183. A V Legon, D J Millen, S C Rogers *J. Chem. Soc., Chem. Commun.*, 1975, 580
184. T Fjeldberg, P B Hitchcock, M F Lappert, A J Thorne *J. Chem. Soc., Chem. Commun.*, 1984, 822
185. T Fjeldberg, M F Lappert, A J Thorne *J. Mol. Struct.*, 1984, **125** 265
186. K-K Lau, A B Burg, R A Beaudet *Inorg. Chem.*, 1974, **13** 2787
187. T C Bartke, A Haaland, D P Novak *Acta Chem. Scand., Ser. A*, 1975, **29** 273
188. L V Vilkov, A V Golubinskii, V S Mastryukov, et al. *Sovremennye Problemy Fizicheskoi Khimii* (Present-Day Problems in Physical Chemistry) (Edited by N I Gerasimov, P A Akishin), Vol. 11, Izd. Mosk. Gos. Univ., Moscow, 1979, p. 59
189. P L Baxter, A J Downs, D W H Rankin, H E Robertson *J. Chem. Soc., Dalton Trans.*, 1985, 807
190. Q Shen, R L Hilderbrandt *J. Mol. Struct.*, 1980, **64** 257
191. G Forgacs, M Kolonits, I Hargittai *Struct. Chem.*, 1990, **1** 245
192. J Dekker, J Boersma, L Fernholt, A Haaland, A L Spek *Organometallics*, 1987, **6** 1202
193. A Greenberg, C Wu *Struct. Chem.*, 1990, **1** 79

Received 27th April 1992

Translated from *Uspekhi Khimii* 61 2172–2186 (1992) U.D.C. 543.544.45

The effect of alternation in chromatographic retention relationships

M S Vigdergauz, E I Petrova
Samarskoe State University

ABSTRACT. The effect of the alternation of the chromatographic retention values has been examined for homologous series of sorbates and stationary phases (the even–odd effect) and for other series formed by the successive addition of identical functional groups to the repeating fragments of an aliphatic molecule or ring, as well as by the displacement of functional groups or alkyl groups along a chain or a ring. Particular attention has been paid to the manifestation of this effect when liquid-crystalline stationary phases are used. It has been shown that the diffference in the concentrations of given substances in natural materials may be partly due to the alternation of the sorption characteristics.

The bibliography contains 70 references.

Contents

I. Alternation of the physicochemical characteristics of homologues 1194
II. Alternation of the gas-chromatographic retention values in homologous series of sorbates (even–odd effect) 1195
III. Even–odd effect in the retention of sorbates by homologous series of stationary phases 1197
IV. Even–odd effect in liquid–liquid chromatography 1198
V. Other forms of alternation of retention values 1198

I. Alternation of the physicochemical characteristics of homologues

In the study of the regularities of the change in the physicochemical properties of substances which are members of homologous series, attention is drawn to the role of the structural factor determined by the characteristics of the configuration of molecules with even and odd numbers of carbon atoms.[1] As a consequence of this influence, the relationship between the physicochemical characteristics and the number of carbon atoms z is given by a zigzag curve, that is alternation of the quantities being studied, depending on the parity of z, is observed.

The influence of the parity of z was first revealed in the study of the regularities of the change in the melting point in the homologous series of n-alkanes.[2,3] The relationship between the melting point and the number z was found to be different for the even and odd homologues. A similar effect was later observed for the aliphatic acid series.[4] Data have been published[5] on the effect of alternation in the change in the melting points and solubilities of dicarboxylic acids. The values of the melting points and solubilities of the numbers of the series with odd values of z are higher than those for the even homologues.

For liquid crystals, the effect of alternation is revealed not only by the melting points but also by the temperatures of other phase transformations: smectic–nematic and nematic–isotropic liquid.[6–11] In addition, in the nematic phase of N-(4-alkoxybenzylidene)-4′-toluidine specimens oriented by a magnetic field, an even–odd effect was detected in the temperature dependence of the parameters of the orientational ordering.[11]

Published data[4,12–15] and their own data were used by a group of authors[16,17] to study the regularities in the influence of the parity of z on the values of the dipole moments, refraction, heats of crystallisation, refractive indices, and size of the crystal cells of aliphatic acids, their methyl esters, and the dimethyl esters of dicarboxylic acids. It was later shown[18] from published data[12,19–22] that a fairly clearly defined alternation of such characteristics as the melting point, density, refractive index, dipole moment, and even boiling point is observed for homologous series of alkylamines, alkylbenzenes, ketones, and esters of carboxylic acids.

One of the possible factors responsible for the alternation of the physical properties of substances (such as the melting point or heat of fusion) is apparently the nature and stability of the packing of the molecules in the crystal.[23] The stability of the packing of the molecules in the crystal in turn depends on their geometry. For example, X-ray diffraction shows that the zigzag chains of the molecules of saturated non-branched hydrocarbons in the crystal are arranged parallel to one another, and that the "convex" parts of one chain enter the "dents" in the other. The physical properties of these substances depend on the parity of the number of carbon atoms, since the symmetry of the individual molecules influences the way in which one layer of molecules in the crystal is superimposed on another. Molecules with an odd value of z have a plane of symmetry passing through the central carbon atom, and the terminal methyl groups are directed in the same direction relative to the axis of the molecule. A chain with an even number of carbon atoms does not have this plane of symmetry, but acquires a centre of inversion, situated between the two central carbon atoms. The terminal methyl groups in these molecules are directed in different directions with respect to the axis of the molecule. This difference in the arrangement of the methyl groups is responsible for the difference in the packing of the layers of molecules.

On crystal formation, hydrocarbons with an even value of z are arranged in such a way that each layer repeats the previous layer (with a slight sideways displacement), whereas in the crystals formed by hydrocarbons with an odd value of z, every second layer has the same arrangement of molecules.

Increase in the chain length eliminates the advantage of one type of packing over another, and for hydrocarbons the even–odd effect gradually decreases, disappearing completely when the number of carbon atoms is sufficiently large.

Similar arguments can be used to explain the even–odd effect in carboxylic and dicarboxylic acids.

II. Alternation of the gas-chromatographic retention values in homologous series of sorbates (even–odd effect)

The possibility of the effect of alternation appearing in the change in the temperatures of the phase transformations in liquid crystals is evidently related to their structural ordering in the solid and liquid states. Since the chromatographic characteristics are also related to the phase transformations, the changes in these characteristics should also show the effect of alternation. The probability of this is greater if the liquid phase has a fairly rigid structure. Kovats[24] initially determined the retention index by a logarithmic interpolation based on the logarithms of the retention volumes of the n-alkanes of the even series, but since the alternation effect was not detected, this was later recognised as unnecessary, and the interpolation began to be carried out on the basis of the retention characteristics of neighbouring n-alkanes.

In the subsequent development of chromatography, when highly efficient columns were introduced (this increased considerably the sensitivity of the determination of the retention characteristics), it was established that the relationship between the retention values and the number of carbon atoms in the molecules of sorbates in a homologous series, previously assumed to be linear, often shows deviations from linearity.[25–29] These deviations may be due to either anomalies in the properties of the sorbates or the corresponding sorption properties of the stationary phases. Detailed study of this question established that the deviations from linearity are related primarily to the characteristics of the molecular structure of the first members of the homologous series and are also determined by the non-constant nature of the increment of the repeating fragment of the molecule. These deviations can be seen particularly clearly when polar sorbates and(or) polar stationary phases are used.

The authors cited[29] also showed that for different stationary phases the difference between (ratio of) the retention values in the series of n-alkylbenzenes and n-alkylcyclohexanes is greatest for the n-propyl-substituted/ethyl-substituted pairs (a similar relationship was found for such physicochemical characteristics as the dielectric constant and surface tension). Sojak and co-workers[30] established that the n-propylbenzene/ethylbenzene pair also has the smallest value of the increment in the retention index on a column containing squalane. This effect was later called the "propyl" effect.[31]

The importance of the parity of z was a factor influencing the retention of homologues was first revealed[32] in a study of the n-alkane–polyethylene glycol system. An experiment carried out on a highly efficient capillary column showed that the relationship between the retention and the number z is given by a broken line, that is alternation of the chromatographic retention values is observed on going from an even to an odd member of the homologous series. Thus strictly speaking this relationship should be represented by two curves, one corresponding to even values of z and the other to odd values. Two anomalous effects, namely the "propyl" effect and the even–odd effect, are shown simultaneously by data on the retention of alkylbenzenes on squalane, acetyl tributyl citrate, and 1,2,3-tris(β-cyanethoxy)propane.[33–36]

The relationship between the chromatographic retention and the number of carbon atoms in the molecule z, with allowance for alternation, can be described by the equation:[37]

$$\lg t'_{R_z} = a_t + b_t z + c_t z^2 + d_t z^3 + D_t \varphi_z. \qquad (1)$$

where t'_{R_z} is the reduced retention time of the member of the homologous series with z carbon atoms in the molecule; a_t, b_t, c_t, D_t are constants; and $\varphi = +1$ for even values of z, or -1 for odd values.

Since the effect of alternation is fairly fine, it can be detected by examining not the retention time but the ratio of the reduced retention times

$$\sigma_\Gamma = t'_{R_z}/t'_{R_{z-1}}$$

or the difference between the retention indices ΔI of neighbouring homologues. In the study of the change in the retention characteristics with change in z for substances belonging to different homologous series, it is necessary to examine the ratio of the reduced retention times or the difference between the retention indices of substances having the same number of carbon atoms in the molecule but belonging to different homologous series. The quantity σ_Γ is related to the difference between the molar free energies of volatilisation from the stationary phase $\delta(\Delta G^\circ)_z$ of two molecules with numbers of carbon atoms in the molecule z and $z-1$ by the equation

$$\delta(\Delta G^\circ)_z = RT \ln \sigma_\Gamma, \qquad (2)$$

where R is the universal gas constant, and T the absolute temperature of the column.

Thus the contribution of the parity of the number of carbon atoms to the retention can be expressed in energy units.

On the graph, the distance between lines corresponding to series of homologues with even and odd values of z is characterised by the alternation criterion A_z:[16,17,37]

$$A_z = \lg \sigma_{\Gamma_{z+1}} - \lg \sigma_{\Gamma_z} = \lg t'_{R_{z-1}} + \lg t'_{R_{z-1}} - 2\lg t'_{R_z}, \qquad (3)$$

where σ_{Γ_z} and $\sigma_{\Gamma_{z+1}}$ relate to homologues with numbers of carbon atoms z, $z-1$ and $z+1$, z respectively. The sign of A_z depends on the parity of z and changes on going to each subsequent homologue.

The influence of the parity of z on the retention of n-alkanes, 1-bromoalkanes, and 2-alkanones by a stationary phase of medium polarity, namely triethylene glycol dibutyrate, was revealed using a highly efficient capillary column.[37] The study was carried out at temperatures of 40 °C and 80 °C. The alternation effect increases in the order: n-alkanes < 1-bromo-alkanes < 2-alkanones. This is clearly demonstrated by the plot of $\sigma(\Delta G^\circ)_z = f(z)$. The clearly defined zigzag character of this relationship for the 2-alkanones disappears on going to the 1-bromoalkanes and then to the n-alkanes. The $\sigma(\Delta G^\circ)_z = f(z)$ relationship for the n-alkanes is given by an almost straight line. The data obtained also indicate that in this case the temperature effect is slight; the influence of temperature is shown only by a displacement of the points on the graph, and the form of the curve giving the dependence of the chromatographic retention characteristics on z remains unchanged. An interesting feature is that the value of $\sigma(\Delta G^\circ)_z$ for 1-bromoalkanes with even values of z is smaller than that for the odd compounds, that is the change in these quantities is the opposite of that for the n-alkanes. This effect can be attributed to the role of the bromine atom in position 1, which makes the hydrocarbon chain longer, that is the number of "chain-forming" atoms in the 1-bromoalkanes with z carbon atoms must be regarded as $z+1$.

Fig. 1 gives graphs showing the influence of the parity of the number of carbon atoms in the molecule on various properties of n-alkanes.[37] It can be seen from Fig. 1 that the general curvature of the dependence of the retention values on z is determined by the regularity of the change in the values of the saturated vapour pressure of the sorbates (curve *1*). The influence of the parity of z on the retention of n-alkanes (curves *2* and *3*) is revealed to a greater extent when polyethylene glycol 400 is used as the stationary phase than when triethylene glycol dibutyrate is used; this is a consequence of the more rigid molecular structure of the first of these stationary phases. The similarity between curves *3* and *4* proves the close relationship between the retention values and the molecular structure of the compounds being considered.

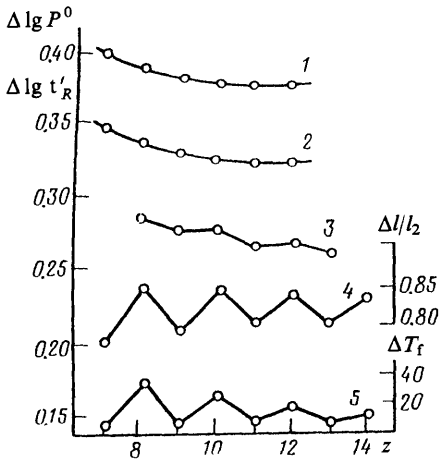


Figure 1. Dependence of various properties of n-alkanes on the number of carbon atoms in the molecule;[37] *1*, homologous difference between the logarithms of the saturated vapour pressures $\Delta \lg P^0$ at 80 °C; *2,3*, homologous difference between the logarithms of the reduced retention times at 80 °C on columns containing triethylene glycol dibutyrate (*2*) and polyethylene glycol 400 (*3*); *4*, the quantity $\Delta l/l_2$, where Δl is the difference between the terminal carbon atoms in the molecule for neighbouring homologues, and l_2 the length of the C–C bond; *5*, homologous difference between the melting points ΔT_f.

The influence of the parity of z on the functional group increment in the molecules of compounds of different homologous series has been studied.[38] The sorbates chosen were n-alkanes, bromoalkanes, aldehydes, and ketones. The study was carried out on a capillary column with triethylene glycol dibutyrate as stationary phase. The retention characteristic was the partial Henry coefficient (the capacity coefficient) $\Gamma' = t'_R/t_0$, where t_0 is the retention time of a substance which is not sorbed. The dependence of $\lg \Gamma'$ on z has the form of a broken line and can be described by an equation analogous to Eqn. (1).

Calculation of the retention increments from published data[39] shows that alternation of the values of ΔI is also observed for homologous series of methyl and chloromethyl esters of n-C_5–C_{12} chlorocarboxylic acids on capillary columns with the stationary phases SE-30 and Carbowax 20M.

The effect of alternation in the chromatographic retention of n-alkanes (C_6–C_{11}) is also observed on packed columns containing trifluoropropylmethylsilicone SKTFT-100 and pentaphenyl ether.[40] The $\sigma_\Gamma = f(t)$ relationship is given by a zigzag line. In particular, for the stationary phase SKTFT-100 the value of σ_Γ lies in the range 1.40–1.58 (uncertainty in the determination 0.01–0.04), and the quantity $\Delta\sigma_\Gamma = \sigma_{\Gamma_{z+1}} - \sigma_{\Gamma_z}$ characterising the range of alternation for following pairs of homologues has the values −0.11, 0.18, −0.14, 0.14.

The effect of alternation becomes particularly marked for polar sorbates and polar stationary phases. The alternation may be clearly defined even for packed columns with medium efficiency. In particular, this phenomenon has been studied in detail for aliphatic acids and their esters.[16,17,41] The regularities in the retention of the methyl esters of aliphatic acids were studied at different temperatures on four stationary phases with different polarity: Apiezon L, Triton X-305, Carbowax 20M, and diethylene glycol succinate (DEGS). The ratios of the retention indices of the sorbates studied on columns containing DEGS and Apiezon L showed a tendency to alternate. The alternation of these quantities is observed in the range $z = 3$–12, and the tendency disappears with further increase in the length of the alkyl group.

The retention of the dimethyl esters of aliphatic dicarboxylic acids on a column containing the high-temperature liquid-crystalline stationary phase bis(*p*-ethoxybenzylideneamino)biphenyl has been studied.[42] Clearly defined alternation of the retention values is observed for the C_4–C_8 series, after which it disappears with increase in the number of CH_2 groups in the molecule.

To investigate the alternation of the t'_{R_z} values, the alternation criterion A_z was calculated. The values of A_z were calculated for a temperature of 190 °C on two stationary phases: the polar DEGS and the non-polar Apiezon L. Alternation of the values of t'_{R_z} is observed only on the polar liquid phase in the range $z = 3$–6 for the dimethyl esters of dicarboxylic acids (t_0 = 190 °C, stationary phase DEGS); alternation of the retention characteristics is also observed in the range $z = 4$–10 for the free aliphatic acids (t_0 = 190 °C, stationary phase diethylene glycol adipate + H_3PO_4).

In the study of the chromatographic behaviour of free aliphatic acids it was shown that lowering the temperature of the column to 160 °C leads to disappearance of the alternation effect, and that the effect is preserved when the temperature is raised to 200 °C.

The alternation of the properties in the series of normal aliphatic acids is attributed to the difference between the configurations of the molecules of the even and odd homologues. In the monocarboxylic acids, the carboxyl group at one end of the molecule is opposite a methyl group for odd values of z) or a methylene group (for even values of z). For dicarboxylic acids, the carboxyl group is opposite a second carboxyl group or a methylene group, depending on whether the value of z is even or odd. Thus if the alternation is determined by the configuration of the molecule, it should be more clearly defined for the dicarboxylic acids and their derivatives. This is confirmed by the results obtained.[16,17] Thus if the range of alternation of the retention values is characterised by the difference

$$\Delta A_z = |A_{z+1}| - |A_z|,$$

then the range will be about 0.01–0.07 for free aliphatic acids, 0.06–0.08 for the methyl esters of aliphatic acids, and 0.16 for the dimethyl esters of dicarboxylic acids. The authors cited[16,17] consider that a definite role in the phenomenon of alternation may also be played by the polymorphism of the aliphatic acids (there exist forms

A, B, and C whose molecules differ in the magnitude of the angle at which the carbon atoms are arranged).

The effect of alternation has been observed[5] in the dependence of the relative retention of n-alkyl-substituted carboxylic acids (n-C_5 – n-C_{16}) on their melting points on a column containing a silicon + 15% stearic acid as stationary phase, the dependence of the relative retention of the methyl esters (n-C_8 – n-C_{18}) on the melting points of the corresponding aliphatic acids on a column containing a silicone grease as stationary phase, and the dependence on the melting points of the absolute specific retention volume of n-alkanols (C_1 – C_8) in a column containing the stationary phase SE-30.

A statistical estimation of the alternation effect has been carried out.[18] For this purpose, the uncertainty in the determination of the quantity used to characterise the chromatographic retention was established. This quantity was the retention increment ΔI equal to the difference between the retention indices I of neighbouring members of a series of sorbates differing in the number of repeating fragments. It was shown for a number of examples that the regularities of the change in the retention values in the series of sorbates studied are preserved when account is taken of the uncertainties in the determination of these quantities. Thus in the range of alternation $\Delta(\Delta I)$ for cycloalkanes on squalane in the range 3 – 13 I units, the uncertainty in the determination of I varies in the range 0 – 1.5 I units. Thus the alternation effect observed in a number of cases is not a consequence of the uncertainty in the determination of the retention indices, but is determined by the characteristics of the structure of the sorbates and the nature of their interaction with the stationary phase.

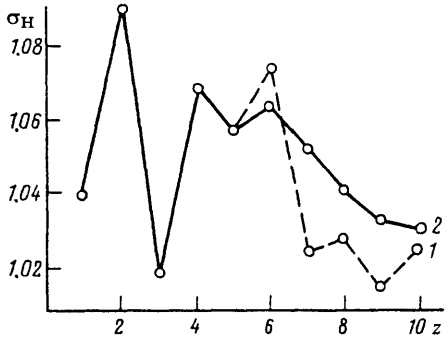


Figure 2. Dependence of the selectivity coefficient on the number of carbon atoms in the lateral alkoxy-group of symmetrical azoxy-ethers for smectic (*1*) and nematic (*2*) meso-phases.

The alternation effect is also revealed by the regularities of the chromatographic behaviour of liquid crystals when they are used both as sorbents and as stationary phases. For example, the alternation effect was detected in a chromatographic study of the thermodynamics of the solution of monohydric aliphatic alcohols in the cholesteryl ester of myristic acid.[43] The authors cited[43] consider that the probable reason for this effect is that when the molecules of non-mesogenic additives are introduced into the structure of a meso-phase there is a difference in the efficiency of the coupling between the molecules and individual sections of the meso-phase. The coupling reduces mainly to an end-type interaction between the molecules of the liquid crystal and the non-mesogenic additive. Increase in the length of the hydrocarbon group of the alcohol will lead to a decrease in the smectogenic character of the cholesteryl myristate molecules.

The selectivity of the stationary phases *p,p'*-methoxyethoxyazoxy-benzene (MEAB) with respect to isomeric alkanes (C_{10} – C_{17}) has been studied;[9,44] geometric isomers and positional isomers were examined. The dependence of the selectivity coefficient σ_H, which is the ratio of the reduced retention times of *trans*- and *cis*-isomers with double-bond position 2 – 8 or the ratio of the reduced retention times of neighbouring *cis*- and *cis*-isomers and *trans*- and *trans*-isomers, on the number z has a zigzag form. This confirms the influence of the parity of z on the ratio of the retention parameters of sorbates having the same number of carbon atoms in the molecule but belonging to different homologous series.

III. Even – odd effect in the retention of sorbates by homologous series of stationary phases

The effect of alternation in chromatography can also be detected by studying the retention of the same sorbates on a number of stationary phases which are members of one homologous series. In particular, this effect has been observed in a study of the separation of close-boiling isomers on columns containing nematic liquid crystals, namely azoxy-ethers. The influence of the parity of z can be examined from different viewpoints; thus it is possible to consider firstly the total number of carbon atoms in the molecule of the liquid crystal, and secondly the number of carbon atoms in both lateral parts; the influence of parity in one side chain on the chromatographic retention can also be examined. Thus symmetrical azoxy-ethers have been used as stationary phases for the separation of *m*- and *p*-xylenes.[45–47] The dimethoxy-derivative (azoxyanisole) has a low selectivity, the diethoxy-derivative (azoxyphenetole) a higher selectivity, and the subsequent homologues approximately the same or a lower selectivity (Fig. 2). If however the asymmetric ether *p,p'*-methoxyethoxyazoxybenzene is used as the stationary phase, the *m* – *p*-selectivity increases considerably and becomes greater than that for azoxyphenetole and its eutectic mixture with azoxyanisole.[48]

The change in the *m* – *p*-selectivity in a series of symmetrical and asymmetrical azoxy-ethers has been studied.[9,49] The value of the selectivity coefficient σ_H, which in this case is the ratio of the reduced retention times of the *m*- and *p*-xylenes, shows alternation not only with change in the number of carbon atoms in the side chains of the azoxy-compounds but also in the dependence on the symmetry of the molecules of the liquid crystals as a whole. The asymmetric azoxy-ethers on the whole have a greater *m* – *p*-selectivity than the symmetrical ones. In the series of asymmetric homologues, MEAB has the greatest *m* – *p*-selectivity.

An even – odd effect has been detected[50,51] in the retention of standard sorbates (ethanol, methyl ethyl ketone, benzene, and nitromethane) on liquid-crystalline stationary phases belonging to the homologous series of nitroazoxybenzenes. Alternation is shown by the values of the linear retention indices of the sorbates studied and the chromatographic polarity factors. The values of the retention parameters are greater for the odd than for the even substituents.

When asymmetric azoxy-ethers are used as stationary phases,[32] alternation is also shown by the values of the universal polarity factors—quantities which are proportional to the reduced retention times of the sorbates and which characterise the chromatographic polarity of the stationary phase with allowance for its sorptive capacity and the duration of the chromatographic analysis.

IV. Even–odd effect in liquid–liquid chromatography

The influence of the parity of z on the sorptive properties of petroleums is related to the corresponding regularities of their composition. Thus the ratio of odd and even n-alkanes in recent sediments and petroleums is different.[53–56] In sediments, molecules with an odd number of carbon atoms predominate, whereas in petroleums, molecules with an odd value of z are present in very small quantities or are not detected at all. It has been proposed[57] that this relationship be characterised by the odd-parity index, which is the ratio of the number of molecules of n-alkanes with odd values of z [odd molecules (O)] to the number of molecules of n-alkanes with even z [even molecules (E)]. The corresponding values of O/E are -5.6 in recent sediments, and $0.9-1.2$ in petroleums.

The odd-parity index is used by many authors as a characteristic of petroleum which makes it possible to identify its origins. Another characteristic of petroleum used for identification is the ratio of the concentrations in it of two alkanes with an isoprene structure, namely pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane).[58,59] For a long time, however, the predominance of even or odd alkanes (with normal or branched structures) in different petroleums was related in the literature only to the organic origin of the petroleum, and no account was taken of the fact that a change in its composition may take place during the migration of petroleum through rocks which are adsorbents. This was first pointed out by Vigdergauz and co-workers.[60] It is confirmed by the results of investigations[61,62] in which the effect of the alternation of the sorptive properties of n-alkanes was studied under liquid–liquid chromatographic conditions. When a mixture of n-alkanes is passed through a column containing silica gel moistened with hexane, a fraction richer in hydrocarbons of the even series will leave the column first, followed by a fraction richer in those of the odd series.

Fig. 3 shows the change in the ratios of the concentrations of neighbouring n-alkanes (containing z and $z-1$ carbon atoms in the molecules) in a comparison of the initial and final fractions of the eluate with the original mixture. The total coefficient of enrichment of the initial fraction of the eluate in n-alkanes of the even series was 1.24 for the chosen conditions.

Studies carried out with different adsorbents moistened with different organic substances gave initial fractions enriched sometimes in the even and sometimes in the odd homologues.

In the work cited,[62] the changes in the compositions of the petroleums were studied by gas–liquid and thin-layer chromatography. It was shown that the process of filtration of the petroleum through rock is accompanied by a change in the even : odd n-alkane ratio and in the pristane/phytane ratio compared with the ratios in the petroleum taken initially.

Finally, a detailed study has been made[63] of the effect of change in the composition of a mixture of hydrocarbons with the isoprene structure on filtration through moistened porous media. The work was carried out under the conditions of frontal liquid–liquid chromatography, which approach most closely the natural conditions of the migration of fluids. The porous medium used was activated silica gel moistened with n-hexane. The studies showed that an even–odd effect is also observed in this case. The concentration of pristane in the initial fractions increases, compared with the concentration of phytane. In subsequent fractions this sorption effect gradually decreases, and the composition of the filtrate approaches the original composition. The effect of change in the composition of the mixture of isoprene hydrocarbons under these conditions is determined both by the solubility of the hydrocarbons studied in the n-hexane wetting the adsorbent and by the adsorption surface of the polar activated silica gel used as the adsorbent.

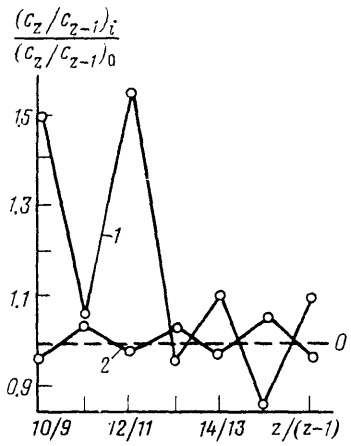


Figure 3. Change in the ratios of the concentrations of neighbouring n-alkanes (with numbers of carbon atoms in the molecules z and $z-1$) in a comparison of the initial (*1*) and final (*2*) fractions of the eluate with the original mixture (0).[60]

V. Other forms of alternation of retention values

A detailed examination of published data showed that the even–odd effect is only a particular case of alternation in chromatography. It is therefore of interest to examine the problem of alternation as a whole, and in particular the position occupied by the even–odd effect in alternation phenomena.

Study of the regularities of retention in different series of sorbates and stationary liquids makes it possible to consider seven cases of alternation of retention values.

1. With increase in the length of a molecule as a result of an increase in the number of repeating fragments (with a functional group on one or both ends of it). The even–odd effect, determined by the number of methylene groups in alkyl chains, is here a particular case.

2. On the successive addition of identical functional groups (or alkyl groups) to the repeating fragments of an aliphatic molecule or the aliphatic part of a molecule.

3. The analogous effect of a cyclic molecule (naphthenic or aromatic rings) and in per-substituted rings or heterocycles.

4. On displacement of a functional group (including hydrocarbon groups), joined to the alkyl chain of a molecule, along the chain.

5. The analogous effect for substituents in a cyclic molecule.

6. On the displacement of a functional group or a more complex fragment (or multiple bond), situated in a chain, along this chain (succession of metamers).

7. The analogous effect in heterocycles containing two heteroatoms.

Thus three types of alternation can be distinguished.

I. On the successive addition of identical fragments to a molecule (point 1).

II. On the successive addition of identical functional groups (or alkyl groups) to the fragments of an aliphatic chain or ring (points 2 and 3).

III. On the "displacement" of these fragments along alkyl chains and aromatic (or naphthenic) rings (points 4–7).

The initial data for the study of the relationships characterising the different types of alternation were the retention index values given in various sources,[64–69] and the published[45] and our own[10,70] values of the *m*–*p*-selectivity coefficients.

The retention characteristics used were the differences between the retention indices of neighbouring compounds in the series of sorbates selected

$$\sigma I = I_{N+1} - I_N,$$

where N is the sequence number of the compounds, and for the case of alternation in a series of liquid-crystalline stationary phases the selectivity coefficient σ_H, representing the ratio of the reduced retention times of *m*- and *p*-xylenes.

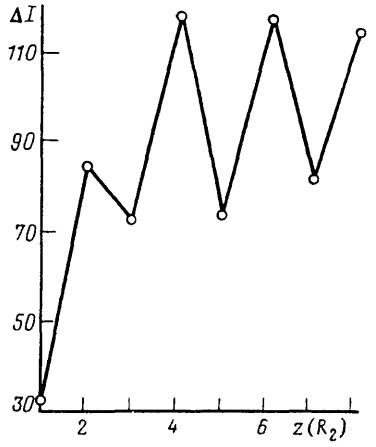


Figure 4. Dependence of ΔI on the number of carbon atoms in the substituent for n-alkyl acetates $CH_3-COO-C_zH_{2z+1}$ (z = 1–9) on a column containing OV-351.[64]

The graphical relationships which we obtained can illustrate the following classification of series of sorbates and stationary liquids in which alternation of the retention values takes place.

1. Series formed by an increase in the length of the aliphatic chain of a molecule as a result of an increase in the number of repeating fragments (structural units); the members of the series are homologues or polymer–homologues $R_1-\varphi-R_2$, where R_1 and R_2 are alkyl groups, and φ a functional group;

a, increase in length on one side of a functional group (or counting from a terminal methyl group); R_1 = const, $R_2 \neq$ const (Figs. 4–6);

b, increase in length in both directions away from a functional group; $R_1 \neq$ const, $R_2 \neq$ const; the side chains may increase in length to equal or different extents (Figs. 2 and 7).

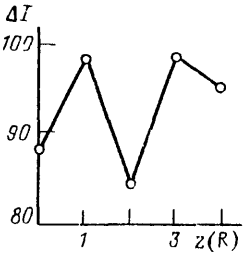
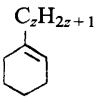


Figure 5. $\Delta I = f(z)$ relationship for n-alkyl derivatives of cyclohex-1-ene  (z = 1–5) on a column containing Apiezon L;[65] temperature of the experiment 100 °C.

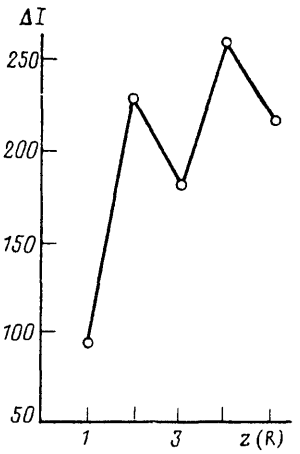
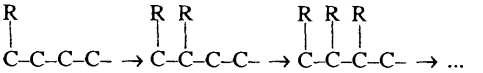
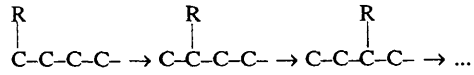


Figure 6. $\Delta I = f(z)$ relationship for di-n-alkylnitrosamines $(n\text{-}C_zH_{2z+1})_2N-NO$ (z = 1–6) on a column containing SE-30;[66] temperature of the experiment 125 °C.

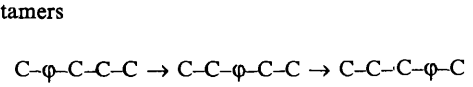
2. Series formed by the successive addition of identical functional groups (or alkyl groups) to the repeating fragments of an aliphatic molecule (or the aliphatic part of a molecule) or to a ring (formation of a polysubstituted chain or poly-substituted ring) (Figs. 8 and 9)



3. Series formed in the movement ("displacement") of functional groups or alkyl groups along a chain or ring (Fig. 10)



Series formed by "displacement" of insertion, that is a sequence of metamers



are included here.

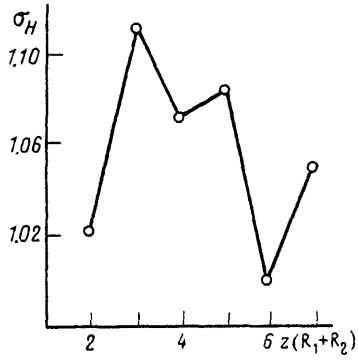
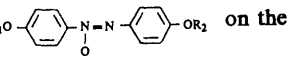


Figure 7. Dependence of the coefficient of $m-p$-selectivity σ_H of dialkoxyazoxybenzenes  on the total number of carbon atoms in both side chains of azoxy-ethers symmetrical and non-symmetrical structures.[10]

4. Obviously, alternation is also observed in isologous series, that is on going from saturated aliphatic hydrocarbons to alkenes and alkynes, and also from alicyclic to aromatic.

Studies have shown that the probability of the appearance of the alternation effect in chromatographic retention relationships is higher, the more polar the sorbates and stationary liquids studied. Thus in the study of retention on non-polar or slightly polar stationary phases (squalane, Apiezon L, SE-30, etc.), alternation is observed for such sorbates as alkyl-substituted cycloalkanes, aldehydes, ketones, and various esters, and is not observed for alkanes, alkenes, alkynes, or alkyl-substituted aromatic hydrocarbons. The range of alternation, defined as the difference between neighbouring values of ΔI in the selected series of sorbates, varies in the ranges 1–20 I units (sorbates—substituted cycloalkanes, aldehydes, ketones, esters of carboxylic acids; stationary phases—Apiezon L, SE-30, DS-550, OV-1), 1–50 I units (sorbates—substituted cycloalkanes, ketones, esters of carboxylic acids, alcohols, alkyl-substituted phospholans, substituted amines; stationary liquids—squalane, Apiezon L, SE-30, DS-550), and 1–100 I units (sorbates—substituted adamantanes, substituted amines; stationary phase—SE-30). On going to polar stationary phases, the effect of alternation becomes stronger and can also be observed for non-polar and weakly polar sorbates. For example, the range of alternation reaches 40 I units for such sorbates as alkylbenzenes, alkylamines, esters of carboxylic and benzoic acids, and alkyl-substituted cycloalkanes on columns containing PEG-4000, OV-351, XF-1150, dibutyl tetrachlorophthalate, and 1,2,3-tris(β-cyanethoxy)propane, 80 I units for alkyl-substituted cycloalkanes, cycloalkenes, and naphthalenes, esters of carboxylic acids, and alkylamines on columns containing PEG-1000, PEG-4000, PEGA, OV-351, and tricresyl phosphate, and 400–200 I units for alkylbenzenes, ketones, and esters of carboxylic acids on columns containing OV-351, XF-1150, tricresyl phosphate, and Reoplex.

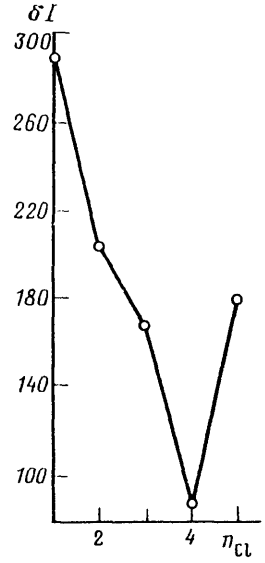


Figure 8. Dependence of δI on the number of chlorine atom for a series of chloro-derivatives of benzene: chlorobenzene, 1,2-dichlorobenzene, 1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene on a column containing Carbowax 20M.[67]

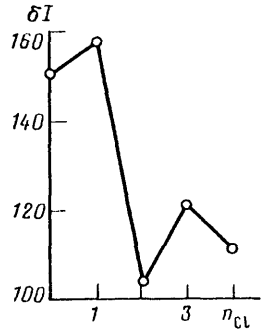


Figure 9. Dependence of δI on the number of chlorine atoms for a series of methyl esters of chloropropionic acids: $C_2H_5-COO-CH_3$, $CH_3-CHCl-COO-CH_3$, $CH_2Cl-CHCl-COO-CH_3$, $CH_2Cl-CCl_2-COO-CH_3$, $CHCl_2-CCl_2-COO-CH_3$, and $CCl_3-CCl_2-COO-CH_3$ on a column containing OV-101;[68] temperature of the experiment 80 °C.

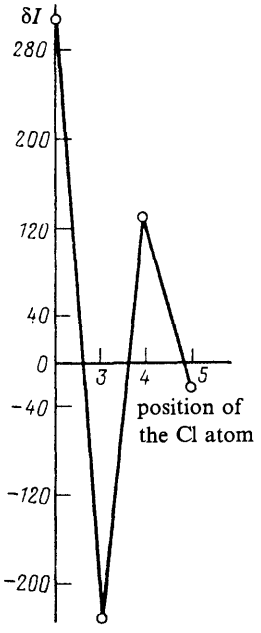


Figure 10. Dependence of δI on the position of the chlorine atom for a series of chlorinated salicylaldehydes on a column containing OV-351;[69] temperature of the experiment 140 °C.

It will be possible to determine more precise dependences of the retention values on the number of carbon atoms in the molecule and other physicochemical characteristics for identification, when more selective stationary phases appear. For a deeper understanding of the reasons for the production of the alternation effect it is necessary to study its relation to the structure of the molecules of the sorbates and stationary phases and the intermolecular interactions in the chromatographic column.

***

Thus the effect of alternation of chromatographic characteristics is observed both in homologous series of sorbates and stationary phases (the even–odd effect) and in other series (for example on the "displacement" of a functional group along an aliphatic chain). The scale of the alternation for a sufficiently rigid molecular structure may reach 10–13 retention index units. The effect is detected in distribution and adsorption chromatography. Further studies may reveal this effect in other forms of chromatography (supercritical fluid, thin-layer, etc.). Different forms of alternation will possibly be detected.

References

1. M S Vigdergauz, E I Petrova *J. Chromatogr.*, 1990, **509** 15
2. A E Chichibabin *Osnovnye Nachala Organicheskoi Khimii* (Basic Principles of Organic Chemistry), Vol. 1, Goskhimizdat, Moscow, 1953, p. 164
3. K Van Nes, H A Van Westen *Aspects of the Constitution of Mineral Oils* (Translated into Russian), Inostr. Lit., Moscow, 1954, p. 116
4. B I Tetyunnikov *Khimiya Zhirov* (The Chemistry of Fats), Pishchevaya Promyshlennost', Moscow, 1966, p. 14
5. R C Crippen *Identification of Organic Compounds with the Aid of Gas Chromatography*, McGraw-Hill Book Co., New York, 1973, 331 pp
6. I V Sushkin, I G Chistyakov, collected papers *Struktura i Svoistva Zhidkikh Kristallov i Vysokomolekulyarnykh Veshchestv* (The Structure and Properties of Liquid Crystals and Macromolecular Substances), Vol. 62, No. 1, Uchen. Zapiski IGPI, Ivanovo, 1967, p. 22
7. S I Zhdanov (Editor) *Zhidkie Kristally* (Liquid Crystals), Khimiya, Moscow, 1979, p. 18
8. Yu B Amerik, B A Krentsel' *Khimiya Zhidkikh Kristallov i Mezomorfnykh Polimernykh Sistem* (The Chemistry of Liquid Crystals and Mesomorphic Polymer Systems), Nauka, Moscow, 1981, p. 68
9. L Sojak, G Kraws, P Farkas, I Ostrovsky *J. Chromatogr.*, 1984, **294** 155
10. R V Vigalok, G G Maidachenko, G A Seichasova, et al., collected papers *Uspekhi Gazovoi Khromatografii* (Gas Chromatography Reviews), No. 4, Part 1, Izd. Inst. Org. Fiz. Khim. im A E Arbuzova, Kazan', 1975, p. 115
11. E A Kopelyan *Zhidkie Kristally i ikh Prakticheskoe Ispol'zovanie. Tezisy Dokladov 6 Vsesoyuznoi Konferentsii* (Summaries of Papers Presented at the Sixth All Union Conference on Liquid Crystals and Their Practical Application), Vol. 3, Chernigov, 1988, p. 349
12. O A Osipov, V I Minin *Spravochnik po Dipol'nym Momentam* (Reference Book of Dipole Moments), Vysshaya Shkola, Moscow, 1971
13. H P Kaufmann *Analyse der Fette und Fettprodukte. B*, Springer Verlag, 1958, p. 148
14. *Kratkaya Khimicheskaya Entsiklopediya* (Short Chemical Encyclopedia), Sovetskaya Entsiklopediya, Moscow, 1963
15. A L Markman, collected papers *Khimiya Lipidov* (The Chemistry of Lipids), No. 2, Izd. FAN, Tashkent, 1970, p. 23
16. J Liepins, M S Vigdergauz, collected papers *Uspekhi Gazovoi Khromatografii* (Gas Chromatography Reviews), No. 5, Izd. Inst. Org. Fiz. Khim. im A E Arbuzova, Kazan', 1978, p. 83
17. A Kamradzis, J Liepins, I Jankovska, J Stradins *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, 1977, No. 1, p. 69
18. M S Vigdergauz, E I Petrova, S V Sosnina, T K Florova *Izv. Vys. Ucheb. Zaved. SSSR, Khim. Khim. Tekhnol.*, 1991, **34**(6) 28
19. B P Nikol'skii (Editor) *Spravochnik Khimika* (Chemist's Reference Book), Vol. 1, Khimiya, Moscow–Leningrad, 1964, 1070 pp
20. B P Nikol'skii (Editor) *Spravochnik Khimika* (Chemist's Reference Book), Vol. 2, Khimiya, Moscow–Leningrad, 1966, 1167 pp
21. A A Potekhin (Editor) *Svoistva Organicheskikh Soedinenii* (The Properties of Organic Compounds), Khimiya, Leningrad, 1984, 518 pp
22. N B Vargaftik *Spravochnik po Teplofizicheskim Svoistvam Gazov i Zhidkostei* (Reference Book on the Thermophysical Properties of Gases and Liquids), Fiz.-Mat. Lit., Moscow, 1963, 708 pp
23. I A Leenson *Chet ili Nechet? Zanimatel'nye Ocherki po Khimii* (Even or Odd? Entertaining Essays in Chemistry), Khimiya, Moscow, 1987, p. 102

24. E Kovats *Helv. Chim. Acta,* 1958, **41** 1915
25. A N Korol' *Nepodvizhnaya Faza v Gazozhidkostnoi Khromatografii* (The Stationary Phase in Gas–Liquid Chromatography), Naukova Dumka, Kiev, 1969, p. 60
26. V G Arakelyan, collected papers *Gazovaya Khromatografiya* (Gas Chromatography), No. 10, Izd. NIITEKhim, Moscow, 1969, p. 38
27. V M Sakharov, V S Voskov, collected papers *Gazovaya Khromatografiya* (Gas Chromatography), No. 10, Izd. NIITEKhim, Moscow, 1969, p. 76
28. L Rohrschneider *Chromatographia,* 1969, **12** 437
29. B I Anvaer, M S Vigdergauz, V I Semkin, collected papers *Novye Adsorbenty dlya Khromatografii* (New Adsorbents for Gas Chromatography), No. 18, Izd. NIITEKhim, Moscow, 1972, p. 38
30. L Sojak, P Maher, J Krupcik, J Janak *J. Chromatogr.,* 1972, **65** 143
31. L Sojak, P Zahradnik, J Leska, J Janak *J. Chromatogr.,* 1979, **174** 97
32. M S Vigdergauz, V I Semkin *Zh. Fiz. Khim.,* 1972, **46**(4) 948 [English translation in *Russ. J. Phys. Chem.,* 1972(4)]
33. L Sojak, J A Rijks *J. Chromatogr.,* 1976, **119** 505
34. L Sojak, J Janak, J A Rijks *J. Chromatogr.,* 1977, **135** 71
35. L Sojak, M S Vigdergauz *J. Chromatogr.,* 1978, **148** 159
36. L Sojak, J Janak *Zh. Anal. Khim.,* 1978, **33** 574
37. M S Vigdergauz, V J Semkin *J. Chromatogr.,* 1978, **158** 57
38. V I Semkin, S K Lezina *Zh. Fiz. Khim.,* 1979, **53**(6) 1537 [English translation in *Russ. J. Phys. Chem.,* 1979(6)]
39. J K Haken, B G Madden, I O O Korhonen *J. Chromatogr.,* 1984, **298** 150
40. E I Petrova, E Yu Gerasimova, S V Sosnina, M S Vigdergauz *Izv. Vys. Ucheb. Zaved. SSSR, Khim. Khim. Tekhnol.,* 1988, **31**(6) 81
41. J Liepins, M S Vigdergauz *Tezisy II Vsesoyuznoi Konferentsii po Metodam Polucheniya i Analiza Biokhimicheskikh Preparatov* (Summaries of Papers Presented at the Second All-Union Conference on Methods for the Preparation and Analysis of Biochemical Products), Izd. NIITEKhim, Cherkassy, 1977, p. 148
42. V A Shcheglova, M S Vigdergauz, V I Romanova *Zh. Anal. Khim.,* 1988, **43** 333
43. N B Kuznetsova, O A Vladimirova, I A Ovechkin, et al. *Tezisy Dokladov Seminara po Khromatografii Zhidkikh Kristallov i Zhidkim Kristallam v Khromatografii* (Summaries of Papers Presented at the Seminar on Liquid Crystals in Chromatography and the Chromatography of Liquid Crystals), Kuibyshev, 1983, p. 28
44. L Sojak, G Kraus, P Farkas, I Ostrowsky *J. Chromatogr.,* 1982, **249** 29
45. H Kelker, E Von Schivizhoffen *Adv. in Chromatogr.* (Editors, J C Giddings, R A Keller), 1968, Vol. 6, p. 247
46. R V Vigalok, A M Tsybulevskii, M S Vigdergauz *Neftepererabotka i Neftekhimiya. Spetsial'nyi Vypusk Posvyashchennyi XI Mezhdunarodnomu Gazovomu Kongressu* (Petroleum Processing and Petroleum Chemistry. Special Edition Dedicated to the Eleventh International Gas Congress), Izd. TsNIITENeftekhim, Moscow, 1970, p. 12
47. M S Vigdergauz, R V Vigalok *Neftekhimiya,* 1971, **11** 141
48. USSR P. 455 276; *Byull. Izobret.,* 1974, (48)
49. N F Belyaev, M S Vigdergauz, G V Dmitrieva *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1989, (1) 15
50. V F Novikov, M S Vigdergauz, collected papers *Khimiya Zhidkikh Kristallov. Primenenie v Khromatografii* (The Chemistry of Liquid Crystals. Applications in Chromatography), Kuibyshev, 1987, p. 77
51. L V Ryazanova, V F Novikov, G G Maidachenko, M S Vigdergauz *Izv. Vys. Ucheb. Zaved. SSSR, Khim. Khim. Tekhnol.,* 1988, **31**(2) 47
52. N F Belyaev, K V Egorova *Izv. Vys. Ucheb. Zaved. SSSR, Khim. Khim. Tekhnol.,* 1989, **32**(2) 74
53. E E Bray, E D Evans, collected papers *Organic Geochemistry* (Translated into Russian), No. 1, Nedra, Moscow, 1967, p. 174
54. B J Mair, collected papers *Organic Geochemistry* (Translated into Russian), No. 1, Nedra, Moscow, 1967, p. 144
55. J Hunt, collected papers *Organic Geochemistry* (Translated into Russian), No. 3, Nedra, Moscow, 1971, p. 217
56. A F Shlyakhov *Gazovaya Khromatografiya v Organicheskoi Geokhimii* (Gas Chromatography in Organic Geochemistry), Nedra, Moscow, 1984, p. 31
57. E E Bray, E D Evans *Geochim. et Cosmochim. Acta,* 1961, **22** 2
58. G I Safonova, L M Bulekova *Novye Metody Issledovaniya Sostava Neftei* (New Methods for Studying the Composition of Petroleum), Moscow, 1972, p. 193
59. A A Petrov *Uglevodorody Nefti* (Petroleum Hydrocarbons), Nauka, Moscow, 1984, p. 63
60. M S Vigdergauz, V I Kozyuro, S K Lezina, V I Semkin *Zh. Fiz. Khim.,* 1981, **55**(8) 2188 [English translation in *Russ. J. Phys. Chem.,* 1981(8)]
61. V I Semkin, S K Lezina, M S Vigdergauz, collected papers *Uspekhi Gazovoi Khromatografii* (Gas Chromatography Reviews), No. 6, Izd. Inst. Org. Fiz. Khim. im A E Arbuzova, Kazan', 1982, p. 147
62. T P Safronova, S G Shvedova *Migratsiya Uglevodorodov i Usloviya Formirovaniya Kollektorov Nefti* (The Migration of Hydrocarbons and the Conditions of Formation of Petroleum Reservoirs), Nauka, Moscow, 1982, p. 5
63. V I Semkin, S K Lezina, M S Vigdergauz *Izv. Vys. Ucheb. Zaved. SSSR, Khim. Khim. Tekhnol.,* 1984, **27**(2) 215
64. J K Haken, I O O Korhonen *J. Chromatogr.,* 1986, **356** 79
65. O Eisen, A Orav, S Rang *Chromatographia,* 1972, **5** 229
66. K Heyne, H Roper *J. Chromatogr.,* 1973, **82** 87
67. J K Haken, I O O Korhonen *J. Chromatogr.,* 1983, **265** 323
68. J K Haken, I O O Korhonen *J. Chromatogr.,* 1984, **284** 474
69. I O O Korhonen *J. Chromatogr.,* 1985, **298** 101
70. N F Belyaev, M S Vigdergauz, K V Egorova, collected papers *Khimiya Zhidkikh Kristallov. Primenenie v Khromatografii* (The Chemistry of Liquid Crystals. Applications in Chromatography), Kuibyshev, 1987, p. 76

Received 17th July 1992

Translated from *Uspekhi Khimii* **61** 2187–2214 (1992) U.D.C. 541.64:678.02:66.095.3

Characteristic features of the chemical kinetics of the formation of interpenetrating polymer networks

Yu S Lipatov, T T Alekseeva
Institute of the Chemistry of Macromolecular Compounds, Academy of Sciences of the Ukraine, Kiev

ABSTRACT. Data on the kinetics of the formation reactions of interpenetrating polymer networks (IPN) are surveyed. They are formed in the course of the simultaneous cross-linking in the reaction system of two three-dimensional networks which do not react chemically. It was established that the kinetics of the formation of the network components forming part of the IPN differ from those for the "pure" networks. The mutual influence of the networks formed on the kinetics of their formation depends on the composition of the IPN, the ratio of the rates of the component reactions, and the order in which the reactions are carried out.

A characteristic feature of the formation of the IPN is that, even in the early stages of the reactions of the system, a thermodynamic incompatibility of the molecular fragments of the component networks arises as a rule.

The bibliography includes 46 references.

Contents

I. Introduction 1203
II. The influence of the components of one network on the kinetics of the formation of the second network during the consecutive generation of interpenetrating networks 1204
III. Kinetics of the formation of interpenetrating networks taking into account the interrelation of the processes and the influence on the microphase separation 1207
IV. Conclusion 1218

I. Introduction

It has now been established that the properties of polymeric materials based on interpenetrating polymer networks (IPN) depend on the thermodynamic compatibility of the constituent networks and the kinetics of the chemical reactions which establish the microphase separation at a particular level.

Analysis of the literature data shows that an increasing number of studies are now being published on this problem. Whereas the structure and properties of the IPN were previously studied mainly in the laboratories of Frisch, Sperling, and Lipatov, which led to the discovery of their principal structural features and a set of properties determined by the microheterogeneity of the IPN, nowadays Hourston, Meyer, Widmaier, and Hsu are engaged in the problem of the creation and study of the IPN. Investigations by Japanese and Chinese investigators have been published. Many polymer compositions for the production of IPN have been tested. For example, Kim et al.[1] investigated modern IPN based on polyurethane–polystyrene or polyacrylates, Hourston and co-workers[2] studied by the ^{13}C NMR method the structure and properties of IPN based on polyurethane-polyphenylsiloxane, Djomo, Morin, and co-workers[3] investigated the mechanical properties of IPN based on polyurethane–poly(methyl methacrylate), Bi Xiping, Li Binyao and co-workers[4,5] studied those based on poly(vinyl acetate)–poly(methyl methacrylate), and Burford et al.[6] investigated by mechanical dynamic spectroscopy IPN based on a cross-linked butadiene or butadienestyrene elastomer and polystyrene. Visscher et al.[7] studied by differential scanning calorimetry and IR spectroscopy new class of IPN based on polyorganophosphazenes and poly(methyl methacrylate), which are biocompatible and resistant to oil. The majority of studies were devoted to the synthesis and investigation of the mechanical and viscoelastic properties[8–11] and the morphology[12–14] of the materials obtained. However, in order to be able to employ the IPN in different technologies, it is essential to understand in detail the kinetics of the hardening reaction and the microphase separation processes in polymeric two-phase systems and the influence of these parameters on the viscoelastic and mechanical properties of such systems.[15,16]

A characteristic feature of interpenetrating networks is that the phase separation processes occur as a result of the formation of heterogeneous networks from an initially single-phase system, so that the degree of microphase separation is determined by the kinetics of the formation of the components. IPN can be obtained in two ways: with simultaneous and consecutive formation of polymer networks. The initial system is usually single-phase—in the simultaneous formation process it is a solution of components forming two networks, while in the consecutive formation process it consists of a swollen gel. Since microphase separation begins simultaneously with the chemical reaction at a certain degree of conversion, the properties of the IPN are determined by the differences between the rates of formation of individual networks, which can be varied within wide limits by altering the hardening temperature for each component, the catalyst concentration, the concentration of the cross-linking agent, the hardening sequence using thermo- or photohardening, and the component ratio in the IPN formed. It is also essential to take into account the fact that in the case of both consecutively and simultaneously formed IPN the formation reactions of one of the networks take place in the matrix of the other.

In the simultaneous formation of IPN, the kinetics of the formation reactions of the constituent networks are different and the reactions proceed via different mechanisms (polyaddition–polymerisation), one of the networks being formed usually at an earlier stage and serving as the matrix for the formation of the other. The network formed first (the matrix network) alters significantly the

conditions in the formation reaction of the second network, becoming segregated as a microphase as a consequence of the resulting thermodynamic incompatibility of the chains of the constituent networks. This affects the diffusion parameters of the formation reaction of the second network.

Although the factors listed above provide grounds for the hypothesis that there are differences between kinetics of the formation of the interpenetrating networks and the individual polymer networks, sufficient attention has not yet been devoted to the study of this problem. Vigorous investigation of the kinetics of the reactions, occurring simultaneously and consecutively via different mechanisms and influencing one another, has begun only in recent years.

II. The influence of the components of one network on the kinetics of the formation of the second network during the consecutive generation of interpenetrating networks

Studies on the formation of IPN began comparatively recently. This is associated primarily with the fact that, on passing from the study of individual polymer networks to IPN, the kinetics become more complex, apparently as a consequence of the rapid increase in the viscosity of the reaction medium during both polycondensation and radical polymerisation and the mutual influence of the two processes occurring in the IPN produced.

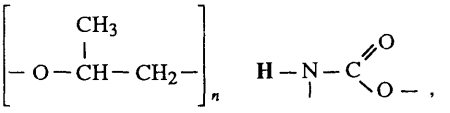
The first studies on kinetics of the formation of IPN were carried out by Djomo et al.[3] in relation to two network polyurethane–poly(methyl methacrylate) polymers. The polyurethane (PU) network was formed from a flexible polyoxypropylene glycol (POPG) block with a molecular weight of 2000 and an aromatic triisocyanate adduct. The catalyst was tin octanoate (OcSn). The poly(methyl methacrylate) (PMMA) network was obtained by copolymerising methyl methacrylate (MMA) and tri(hydroxymethyl)-propane trimethyacrylate using a radical polymerisation initiator 2,2-azobisisobutyronitrile (AIBN). The PU network was formed first at room temperature and this was then followed by the formation of the PMMA network at 50 °C. The influence of all the components of the PMMA network on gel formation in the PU network was studied in succession and a similar study was made of the influence of the components of the PU network on gel formation in the PMMA network. The influence of the OcSn catalyst on the rate of formation of the PMMA network was investigated. It was observed that the components of the PMMA network do not affect the gel formation in the PU network, whereas the components of the PU network diminish the gel formation time from 180 to 30 min. This is induced by the increase in viscosity of the reaction medium, which increases the rate of formation of the PMMA network (V_p) in the presence of the components of the PU network as a result of the decrease in the termination rate constant (K_t) in accordance with the equation[17]

$$V_p = \frac{K_p[M]\sqrt{V_{in}}}{\sqrt{K_t}}, \qquad (1)$$

where [M] is the monomer concentration, K_p the chain propagation rate constant, V_p the rate of chain propagation, V_{in} the rate of initiation, and K_t the termination rate constant.

The influence of the OcSn catalyst on the rate of formation of the PMMA network was studied in greater detail by Meyer.[18] Data for the electrical conductivity of the system led the author to the conclusion that the catalyst does not affect the rate of decomposition of the initiator but does accelerate the polymerisation and copolymerisation of the methacrylates as a result of the polarisation of the monomer double bonds and facilitates the addition of radicals to the latter, inducing thereby an acceleration of the formation reaction of PMMA in the presence of the OcSn catalyst.

The possibility of the formation of a chemical bond between the PU and PMMA networks has also been studied. The presence in the reaction medium of two components of the PU network–polyoxypropylene glycol and the triisocyanate adduct, i.e.



containing a mobile hydrogen atom which can be abstracted by a radical, suggests a possible way in which the reaction may be transmitted, which can be represented schematically as follows:

Stage I:

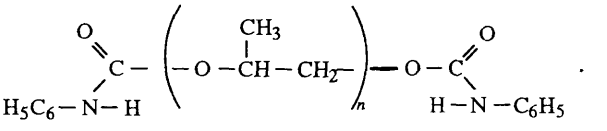
$$Ac^{\cdot} + T \longrightarrow Ac + T^{\cdot}.$$

Stage II:

a) $T^{\cdot} + Ac \rightarrow T \sim Ac^{\cdot}$;

b) $T^{\cdot} + Ac^{\cdot} \rightarrow T \sim Ac$,

where Ac is the MMA monomer, T the component containing the oxypropylene or urethane group, and $Ac^{\cdot}$ and $T^{\cdot}$ are the corresponding radicals. If reactions (IIa) and (IIb) occur, then a chemical bond is formed between PU and PMMA. To confirm this hypothesis, a mixture of methacrylate monomers with different amounts of the α,ω-phenylurethane–POPG adduct was polymerised under the experimental conditions described above:



The products were extracted with a solvent and were analysed by IR spectroscopy. It was observed that the PU component is extracted to an extent greater than 90% (of the amount introduced). For the system containing 20% PU and 80% PMMA, 1.8% PU remained after extraction in the poly(methyl methacrylate) network. This is a low value, so that even if a chemical graft does exist, it is so small that its influence on the macroscopic properties of the IPN is insignificant.

The above study[18] constituted the first step in the investigation of the complex IPN systems. The author showed that it is essential to take into account the influence of each component of one network on the formation of the second network, and conversely, as well as the possibility of side reactions, which may disturb or prevent the formation of one of the networks.

The influence of the concentration of the cross-linking agent and the initiator for the polyacrylate network, of the NCO/OH ratio, and of the component ratio PU/PMMA on the transparency and the viscoelastic properties of the resulting IPN and semi-IPN was demonstrated in subsequent studies.[19–22] Fourier transform IR

spectroscopy[23] was used to investigate the kinetics of the formation of IPN and semi-IPN based on PU and PMMA, obtained as described by Meyer.[3] The method makes it possible to study the kinetics of the simultaneous formation of IPN (the NCO group absorbs in the region of 2275.5 cm^{-1}, while the C=C bond absorbs at 1639 cm^{-1}). The authors[23] studied the influence of the various factors (temperature, concentration of the cross-linking agent, concentration of PU in solution) on the formation of individual PU and PMMA networks forming part of the composition of the IPN. In the study of the PU network in ethyl acetate (EA) with the concentration ratio PU/EA = 25/75 wt.%, the rate of formation of PU increased with increase in the OcSn catalyst concentration from 0.38 to 1.0 wt.% but a further increase in catalyst concentration to 2 wt.% did not affect the rate of formation of PU. It has also been shown that an increase in the PU content in ethyl acetate for a constant catalyst content increases the rate of formation of the PU network and that the temperature at which the PU network is formed has a similar effect. In the study of the formation of PMMA it was observed that the cross-linking agent accelerates the formation of the network structure of the PMMA compared with the linear polymer and that under these conditions the onset of autoacceleration shifts towards shorter times, whilst the presence of the OcSn catalyst intensifies the copolymerisation effect.

The study of the simultaneously formed IPN having the composition PU/PMMA = 34/66 (wt.%) by Fourier transform (FTIR) IR spectroscopy showed that the nature of the PU and PMMA kinetic curves does not differ from the initial curves and it was concluded on this basis that there is no chemical interaction between the two IPN networks.

Subsequently the IPN network based on the same PU–PMMA system was investigated by FTIR spectroscopy[24] under conditions of stepwise polymerisation. Polyurethane was polymerised at room temperature, while PMMA was polymerised at 60 °C. The influence of the catalyst concentration and of the PU/PMMA ratio on the rate constants for the urethane formation reaction in the IPN at room temperature was investigated. In the study of the kinetics of the formation of the PU network in the IPN for the component ratio PU/PMMA = 34/66 (wt.%) with the reactions occurring simultaneously, it was observed that the rate of urethane formation increases by a factor of 8 when the temperature is raised to 60 °C. The order of the reaction was found over a wide range of NCO conversions. The authors believe that the equation

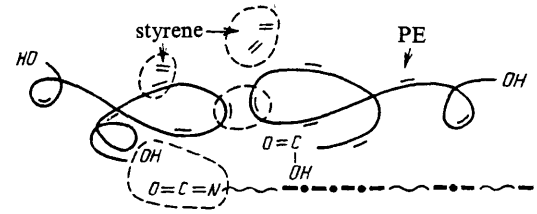
$$d[NCO]/dt = K[OcSn][NCO]^{1.5},$$

describes satisfactorily the formation of the PU network in the IPN under the conditions of both stepwise and simultaneous formation of both networks.

The search for new ways of synthesising IPN led Derrough et al.[25] to a simple but novel solution of the problem of synthesising IPN via a radical mechanism *in situ*. The butyl acrylate or methyl methacrylate (MMA) and diallyl carbonate–bisphenol A (DACBA) monomers were used to repair the IPN. The novelty of the method of synthesis consists in the choice of compounds which initiate the reaction only in a specific temperature range. AIBN, which operates at temperatures above 50 °C, was chosen for butyl acrylate or methyl methacrylate, while t-butylperoxy-3,5,5-trimethylhexanoate (TBPTMH), which initiates the reaction above 95 °C, was chosen for bisphenol A. The polymerisation mixture of MMA and DACBA in proportions of 50/50 (wt.%), containing the AIBN and TBPTMH initiators, was investigated by FTIR spectroscopy. The degree of conversion in the reaction was calculated from the change in the absorption band in the region of 1639 cm^{-1} characteristic of the C=C bond in MMA, with a shoulder at 1649 cm^{-1}, which corresponds to the allyl monomer. At 50 °C, the intensity of the 1639 cm^{-1} peak diminishes and reaches the base line, which corresponds to more than 95% conversion of the C=C bond in methyl methacrylate over a period of 2 h. With increase in temperature, the shoulder is unexpectedly transformed into an isolated peak, the intensity of which does not change so long as the temperature of the reaction medium does not reach 95 °C. After the attainment of this temperature, the peak intensity diminishes, indicating the polymerisation of the second component. After the introduction of the cross-linking agent, it is also possible to obtain the full IPN.

The influence of the methacrylate radicals on DACBA in the polymerisation of methyl methacrylate at 50 °C was investigated. UV analysis did not reveal the presence of the aromatic DACBA rings in the PMMA polymer chain. The nature and concentration of the radicals produced during the formation of the IPN were also investigated by the EPR method.[25] The results of this investigation agreed with the IR spectroscopic data. Consequently the authors clearly showed that the half-IPN or IPN can be obtained via a single mechanism (a radical mechanism) using different initiators. It would be of interest to have information about the phase state of the given IPN.

Hsu and Lee[26] investigated experimentally and theoretically the kinetics of the formation of IPN from polyurethane and an unsaturated polyester (PE). The PU component was obtained from a diisocyanate, a polyol, and a diol containing rigid and flexible segments; the PE component was obtained from an unsaturated polyester with styrene as the cross-linking agent involving the C=C bond in the polyester. The formation of a graft between the two PU and PE phases via the reaction of the NCO groups with the terminal OH or COOH groups of the PE molecules is possible. Such systems can be classified as graft IPN, which are illustrated schematically below.



The studies were carried out on an DSK-2S differential scanning calorimeter under isothermal and adiabatic conditions. The kinetics were studied for IPN obtained as a result of the RIM process (reaction injection moudling) and the usual casting. The kinetic measurements on the formation of the IPN by differential scanning calorimetry under isothermal conditions demonstrated that, as a consequence of different reaction mechanisms (polyaddition and radical polymerisation), the formation of urethane always begins after mixing the components and takes place under conditions where the PE phase does not yet react or only partly reacts, the PU being formed in solution in the components of the PE network, while the PE phase is frequently formed under conditions where the PU has been already fully or partly formed, i.e. the radical polymerisation of the polyester takes place fully or partly in the polymerised PU phase. However, the question of phase separation was not considered in the above study.

Fig. 1 shows that, with increase in the PU content in the IPN from 25/75 to 75/25 (wt.%), the peak for the PE reaction shifts to the right, which characterises the increase in the induction period due to the formation of the PE network, while the broadening of the peak indicates an increase in reaction time. This means that the diffusion of the PE reagents becomes hindered as the content of the PU network increases.

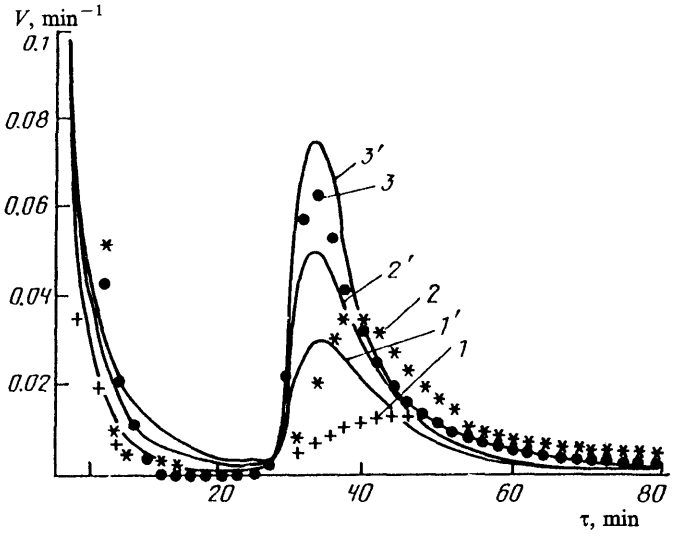


Figure 1. Time (τ) variation of the rate of reaction (V) for different ratios PU/PE in the IPN at T = 80 °C obtained experimentally (curves *1*–*3*) and calculated theoretically (curves *1'*–*3'*); PU/PE (wt.%): *1*, 75/25; *2*, 50/50; *3*, 25/75.[26]

The study of the formation of IPN under adiabatic conditions, modelling the RIM process, showed that the reaction takes place consecutively and the time variation of the degree of conversion of the components has the S shape characteristic of radical polymerisation for the component ratio PU/PE = 50/50 (wt.%). With increase in the fraction of the PU component in the IPN to 75/25 wt.%, the form of the curve changes, since the urethane formation reaction predominates in the overall process.

Using models based on the additive contributions of the initial components of the IPN, the authors[26] carried out a theoretical calculation for the model reaction under isothermal and adiabatic conditions involving the IPN investigated. In the calculation for the model reaction, use was made of the Arrhenius equation and a number of assumptions which disregarded the mutual influence and interaction of the two polymer network structures formed in the system, were made.

The kinetic parameters of the PU reaction were calculated from the increase in the temperature of the reaction system under adiabatic conditions using the equation

$$\ln\frac{dT_u}{dt} = \ln\left[\frac{\Delta H_u A_u}{P_u C_{pu}}\right] + \frac{E_u}{RT_u} + n\ln\left[\frac{T_{ad} - T_u}{T_{ad} - T_{uo}}\right] ,$$

The variables dT_u/dt, $1/T_u$, and $[(T_{ad} - T_u)/\Delta T_{ad}]$ can be calculated from the time variation of the temperature in the adiabatic polymerisation. Using the multilinear regression method, the order of the reaction n, the activation energy E_u, and the pre-exponential factor of the rate constant A_u were calculated.

The kinetic parameters of the radical polymerisation of the polyester were calculated by Lee's method[27] from the equation

$$\left(2fI_0A_p\right)\exp\left(-\frac{E_p}{RT}\right) = \frac{K_d\exp[-K_d(t_m - t_z)]}{1 - \exp[-K_d(t_m - t_z)]} ,$$

where f is the effectiveness of the initiator, I the concentration, K_d the decomposition rate constant, and t the induction period.

The authors concluded that the theoretical calculations for the reactions of pure PU and PE agree well with experimental data obtained by differential scanning calorimetry under isothermal conditions. Slight discrepancies between the theoretical calculation and experiment are observed for the IPN having the composition PU/PE = 25/75 (wt.%), while an increase in the content of the PU network in the system to 50/50 (wt.%) increases the discrepancies, which become appreciable for the ratio PU/PE = 75/25 (wt.%). The authors attribute this to the fact that in the theoretical calculations no account was taken of the interaction between the components. Discrepancies with experiment are observed particularly for the PE polymerisation, which is probably associated with the effect of diffusion in the region of high conversions. The mathematical description of the model reaction for the IRM process under adiabatic conditions agrees well with experimental results, which can be explained by the high rate of the reaction under adiabatic conditions.

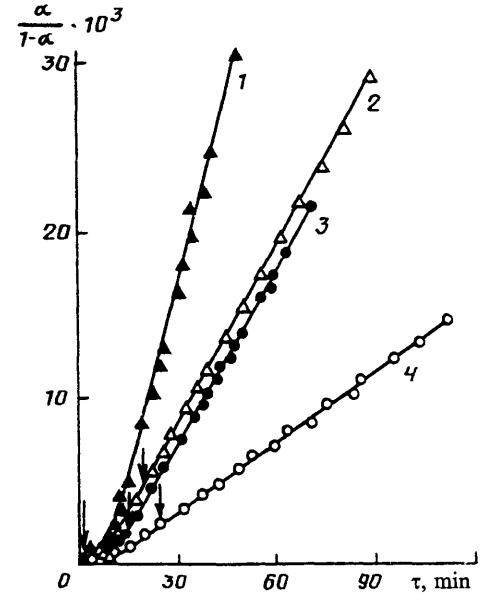


Figure 2. Transformed kinetic curves for the copolymerisation of styrene with divinylbenzene in a semi-IPN; the arrows indicate the onset of phase separation; PBMA content at T = 90 °C (wt.%): *1*, 40; *2*, 15; PBMA content at T = 80 °c (wt.%): *3*, 30; *4*, 15.[28]

III. Kinetics of the formation of interpenetrating polymer networks taking into account the interrelation between the processes and the influence on the microphase separation

The mutual influence of the kinetics of the formation of the polystyrene–divinylbenzene copolymer in the presence of poy(butyl methacrylate) (PBMA) and the microphase separation in the resulting IPN was investigated for the first time[28] in relation to a semi-IPN. Fig. 2 illustrates the linear forms of the kinetic curves for the copolymerisation of styrene with divinylbenzene in the semi-IPN for different proportions of the PBMA. The authors explain the absence of a break in the kinetic curves at the phase separation point by the fact that the microphase separation process in the semi-IPN produced proceeds via a spinodal mechanism, whereupon no visible volume effects are observed[29] and under such conditions the microphase separation (MPS) does not affect the rate of reaction. It has been established that, with increase in the content of PBMA in the mixture, the time of the onset of the MPS diminishes significantly, while an increase in temperature by 30 K likewise shortens the time of the onset of the MPS, the degree of conversion of the copolymer increasing under these conditions. It has also been shown that phase separation begins for low conversions of styrene in the range 0.1–8.0%. The authors conclude that there is a close relationship between the reaction kinetics, the degree of conversion, and the MPS in the system, the kinetics of the formation of the IPN exerting a significant influence on MPS processes, determining the onset of MPS.

Table 1. Physicochemical characteristics of the polyurethane network in the semi-IPN with the composition PBMA/PU = 15/100 (%).[30]

No. of specimen	Composition	T_h, °C	c_{ct}, wt.%	$10^4 K_r$, kg mol^{-1} s^{-1}	τ_{MPS}, min	α_{MPS}
1	PU	60	0.005	3.46	—	—
2	PU	60	0.010	7.63	—	—
3	PU	40	0.010	1.90	—	—
4	semi-IPN	60	0.005	1.30	100	0.13
5	semi-IPN	60	0.010	2.62	43	0.23
6	semi-IPN	60	0.050	8.10	28	0.39
7	semi-IPN	80	0.010	7.05	30	0.56
8	semi-IPN	40	0.010	0.73	290	0.48

Notation: T_h is the hardening temperature, c_{ct} the catalyst concentration, K_r the reaction rate constant, τ_{MPS} the time of the onset of the MPS, and α_{MPS} the degree of conversion at the instant of the onset of the MPS.

A study[30] of the formation of polyurethane in the presence of 15% PBMA was devoted to the establishment of the relationship between the kinetics of the hardening of the half-IPN and the MPS during the formation of the polymeric two-phase system. Analysis of the results, presented in Table 1, shows that the onset of the MPS depends directly on the rate constant of the urethane formation reaction. Variation of the rate of reaction achieved by varying the catalyst concentration alters the degree of conversion at which phase separation begins from 23 to 39%, while variation of the rate of reaction effected by varying the temperature (40–80 °C) leads to the considerable scatter in the degrees of conversion (from 23 to 56%). The transformed kinetic curves presented in Fig. 3 are characterised by the presence of two sections, which indicates a change in the rate of reaction in the system after the attainment of a definite degree of conversion. Comparison of experiments 1 and 4, 2 and 5, 3 and 8 reveals a decrease in the rate of urethane formation by a factor of 3 in the presence of PBMA, but the nature of the transformed kinetic curves remained qualitatively the same as before. The degree of conversion at which MPS begins does not agree with the degrees of conversion at which a break is observed in the transformed curves (except for experiment 8). The results do not indicate a change in the reaction kinetics when MPS begins or in the vicinity of the degree of conversion corresponding to this process, which indicates the occurrence of MPS via the spinodal mechanism in the half-IPN formed.[31] Consequently the results agree with those of Lipatov and Grigor'eva,[28] confirming unambiguously that the MPS depends significantly on the reaction kinetics, regardless of the type of reaction (radical polymerisation or polyaddition) and that a change in the kinetics of the formation of the two-phase system influences its viscoelastic properties.

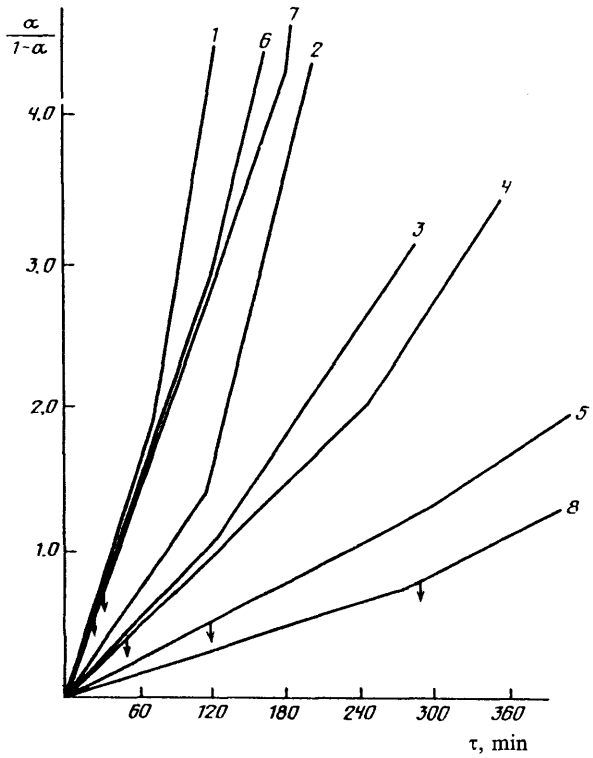


Figure 3. Transformed kinetic curves for the polyurethane network (curves *1–3*) in the semi-IPN based on polyurethane and PBMA (curves *4–8*); the significance of the symbols is indicated in Table 1.[30]

The kinetics of the formation of IPN based on polyurethane and polyurethane acrylate (in the IPN) were investigated for the first time by the method of distorted total internal reflection (DTIR) in the IR region with simultaneous hardening for different PU/OUA ratios (OUA = oligourethane acrylate). The transformed kinetic curves for the formation of polyurethane were linear up to a degree of conversion of 50%, which shows that the urethane formation reaction obeys a second-order equation. The initial slope of the curves (Fig. 4) depends significantly on the amount of oligourethane acrylate in the reaction mixture. Differentiation of these curves yielded the dependence of $|\partial\alpha/\partial\tau|$ on the composition, characterising the influence of the component ratio in the reaction mixture on the rate of the urethane formation reaction (Fig. 5). Fig. 5 shows that small amounts of added OUA play the role of an inhibitor of this reaction. For comparable amounts of the components in the OUA mixture, the formation of polyurethane is initially accelerated sharply, but, after the elapse of 45–60 min, the rate of formation of PU in the presence of PUA falls to values lower than in the individual PU.

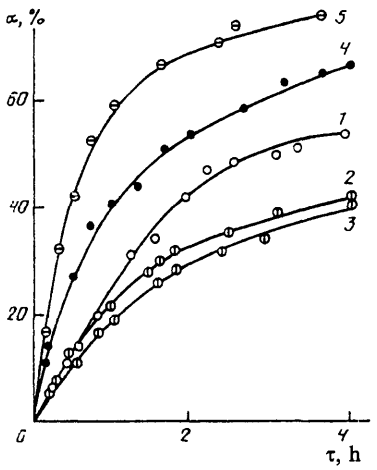


Figure 4. Kinetic curves for the hardening of pure polyurethane (curve *1*) and polyurethane in the IPN system; PUA (wt.%): *2*, 1; *3*, 5; *4*, 50; *5*, 70.[32]

Spectroscopic studies showed that the observed effect is not associated with the chemical interaction between unlike networks, since the spectra of the hardened IPN of different composition can be obtained by superimposing the spectra of the individual networks. On the other hand, some deviations from additivity, observed in the region of the stretching vibrations of the C=O and NH groups, indicate a redistribution of the network of physical bonds as the composition of the IPN is altered.

In IPN with comparable amounts of the components, the MPS process begins usually before the onset of gel formation in the individual networks, is fairly rapid, and is characterised by a high extent of completion. For both low and high OUA contents in the mixture, gel formation begins during the first 5–6 min of the reaction. The rapidly growing PUA network, segregated in the course of the MPS, displaces the reacting components of the first network (PU), intensifying their self-association and increasing the concentration of the reactants in the microregions, which accelerates the formation of polyurethane. Furthermore, the PUA segregated as a separate phase can play the role of a filler, which exerts an orienting influence on the components of the first network adsorbed on its surface, which can also accelerate its formation. The retardation of the polyaddition reaction at later stages of the formation of the IPN having this composition can apparently be explained by the fact that, as the reacting components are exhausted in the PU microregions, the process is controlled by the rate of diffusion of the components through the interface.

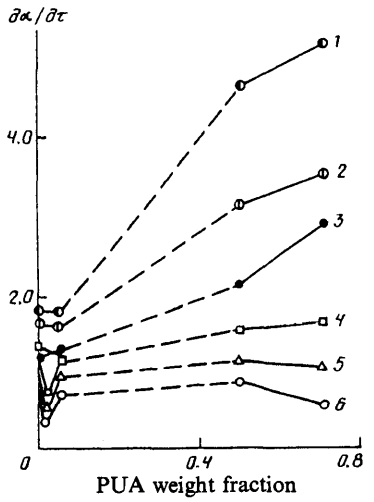


Figure 5. Concentration variation for the IPN; hardening time (min): *1*, 10; *2*, 20; *3*, 30; *4*, 45; *5*, 60; *6*, 90.[32]

For low contents of one of the components of the IPN, the MPS process is much slower. During the period investigated, the OUA has insufficient time to become segregated as a separate phase and the weakening of the bonds between the urethane groups and the appearance of free C=O groups (shoulder at 1740 cm^{-1}) indicates a significant redistribution of the intermolecular interactions after the introduction of small amounts of OUA.

These investigations showed that, in the formation of the IPN, the same component (OUA) can accelerate or retard the formation of the PU network depending on its fraction in the reaction mixture. We believe that this phenomenon is based on the dependence of the rate and the degree of completion of the MPS process on the composition of the reaction mixture. However, it has been shown[28,30] that the degree of MPS is a function of the rate of reaction. The onset of the MPS has been determined[30] during the reaction by the method of the appearance of turbidity points on an FPS-3 photocalorimeter. The experimental data (Table 1) show that, with increase in the rate constant for the formation of the PU network, the time of the onset of the MPS diminishes synchronously, which confirms unambiguously the dependence of the MPS on the reaction kinetics, whereas no breaks, which would indicate a change

in the rate of urethane formation at the instant of the onset of the MPS, are observed on the transformed kinetic curves for the formation of polyurethane at the point corresponding to the onset of the MPS (indicated by an arrow in Fig. 3).

The mutual influence of the kinetics of the formation of two unlike interpenetrating networks has been investigated in recent studies.[33–36]

Interpenetrating networks based on network polyurethane and an unsaturated polyester with styrene in molar proportions of 1 : 2 have been studied by FTIR spectroscopy[33] for simultaneous and consecutive reactions at 60 °C. Styrene served as an agent cross-linking polyester chains via the C=C bonds. Fig. 6 presents typical curves for the time variation of the degree of conversion for two phases (PU and PE) in the case of simultaneously produced IPN with a low-temperature radical polymerisation initiator for the component ratios PU/PE = 50/50 and 30/70 (wt.%). Similar kinetic curves are presented in Fig. 7 for the stepwise polymerisation of IPN with a high-temperature initiator.

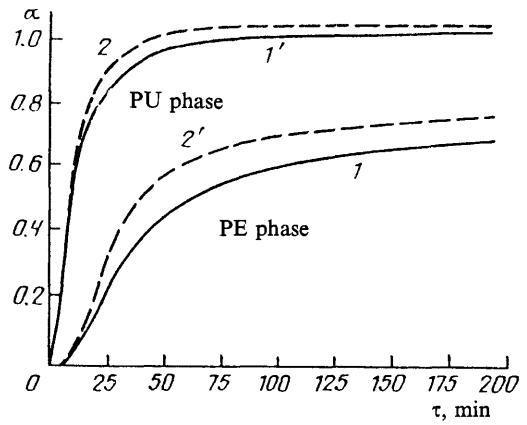


Figure 6. Time variation of the degree of conversion (α) for different PU/PE in the case of simultaneously formed IPN at T = 60 °C: *1*, 50/50; *2*, 30/70 (wt.%) (for polyurethane); *1′*, 50/50; *2′* 30/70 (wt.%) (for polyester).[33]

The use of the latter at 60 °C decreases the rate of reaction of the polyester component with the consecutive formation of IPN. It is of interest to note that, for both consecutively and simultaneously formed IPN, both reactions are accelerated with increase in the content of the polyester component 50 to 70 wt.%. The authors attribute this effect on the reaction of the polyester phase to the increased concentration of double bonds and, for the reaction of the polyurethane phase, to the fact that the rate of consumption of the NCO groups increases with the increase in the amount of the polyester component, since the NCO groups react with the OH groups of the polyol in the polyurethane phase and with the terminal OH groups of the unsaturated polyester. Consequently the degree of conversion in the polyurethane phase increases in proportion to the concentration of the polyester in the IPN, which indicates chemical interaction between the unlike polyurethane and polyester network structures and the given system can be classified as a graft IPN.

The polymerisation of the polyurethane in the IPN takes place in solution in the initial components of the polyester which have not yet reacted or have only partly reacted. On the other hand, the polymerisation of the polyester frequently takes place under conditions where the polyurethane network has been partly or fully formed, i.e. the polyester network is formed in the presence of the hardened second network, which is believed[33] to be in the solid state. Thus, when the IPN is created, there exists a "solvent effect" in the formation of the polyurethane network and a "solid effect" in the formation of the polyester network, which can influence the mechanism of the reactions occurring.

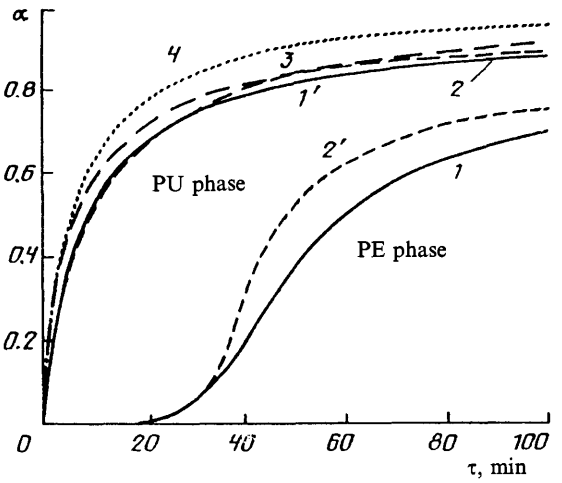


Figure 7. Time variation of the degree of conversion for different PU/PE in the case of consecutively formed IPN at T = 60 °C: *1–4*, for polyurethane; (*1′*, and *2′*) for polyester; *1*, PU/PE = 50/50; *2*, PU/PE = 30/70; *3*, PU/PE = 30/70; *4*, PU/PE = 50/50 (wt.%) [NCO/OH stoichiometric proportions (curves *1* and *2*)].[33]

Within the framework of formal kinetics, the authors obtained an equation for the overall rate of reaction in three possible versions: styrene–styrene, styrene–PE, PE–PE. The rate of reaction of the styrene monomer, the rate of conversion of the C=C bonds in the unsaturated polyester, and the rate of conversion of all the double bonds can be expressed thus:

$$-dc_S/d\tau = k_{SS}\cdot c_S\cdot c_S + k_{ES}c_E\cdot c_S,$$

$$-dc_E/d\tau = k_{SE}c_S\cdot c_E + k_{EE}\cdot c_E\cdot c_E,$$

$$-dc/d\tau = -(dc_S/d\tau + dc_E/d\tau) = k_{SS}\cdot c_S\cdot c_S + k_{ES}c_E\cdot c_S + k_{SE}c_S\cdot c_E + k_{EE}\cdot c_E c_{E'},$$

where S represents styrene, E represents the C=C bonds in the unsaturated polyester, S˙ and E˙ are the radicals in styrene and the polyester, c is the concentration, and k the rate constant. The rates of reaction can be determined experimentally from IR spectra.

Since the structure of the network in the polyester phase depends on the copolymerisation mechanism, information about the dependence of the degree of conversion of the polyester in the polyester phase is very important. Fig. 8 illustrates such dependences. If it is assumed that the contribution of the rate of the PE–PE

reactions to the overall rate is insignificant, then the rate of reaction of the styrene monomer can be expressed as follows relative to the rate of reaction of the C=C bonds in the polyester:

$$\frac{dc_S}{dc_E} = 1 + r_S \frac{c_S}{c_E}, \quad r_S = k_{SS}/k_{SE}.$$

If the copolymerisation takes place under azeotropic conditions, i.e.

$$c_E/c_S = 1 - r_S ,$$

then

$$\frac{dc_S}{dc_E} = \frac{c_S}{c_E} , \qquad \text{(curve 1)}$$

while for the alternative copolymerisation we have

$$\frac{dc_S}{dc_E} = 1 . \qquad \text{(curve 2)}$$

Experimental data for IPN show (Fig. 8, curve *3*) that the PE–PE reaction in the polyurethane network is more favourable at low conversions than the styrene–PE and styrene–styrene reactions. This is probably associated with the fact that the polyurethane phase can intensify the intermolecular reactions of the polyester molecules. On the other hand, at high conversions the styrene–styrene reaction is more favourable than the reaction involving the C=C bonds in the polyester.

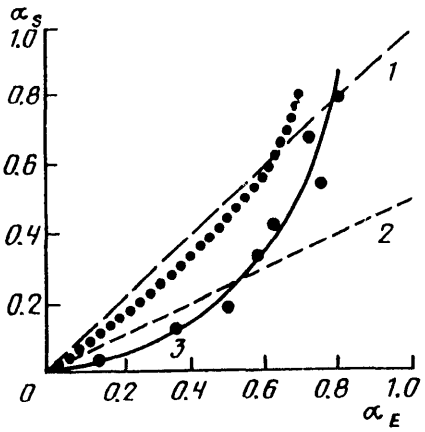


Figure 8. Dependence of the degree of conversion of styrene on the degree of conversion of C–C bonds for the PU–PE reaction in the IPN at T = 60 °C calculated theoretically for copolymerisation under azeotropic conditions (curve *1*) and for alternating copolymerisation (curve *2*) and determined experimentally for the 30/70 (wt.%) composition.[33]

The authors[33] concluded that the kinetics of the urethane formation reaction in bulk differ from the kinetics of the reaction in solution. However, if the IPN is created, the "solvent effect" operates in the formation of the polyurethane network and the "solid effect" operates in the formation of the polyester network, the two effects altering the mechanisms of both reactions. However, as regards the formation of the polyurethane in the presence of the polyester component, the authors do not take into account the "solvent effect" in their explanation of the increase in the rate of urethane formation with increase in the content of the polyester component in the IPN.

Fully grafted, half-grafted, and non-grafted IPN have been obtained[34] for three unsaturated polyesters and a polyurethane. The kinetics of the formation of the IPN as well as the rheological and morphological properties of the IPN obtained were investigated by differential scanning calorimetry, electron microscopy, and dynamic mechanical spectroscopy. The polyurethane component was obtained from diphenylmethane diisocyanate (MDI) and polycaprolactonetriol. The polyester component was obtained from the unsaturated polyester in the presence of styrene. The unsaturated polyester was synthesised from maleic anhydride and propylene glycol. The industrial non-block polyester contained terminal OH and COOH groups, the synthesised polyester contained only COOH groups, and the third type of unsaturated polyester was blocked using phenyl isocyanate.

Consequently fully grafted IPN were obtained on the basis of the industrial polyester, since there is a possibility of the interaction of the terminal OH and COOH groups with the NCO groups of the diisocyanate. Half-grafted IPN were obtained from the synthesised polyester as a result of the reaction of the COOH and NCO groups, while the blocked polyesters yielded non-grafted IPN.

Studies on such complex systems have shown that a better phase compatibility is characteristic of the fully grafted IPN, in contrast to the grafted and non-grafted IPN. It is manifested in the temperature variations by a broad peak in the range between 60° and 120 °C. The half-grafted IPN have three distinct peaks at 38°, 74°, and 120 °C, while the non-grafted IPN exhibit a high and broad peak at 50 °C and a shoulder at 99 °C. As the chemical interaction between the phases intensifies, the modulus of shear G' increases under these conditions. Thus the authors concluded that the interaction between the two phases plays an important role in decreasing the spreading of the phase separation between the polyurethane and polyester networks and also affects the kinetics of the formation of the IPN itself.

The relation between the kinetics of the formation of the two unlike three-dimensional structures in the IPN was also investigated for polyurethane–polyester acrylate.[35] The rate of hardening of polyurethane was determined by the ratio of the tri(hydroxymethyl)-propane–tolylene diisocyanate adduct and the oligoglycol, while the rate of hardening of polyester acrylate (PEA) was specified by the concentration of the initiator AIBN (0.01% for series I, 0.5% for series II, and 3.0% for series III). The kinetics of the formation of the IPN were investigated by the DTIR method. Figs. 9 and 10 illustrate the kinetic curves for the hardening of the polyurethane and PEA networks separately and in the blend. Judging from the slopes of these curves, the rates of cross-linking of unlike networks in the IPN, obtained by the single-stage method, are not independent.

Special experiments showed that the mutual influence is not associated with the chemical interaction between the networks. The authors determined the rate of hardening $\partial\alpha/\partial\tau$ of polyurethane or PEA at each point on the curve from the dependence of $\partial\alpha/\partial\tau$ on the composition of the IPN for different contents of the initiator at fixed time intervals elapsed since the beginning of the reactions. It was shown that the rate of urethane formation in the IPN depends, especially in the initial stages, on the concentration of the oligoester

acrylate and on the rate of its hardening. In the presence of small amounts of additives, the PEA network retards the cross-linking of the polyurethane. The oligoester acrylate inhibits the cross-linking in the series I specimens, where it is hardened at a lower rate than the individual polyurethane. In the series II specimens, the oligoester acrylate hardening at a higher rate inhibits the cross-linking of the matrix network less effectively. In series III, the retardation of the urethane formation reaction is observed over a wide range of compositions.

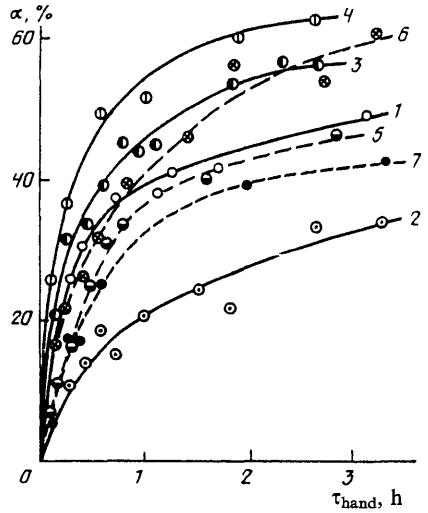


Figure 9. Kinetic curves for the hardening of pure polyurethane (curve *1*) and the polyurethane in the IPN for different PEA contents (wt.%): *2*, 0.5; *3*, *6*, and *7*, 2; *4*, 20; *5*, 0.3; curves *1*–*4* refer to series I, curves *5* and *6* to series II, and curve *7* to series III;[35] τ_{hard} = hardening time.

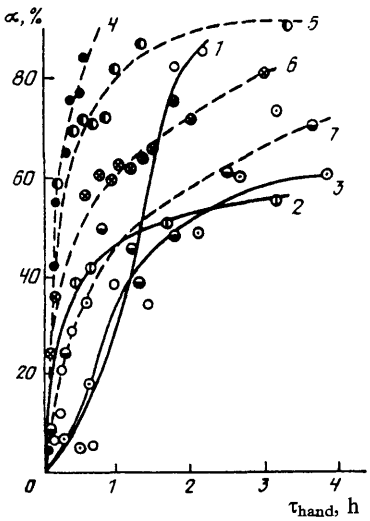


Figure 10. Kinetic curves for the hardening of pure PEA (curves *1* and *4*) and the PEA in the IPN for different PU contents (wt.%): *2*, and *6*, 30; *3*, and *7*, 50; *5*, 10; curves *1*–*3* refer to series I and curves *4*–*7* to series II.[35]

In the range of average compositions, the oligoester acrylate (OEA) accelerates the cross-linking of the polyurethane already in the initial stages of the reaction and the effect depends on the rate of hardening of the OEA. The rate of formation of PEA in the IPN is determined in its turn both by the initiator concentration and by the content of polyurethane. In the series I IPN, the polyurethane hardening at a higher rate initiates the cross-linking of the OEA in the experimental range of compositions. On the other hand, in series II, where the rate of its hardening is lower than that of the OEA, it behaves as an inhibitor of this process.

As the reaction mixture is hardened, the chemical composition and the system of intermolecular interactions continuously change. At a certain degree of conversion, the growing networks become thermodynamically incompatible. Following the onset of microphase separation, the influence of the PEA network on the hardening of the polyurethane should weaken. Indeed, the rate of hardening of the adduct in the IPN approaches the rate of hardening of the pure polyurethane as the reaction develops. After a time, microregions of the "rigid block" type arise in the segregated polyurethane phase, which is indicated by the appearance in the spectrum of bands due to the self-associated urethane groups at 1710 to 1720 cm^{-1}.

On the basis of the results, the authors conclude that, for the simultaneously formed IPN, the rates of hardening of unlike networks are related via the microphase separation process. In IPN with small amounts of the second network, the time of the onset of microphase separation increases sharply and the hardening of the IPN having this composition is characterised by a low degree of segregation of the components and by diffuse phase boundaries.

It is of interest to investigate the kinetics of the formation of simultaneously produced IPN based on polyurethane and polystyrene (PS) by IR spectroscopy.[36] The effects of temperature, of the concentrations of the catalyst, the initiator, and the cross-linking agent for polystyrene, and of the PU/PS ratio on the rates of the formation reactions of polyurethane and polystyrene were investigated. The kinetic results for the urethane formation reaction obtained spectroscopically agree with data obtained by chemical titration. It was shown that, with increase in the ratio PU/PS, the rate of formation of polyurethane increases and the rate of formation of polystyrene diminishes. The variation of the concentration of the catalyst (OcSn) affects the rate of formation of polyurethane but not the rate of formation of polystyrene in simultaneous reactions. The radical polymerisation reaction behaves similarly.

The authors observed that the rate of urethane formation and the rate of the radical polymerisation of styrene are higher for the pure systems than in the IPN. The results obtained for the polymerisation of styrene are surprising, since the catalyst and initiator concentrations in the polyurethane–polystyrene system investigated were chosen in such a way that the rate of formation of polyurethane should be much higher than the rate of formation of the polystyrene. Consequently the polystyrene in the IPN is formed when the degree of conversion of the polyurethane reaches 40–60%, depending on the conditions in the formation of the IPN, and the viscosity of the medium is high. The rate of termination of radical polymerisation is known to diminish sharply with increase in the viscosity of the medium and the rate of formation of polystyrene in the IPN after autoacceleration should therefore be higher than the rate for the pure polystyrene, which was not observed in the above study.

One should also note that the authors[36] do not attempt to explain the influence of the catalyst of initiator, when they are varied, on the formation of polystyrene or polyurethane. However, it has been shown[35,37] that these two processes are so interrelated that a change in the rate of urethane formation is reflected in the rate of formation of polystyrene in the IPN.

A more detailed study of the kinetics of the formation of IPN and semi-IPN confirmed the close relation with microphase separation.[37] It was shown that the rates of formation of the two three-dimensional structures via different mechanisms (polyaddition and radical polymerisation) in the IPN and the formation of the network and linear polymers in the semi-IPN are interrelated: a change in the formation of one of the networks affects significantly the rate of hardening of the second network or the linear polymer. In addition, two processes are superimposed under these conditions: the physical microphase separation process is superimposed on the chemical IPN formation processes.

Table 2. Composition and parameters of the microphase separation in the semi-IPN based on polyurethane and PBMA.[37]

PU/PBMA, wt.%	$I \times 10^2$, M	$K \times 10^3$, % s^{-1}	τ_{MPS}, min	α_{MPS}	
				PU	PBMA
75/25	0.74	0.7	70	0.57	0.034
75/25	0.48	0.83	65	0.50	0.040
75/25	2.96	2.66	55	0.38	0.062
75/25	5.40	3.80	45	0.36	0.080
75/25	10.80	6.60	35	0.21	0.091
65/35	5.40	2.20	65	0.37	0.110
85/15	5.40	5.50	60	0.45	0.28

Notation: I is the initiator concentration and K the rate constant for polymerisation to PBMA before autoacceleration.

The objects of study were semi-IPN and IPN. The semi-IPN was obtained by the method involving the formation of the network polyurethane from polyoxypropylene glycol with a molecular weight of 2000 and an adduct [the product of the interaction of tri(hydroxymethyl)propane with tolylene diisocyanate in proportions of 3 : 1] in the presence of butyl methacrylate (BMA), in which the radical polymerisation initiator (AIBN) had been dissolved beforehand. The catalyst concentration for the urethane formation reaction was constant in all the experiments and equal to 1.4×10^{-4} M. The kinetics of the formation of polyurethane and poly(butyl methacrylate), individually and as part of the composition of the semi-IPN, were investigated at 60 °C using a DAK-1-1A differential calorimeter. The onset of the MPS during the reaction was determined simultaneously for the same systems and under the same kinetic conditions by the method of turbidity points using an FPS-3 photocalorimeter. The composition of the semi-IPN obtained and the time of the onset of the MPS are given in Table 2. Assuming the additivity of the contributions of the heats of formation of each component of the semi-IPN to the overall heat evolution in the reaction, the heat evolution area corresponding to the formation of PBMA in the semi-IPN and the degree of conversion into the PBMA in the half-IPN were determined. The area under the heat evolution curve corresponding to urethane formation was calculated from the degree of conversion obtained by an independent method (back titration of the NCO groups).[38] The kinetic curves for the formation of polyurethane and PBMA in the half-IPN thus obtained for the ratios 75/25 wt.%) in the presence of different initiator concentrations (Fig. 11) show that, for simultaneously occurring reactions, the rate of formation of the polyurethane diminishes with increase in the initiator concentration as does the rate of formation of PBMA compared with the rate of formation of the individual polyurethane network. Evidently the retardation of the polyurethane network formation reaction in the semi-IPN formed can be attributed to the increase in the viscosity of the PBMA reaction system. The rate of polyurethane formation is lower, the higher the rate of formation of PBMA (Fig. 11). Polymerisation to give PBMA takes place in a matrix consisting of a mixture of the polyurethane formed at the given instant and the components from which it is synthesised, i.e. the polymerisation reaction takes place, as it were, in a "dilute" system, as a result of which the initial rate of formation of PBMA is diminished compared with the pure polymer. However, subsequently the rate of formation of PBMA in the semi-IPN becomes higher than for the pure PBMA, which is clearly seen from the variation of the reduced rates of formation of the initial PBMA and the PBMA in the IPN (Fig. 12). This increase in rate may be associated with the overall increase in the viscosity of the reaction system.[17] During the formation of the semi-IPN, the viscosity increases so much that it leads to a sharp decrease in the termination constant (K_t) relative to the propagation constant (K_p) and hence to an increase in the ratio K_p/K_t and in the rate of chain propagation V_p in accordance with Eqn. (1).[17]

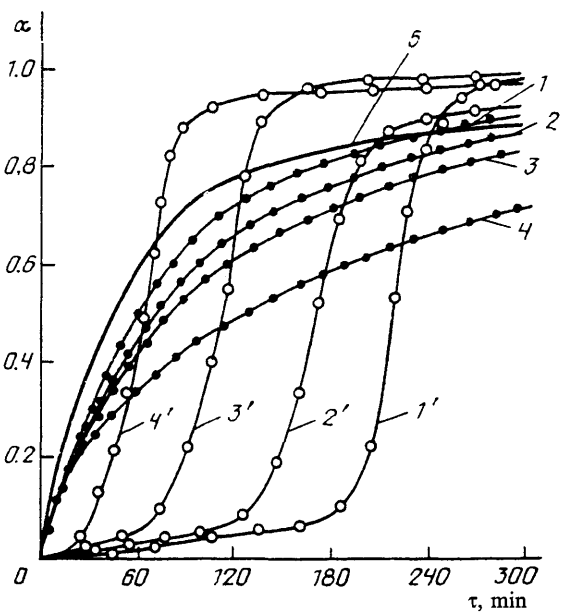


Figure 11. Kinetics of the formation of polyurethane (curves *1–4*) and PBMA (curves *1′–4′*) in the semi-IPN with the composition PU/PBMA = 75/25 for different initiator concentrations $I \times 10^2$(M): *1*, 0.74; *2*, 1.48; *3*, 2.96; *4*, 10.8; *5*, polyurethane.[37]

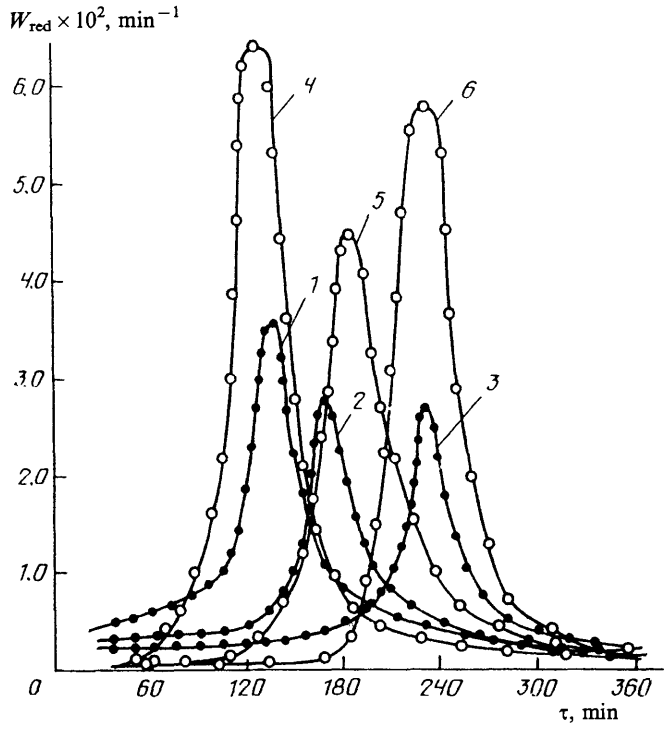


Figure 12. Time variation of the reduced rate of polymerisation (W_{red}) of butyl methacrylate at different molar initiator concentrations $I \times 10^2$ for the pure methacrylate (curves *1*–*3*) and the methacrylate in the semi-IPN with the composition 75/25 (curves *4*–*6*): *1*, and *4*, 2.96 M; *2*, and *5*, 1.48 M; *3*, and *6*, 0.74 M.[37]

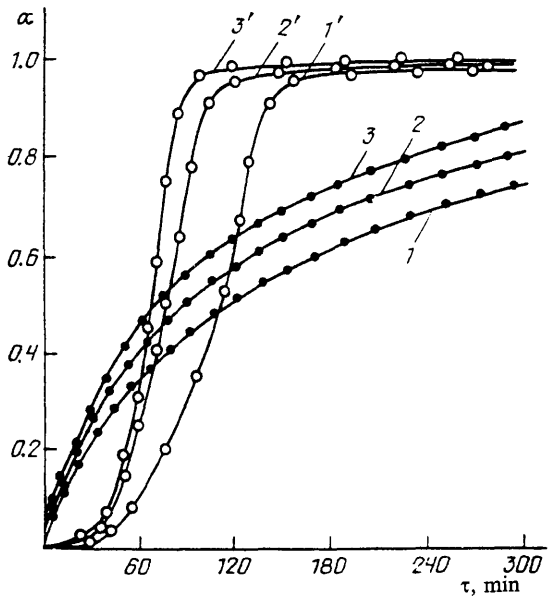


Figure 13. Kinetics of the formation of polyurethane (curves *1*–*3*) and PBMA (curves *1′*–*2′*) in the semi-IPN for $I = 5.4 \times 10^{-2}$ M and different component ratios (wt.%): *1*, and *1′*, 65/35; *2*, and *2′*, 75/25; *3*, and *3′*, 85/15.[37]

Fig. 13 presents kinetic curves for polyurethane and poly(butyl methacrylate) in different proportions in the blend at constant initiator and catalyst concentrations. The calculated reduced rates (W_{red}) for PBMA in the blend show that the rate of formation of PBMA increases in the sequence 65/35 < 75/25 < 85/15 compared with the initial rate, which is associated with the increase in the viscosity of the system. In the experiment with the 85/15 (wt.%) ratio, the viscosity was higher than in the experiment with the 65/35 (wt.%) ratio. Hence K_t diminished and K_p and V_p increased. As can be seen from Fig. 13, the rate of formation of polyurethane under these conditions in the blend diminishes in the sequence 85/15 > 75/25 > 65/35 compared with initial rate.[37]

If one adopts the concept already formulated and assumes the existence of a relation between the kinetics of the formation of the IPN and the microphase separation processes, then it is evident that there exists a distinct relation between the kinetics of the formation of the IPN and its structural characteristics. Such a relation has been established for semi-interpenetrating networks based on cross-linked polyurethane and PBMA formed in a polyurethane network matrix by the radical polymerisation of the monomer.[39]

Table 3 presents some data concerning the conditions in the formation of networks and their structural characteristics determined from low angle X-ray scattering data.[40] The polyurethane formation reaction in the given system begins before and terminates after the butyl methacrylate polymerisation reaction. As can be seen from the data in Table 3, with increase in the initiator concentration and hence in the overall rate of reaction, the heterogeneity distance l_s and the extent of the transition layer also increase. These data can be interpreted as follows. The increase in the rate of formation of PBMA leads to a faster onset of the thermodynamic incompatibility of the components of the interpenetrating network considered (we neglected here the differences between the molecular weights of the PBMA associated with the differences in the rate of initiation). There is then a rapid increase in the viscosity of the reaction system. Against the background of the simultaneous formation of the polyurethane network, these factors retard the microseparation process as a consequence of both the increase in viscosity and the fixation of the microphase separation regions arising on formation of the polyurethane network. The larger dimensions of the inhomogeneity regions and the greater extent of the transition layer are "quenched" as a result.

Table 3. Composition of the semi-IPN based on polyurethane and PBMA and their structural parameters.[39]

No. of specimen	PU/PBMA	$I \times 10^2$, M	Method of synthesis of the IPN	l_s, Å	E^2, (Å)^2
1	75/25	0.74	simultaneous	68	38
2	75/25	5.4	" "	70	27
3	75/25	10.8	" "	75	60
4	85/15	5.4	" "	65	37
5	65/35	5.4	" "	81	61
6	75/25	5.4	stage I–photopolymerisation, stage II–thermopolymerisation	66	21
7	75/25	5.4	stage I–thermopolymerisation at 25 °C, stage II–photo-polymerisation	72	65

Notation: l_s is the heterogeneity parameter and E^2 the thickness of the transition layer.

Indeed it is known[41] that, on spinodal separation, the boundary between the microphase regions in the initial stages is diffuse, but subsequently the differences between the compositions of these regions and the boundary become more distinct. Judging from the experimental data for the structure of the IPN, the observed structural parameters are consistent with this finding. The sooner is the structure of the IPN fixed as a consequence of the inhibition of the microphase separation process, the greater are the micro-heterogeneity distances and the thickness of the transition layer. Indeed, for the same rate of initiation but for a different PU/PBMA ratio [85/15 and 65/35 (wt.%)] in those cases where the content of PBMA is higher, separation is evidently slower, the transition layer is more extensive, and the heterogeneity distance is longer. We also observed a difference between the structural characteristics of consecutively formed IPN, based on the same components, under the conditions of the polymerisation of butyl methacrylate in the matrix of a polyurethane network formed previously.

Thus one may claim that there exists a relation between the structure of the hardened IPN and the kinetics of the formation of the constituent networks, the latter determining the possibility of the occurrence of the microphase separation process. However, since, apart from the factors which we have examined, the microphase separation is influenced also by others (including the change in the thermodynamic compatibility as a function of the composition and the degree of conversion which we did not take into account), a more detailed treatment of the above data does not appear desirable.

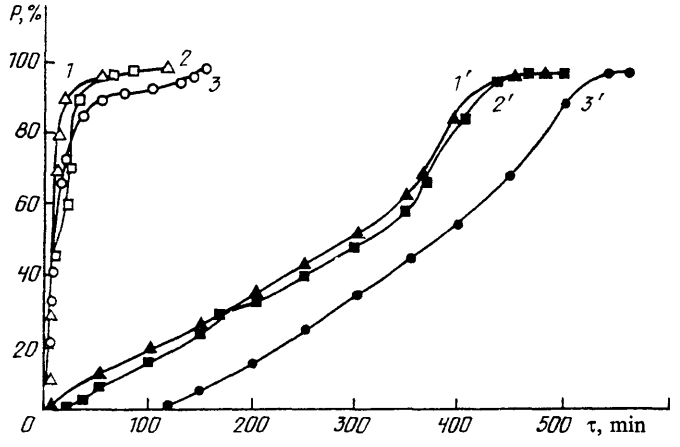


Figure 14. Time variation of the degree of conversion (P) in the formation of the semi-IPN with the composition PU/PS = 30/70 (wt.%) for different polyurethane formation times before the onset of the radical polymerisation of styrene: *1*, and *1′*, 5 min; *2*, and *2′*, 15 min; *3*, and *3′*, 2 h; *1*–*3*, polyurethane; *1′*–*3′*, polystyrene.[42]

The kinetics of the formation of polyurethane and polystryene as part of the composition of a semi-IPN as well as the influence of different kinetic conditions in the formation of the half-IPN on the phase separation in the system have been investigated[42] by FTIR spectroscopy. In order to obtain the half-IPN with the composition PU/PS = 30/70 (wt.%), a mixture of the initial components was maintained at room temperature for different times τ (5 min, 15 min, and 2h) and then the temperature was raised to 70 °C and the mixture was polymerised until the complete disappearance of double bonds. Fig. 14 presents kinetic curves for the formation of polyurethane and polystyrene. Evidently, for times of 5 and 15 min, the polyurethane network and polystyrene are formed simultaneously but at different rates, whereas for τ = 2 h polystyrene is formed in the fully polymerised polyurethane network. The different kinetic conditions in the formation of polyurethane influenced the phase separation in the system, which is clearly seen from the time variation of the transmittance (T, %) (Fig. 15). The system loses transparency on simultaneous formation of polyurethane and polystyrene (τ = 5 min) when the degree of conversion into polystyrene is about 2%. When the semi-IPN is obained consecutively (τ = 2 h), the system remains transparent, but for τ = 15 min a tendency towards a decrease in transmittance (T, %) is observed at later stages in the formation of the half-IPN.

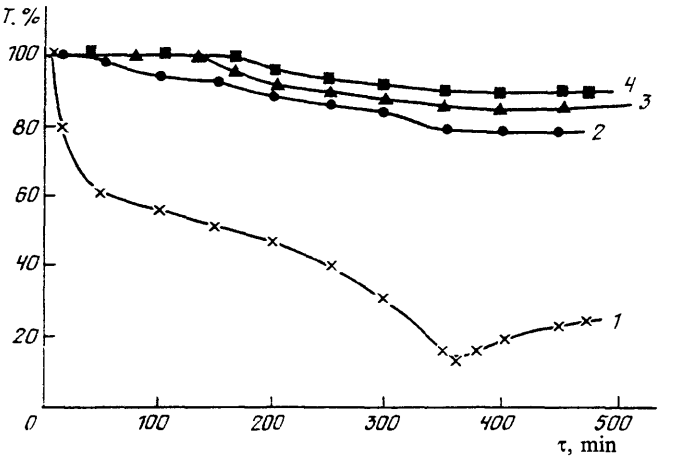


Figure 15. Transmittance (T) curves for the semi-IPN with the composition PU/PS = 30/70 (wt.%) at 70 °c for different polyurethane formation times before the radical polymerisation of styrene: *1*, 5 min; *2*, 15 min; *3*, 2 h; *4*, 6 h.[42]

The introduction of polymerised polystyrene and polyurethane in an amount of 0.5–1% in the first minute induces phase separation in the reaction system. The authors also showed that, with increase in M_n for polystyrene, phase separation is manifested sooner and becomes explicit (Fig. 16). Thus the authors conclude that, when the reaction mixture is separated before the onset of gel formation in polyurethane, the half-IPN are turbid. If separation takes place after gel formation, then transparent IPN are produced, i.e., using certain kinetic parameters it is possible to obtain materials with a wide range of properties.

In order to investigate further the influence of the kinetics of the formation of IPN on the microphase separation, a study was made of IPN based on two networks: polyurethane and a loosely cross-linked butyl methacrylate in the presence of triethylene glycol dimethacrylate (TGM-3).[43] The composition of the IPN and the concentrations of the cross-linking agent (TGM-3), the initiator, and the catalyst are presented in Table 4. The kinetics of the formation

of the IPN were investigated by the calorimetric method described above. The kinetic curves for the initial polyurethane and PBMA and the copolymer with the cross-linking agent TGM-3 having different contents of the latter are presented in Fig. 17. Fig. 17 shows that the initial section on the kinetic curves for the radical polymerisation of butyl methacrylate and the butyl methacrylate–TGM-3 copolymer remains unchanged, so that the introduction of a small amount of the cross-linking agent (up to 0.15 M) does not affect the initial rate of polymerisation of butyl methacrylate but does influence the degree of conversion (α_a) at which autoacceleration begins. With increase in the concentration of TGM-3, the degree of conversion falls, but, after the attainment of a definite value of α_a, the rate of formation of the copolymer increases with increase in the amount of cross-linking agent. This is usually explained by the decrease in the rate of the chain termination reaction when the rate of initiation and the rate of chain propagation are altered slightly. Kinetic curves for polyurethane and PBMA have been obtained by the method described for simultaneously produced IPN with the compositions 75/25 and 65/35 (wt.%) (Fig. 18) in the presence of different concentrations of the initiator and cross-linking agent (Table 4). The experimental data show[43] that the rate of formation of the butyl methacrylate–TGM-3 copolymer in the IPN diminishes in the initial stage owing to the dilution by the components of the polyurethane network but subsequently increases compared with the initial value and the degree of conversion at the onset of the autoacceleration (α_a) diminishes under these conditions. It has been observed that the rate of polymerisation of the copolymer in the IPN changes after the start of autoacceleration with increase in the initiator concentration (Fig. 18, curves *2* and *3*) and a slight decrease in the degree of conversion after the onset of autoacceleration is observed. Under these conditions, the rate of urethane formation also diminishes slightly (curves *1*–*3*). The change in the rate of formation of the loosely cross-linked PBMA in the IPN owing to the variation of the initiator and cross-linking agent concentrations is manifested more markedly on the kinetic curves for the formation of polyurethane in the IPN for the component ratio 65/35 (wt.%) (Fig. 19).

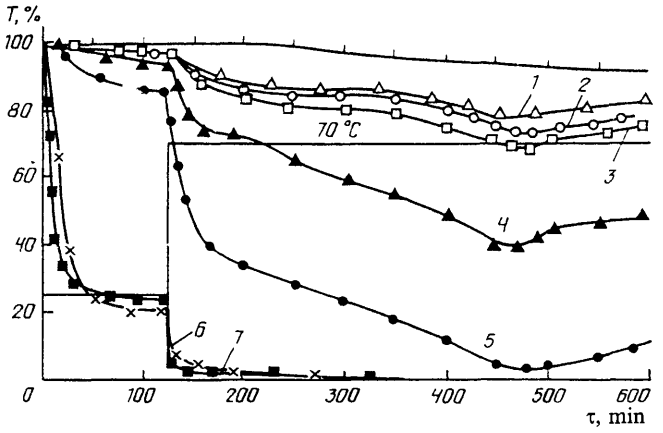


Figure 16. Transmittance (*T*) curves for the semi-IPN with the composition PU/PS = 30/70 (wt.%) at 70 °C with 0.5% polystyrene having different molecular weights M_n: *1*, 2000; *2*, 4900; 3, 22 000; *4*, 27 000; *5*, 40 300; *6*, 52 000; *7*, 105 000.[42]

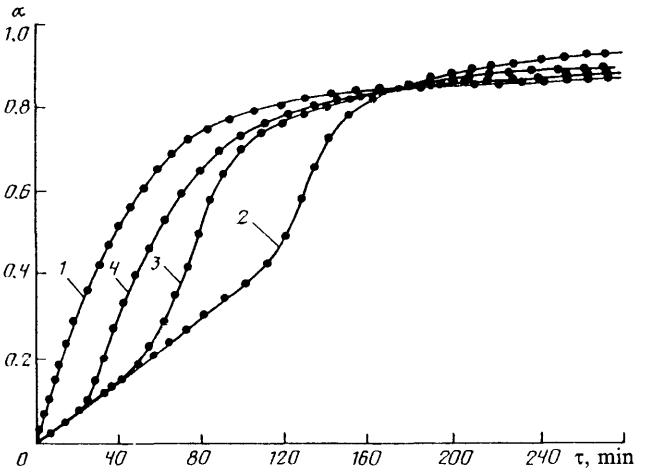


Figure 17. Kinetics of the formation of polyurethane (curve *1*) and PBMA (curve *2*) and of the copolymerisation of butyl methacrylate with triethylene glycol dimethacrylate: *2*, $I = 2.96 \times 10^{-2}$ M; *3*, PBMA + TGM-3; $I = 2.96 \times 10^{-2}$ M, [TGM-3] = 0.031 M; *4*, PBMA + TGM-3, $I = 2.96 \times 10^{-2}$ M, [TGM-3] = 0.156 M.[43]

Table 4. Physicochemical parameters of the IPN based on polyurethane and PBMA.[43]

PU/PBMA (wt.%)	$I \times 10^2$, M	[TGM]*, M	τ_{MPS}, min	α_{MPS}	
				PU	PBMA
75/25	2.96	0.031	60	0.51	0.045
75/25	2.96	0.156	56	0.47	0.050
75/25	5.40	0.031	57	0.44	0.200
65/35	2.96	0.031	60	0.47	0.030
65/35	2.96	0.156	56	0.42	0.050
65/35	5.40	0.031	38	0.28	0.070
50/50	2.96	0.156	70	0.37	0.040

*[TGM] is the concentration of the cross-linking agent.

The calculated reduced rates (W_{red}) for PBMA in the blend for different component ratios show that the rate of formation of PBMA increases in the sequence 50/50 < 65/35 < 75/25 (wt.%). Under these conditions, the dependence of the maximum reduced rate on the PU/PBMA ratio is linear (Fig. 20) and is correlated with data obtained for the semi-IPN. The explanations are similar: with increase in the viscosity of the system, the termination constant diminishes and the chain propagation constant increases with the corresponding increase also in the rate of formation of the copolymer in conformity with Eqn. (1) presented above. The rate of formation of polyurethane diminishes in the sequence 75/25 > 65/35 > 50/50 (wt.%).

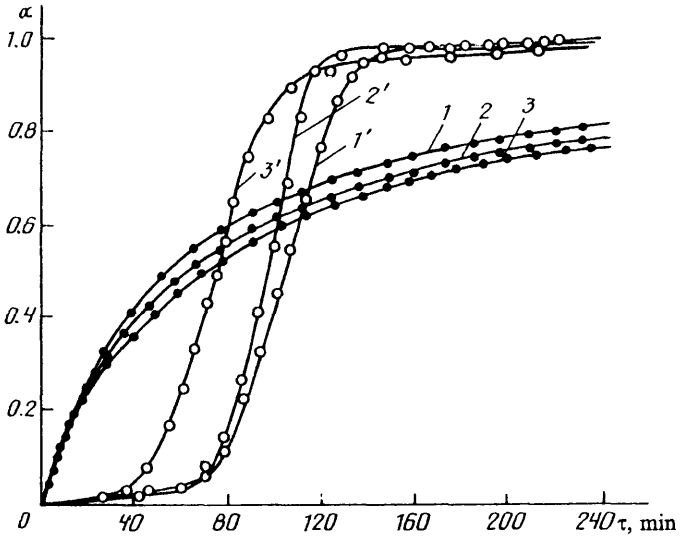


Figure 18. Kinetics of the formation of polyurethane (curves *1*–*3*) and of the cross-linked PBMA (curves *1'*–*3'*) in the IPN for PU/PBMA = 75/25 (wt.%) and different TGM-3 and initator concentrations: *1*, and *1'*, $I = 2.96 \times 10^{-2}$ M, [TGM-3] = 0.031 M; *2*, and *2'*, $I = 2.96 \times 10^{-2}$ M, [TGM-3] = 0.156 M; *3*, and *3'*, $I = 5.4 \times 10^{-2}$ M, [TGM-3] = 0.031 M.[43]

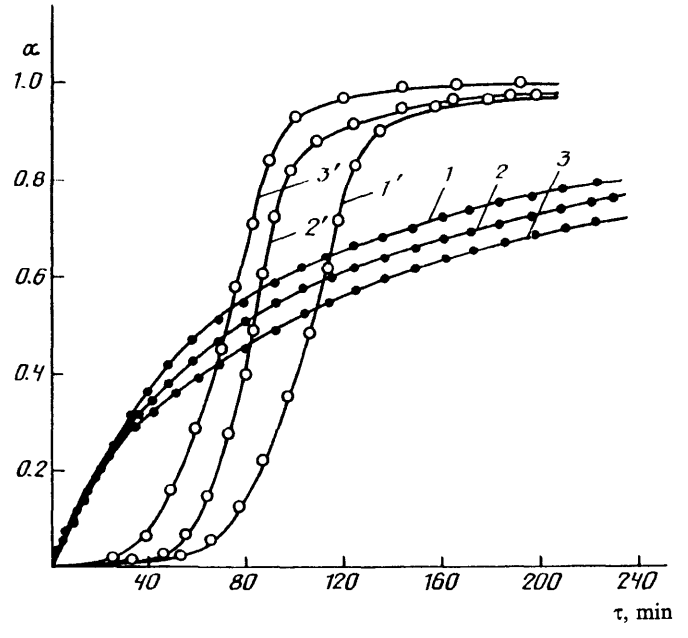


Figure 19. Kinetics of the formation of polyurethane (curves *1*–*3*) and of the cross-linked PBMA (curves *1'*–*3'*) in the IPN for the ratio PU/PBMA = 65/35 (wt.%) and different TGM-3 and initiator concentrations: *1*, and *1'*, $I = 2.96 \times 10^{-2}$ M, [TGM-3] = 0.031 M; *2*, and *2'*, $I = 2.96 \times 10^{-2}$ M, [TGM-3] = 0.156 M; *3*, and *3'*, $I = 5.4 \times 10^{-2}$ M, [TGM-3] = 0.031 M.[43]

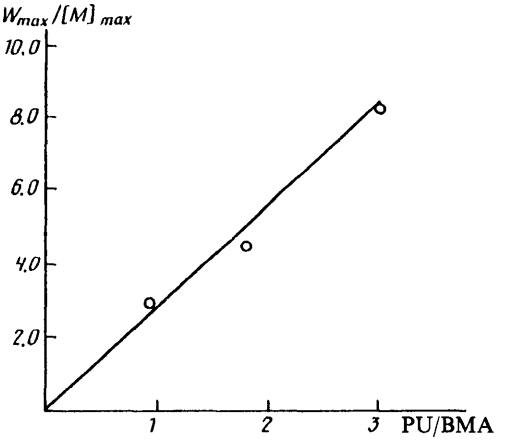


Figure 20. Dependence of the maximum reduced rate of polymerisation of butyl methacrylate in the presence of TGM-3 in the IPN on the component ratio.[43]

Analysis of the data obtained on the kinetics of the formation of polyurethane and PBMA in the case of the simultaneously produced semi-IPN and IPN leads to the conclusion that the introduction of the cross-linking agent for the second polymer network accelerates the formation of the second network, which is reflected directly in the kinetics of the formation of the first network. This is manifested more strikingly with increase in the amount of the second network. The features of the kinetics of the formation of the two networks remain unchanged as the component ratio PU/PBMA varies both in the IPN and in the semi-IPN.

We shall now consider the influence of microphase separation in semi-IPN and IPN and the kinetics of the reactions in the given system. The onset of the MPS was determined simultaneously for the same systems and under the same kinetic conditions in the course of the reaction by the method of turbidity points on an FPS-3 photocalorimeter.[37,43] Tables 2 and 3 present data characterising the microphase separation occurring during the formation of the semi-IPN and the IPN. Analysis of the data presented shows that the time to the onset of the MPS diminishes almost linearly with increase in the concentration of the initiator of the polymerisation of PBMA in the semi-IPN. Calculation of the rate of reaction of PBMA along the initial section (up to the onset of autoacceleration) shows that there is also a linear relation between this quantity and the time of the onset of the MPS. It follows from Table 2 that, for a constant initial composition of the system, the degree of conversion into the polyurethane diminishes at the instant of phase separation with increase in the rate of polymerisation, while the degree of conversion of PBMA increases. The weight fractions of the components in the phase separation were determined from the initial system composition for different rates of polymerisation.[37] Evidently the fraction of polyurethane then falls while that of PBMA increases, which is associated with the influence of the initiator concentration, examined above, on the ratio of the reaction rates. Compatibility is known to be determined not only by the component ratio but also by the ratio of the molecular weights. Evidently the amount of polymer formed at the instant of phase separation, and not the molecular weight, plays a decisive role in the appearance of

incompatibility. We may note that the weight fraction of polyurethane in the semi-IPN at the instant of phase separation is significantly greater than its value in the initial system (of the order of 0.9), which also suggests that the accumulation of PBMA is the decisive factor in the PMS. The higher the rate of polymerisation leading to PBMA, the higher the degree of conversion into PBMA at the phase separation point, and the lower the fraction of polyurethane for which separation begins, while the time up to the onset of the MPS in the system diminishes.

The onset of the MPS depends also on the ratio of the polyurethane and PBMA components in the semi-IPN. For the component ratio 85/15 (wt.%), the degree of conversion up to the onset of MPS is indeed higher for both components than for the ratio 75/25 wt.%, while in the case of the ratios 65/35 and 75/25 wt.%) the degrees of conversion are similar. At the same time the weight fraction of the polyurethane at which MPS begins proved to be smallest for the 65/35 ratio and greatest for the 85/15 (wt.%) ratio. Account must be taken of the fact that the rate of MPS in a highly viscous medium is clearly lower than the rates of the reactions and may therefore lag in time behind the degree of conversion at which this would have occurred under equilibrium conditions uncomplicated by the reaction occurring in the previous period.

The study of the influence of microphase separation on the kinetics of the formation of IPN showed that, for a constant composition of the components, the degree of conversion into polyurethane at the instant of phase separation falls with increase in the rate of formation of PBMA and the degree of conversion into PBMA increases, the influence of the initiator concentration being more marked compared with that of the cross-linking agent. Such behaviour can be traced for two component compositions — 75/25 and 65/35 (wt.%). The time up to the onset of MPS in the system diminishes sharply only for the component ratio 65/35 (wt/%) with increase in the initiator concentration to 5.4×10^{-2} M. When the component ratio is altered at constant initiator and cross-linking agent concentrations, the time of the onset of MPS increases to 70 min and the degree of conversion into polyurethane diminishes from 0.49 to 0.37 and that into PBMA varies in the range 0.04 – 0.05.[43]

Consequently, an increase in the rate of polymerisation, which increases the degree of conversion into PBMA, reduces the time before the onset of phase separation. However, the most significant conclusion arising from the analysis of the rates of reaction and the times of the onset of MPS is as follows. As can be seen from the kinetic data, both before the onset of MPS and afterwards, the nature of the kinetic curves remains unchanged, i.e. the MPS is not reflected in the rates of the continuing reactions. This means that, in the region becoming segregated, the MPS alters the composition to one close to the average composition of the system, i.e. in each segregated phase the ratio of the reacted and unreacted components is approximately the same. This situation can occur only in the case of a microphase separation which proceeds via the spinodal mechanism and is in its initial stage. Evidently, the microheterogeneous system, arising as a result of the formation of the network, is then chemically "quenched",[44] which prevents further phase separation after the attainment of a definite degree of conversion. Otherwise the microphase separation would have progressed further and deviations of the rates of reactions from those in the initially separating system should have been observed, and this is not the case up to high degrees of conversion.

Thus one may conclude that the simultaneously occurring chemical formation reactions of polymer molecules constituting the semi-IPN and the IPN and the physical microphase separation processes take place under non-equilibrium conditions.

This makes it possibile to represent in the following way the process leading to the formation of the IPN. When the IPN is synthesised, the initial reaction system consists of a homogeneous mixture of components capable of forming two independent three-dimensional networks in the course of the chemical reactions occurring via different mechanisms. After the attaiment of a definite degree of conversion, as a rule before the attainment of the sol – gel transition point, the growing fragments of the constituent networks become incompatible in the system. The condition for this is the attainment by the thermodynamic interaction parameter χ_{23} of the critical value predicted by the theory. The initial phase separation conditions are specified by the conditions for the transition of the parameters χ_{23} from negative (region of compatibility) to positive (region of incompatibility) values or by the conditions under which χ_{23} becomes zero for the given system composition and at the given temperature. In most cases, this takes place in the initial stages of the reaction in the kinetic region. However, phase separation takes place from the very beginning under non-equilibrium conditions, because it occurs simultaneously with the developing chemical reaction, altering the parameter χ_{23} and thus the phase separation conditions. The rate of attainment of the critical value of the parameter χ_{23} is determined by the rates of the two independent reactions, while the phase separation process begins before the completion of gel formation in the constituent networks.

In the initial period of the reaction (low degrees of conversion), the onset of phase separation is determined solely by the rate of reaction, i.e. by the rate of formation of the polymer and the increase in its molecular weight. However, the cross-linking of sections of the growing chains into a continuous network and the rapid increase, as a consequence of gel formation, in the viscosity of the system have an inhibiting effect on the phase separation, which thus becomes possible only in a definite range of conversions and in a time interval which is a function of the rates of the constituent reactions. Since the cross-linking reactions continue in the time interval $\Delta\tau$, the phase separation then proceeds under non-equilibrium conditions, because the composition of the phases and their proportions vary with time in the reaction system. Thus the real situation arising in the formation of the IPN differs significantly from the case of "chemical quenching" examined theoretically by Frisch and Binder, in which it is assumed that the hardening time is much shorter than the relaxation time of the system in the phase separation.[44]

Both processes — the chemical reaction and the phase separation — take place simultaneously. This determines the nature of the structures which develop and are transformed at different stages of the reaction in the phase separation. The structure produced as a result of the reaction is characterised by a periodicity and order typical for structure arising in phase separation via the spinodal decomposition mechanism[45] The kinetics of the phase separation are described approximately in the initial stages by the linear Cahn – Hilliard theory despite the fact that this entails continuous changes in the degree of conversion, i.e. a drift of the system along the phase diagram implying continuous variation of the parameter χ_{23} and of the composition of the phases being separated. Thus yet another fundamental feature of the formation of the structure is established. It consists of a continuous sequence of structures differing in composition not only in the early stages of the phase separation but, according to the theory, also as a

consequence of the chemical reaction.[46] Thus the structure arising during the reaction is a result of a non-equilibrium phase transition of the liquid–liquid type and the final result of this transition is determined by the system composition (the ratio of the networks, the rates of the reactions, and the degree of the non-equilibrium phase separation during the time interval $\Delta\tau$).

It follows from the foregoing that, from the thermodynamic point of view, IPN are non-equilibrium systems. However, phase separation microregions, which can be described as quasi-equilibrium regions, are manifested in them. Indeed, each of the two experimentally observed phases has a glass point different from the glass points of the constituents. Each given phase contains both constituents. We can consider such a phase as a region in which the state of the molecular blending of the components (compatibility), corresponding to the equilibrium conditions preceding the given state of the entire system, has been "frozen". Overall, this is a thermodynamically non-equilibrium two-phase system whose state is determined by the conditions for incomplete microphase separation. However, each phase is in a quasi-equilibrium state. The structure of the IPN is microheterogeneous and molecular blending of the components takes place in the constituent phases.

IV. Conclusion

Analysis of the data presented shows that the principal experimentally demonstrated fact in the formation of IPN is at the present time the influence of the kinetics of the formation of the constituent networks in the IPN on the kinetics of the microphase separation and also the occurrence of the MPS under non-equilibrium conditions in the chemically varying system. However, this postulate has been formulated in a qualitative form.

The previous literature describes no attempts at a formal analysis of the kinetics of the network formation reactions taking into account the factors which influence the kinetics and which were examined above.

Numerous data essential for the understanding of the mechanisms of the formation of IPN are lacking. Thus, in radical three-dimensional polymerisation, the role of the reaction involving chain transfer to the second network, being formed via a non-radical mechanism or already formed (consecutive hardening), was not established. An appropriate study of the kinetics of the formation of the network in the matrix already produced (consecutively formed IPN), which strictly speaking should have preceded the investigation of the kinetics of the simultaneous reactions, was not carried out.

Although the fundamental role of MPS in the kinetics and their mutual influence has been established, the fundamenal problems arising in this connection have still not been studied. These include the following. Despite the fact that the degree of the MPS in the IPN may be estimated quantitatively,[41] it has not been estimated at different degrees of conversion of the systems for which the kinetics have been investigated. It is not clear in which stage and at what degree of conversion the MPS is frozen as a function of the kinetic conditions in the formation of the networks (rate, composition, and temperature). There are no data on the kinetics of the MPS after its onset.

It is also not clear in what way the reaction takes place after the MPS in MPS regions of different composition and how the chemical interaction between the phases is achieved. We have no information about the influence of the constituent networks and the MPS on the conversion at the gel point. Accordingly, and this is very important for the estimation of mechanical properties, the density of the constituent network is unknown under the conditions of the mutual influence of the kinetics of the reactions and the kinetics of the MPS on the formation of the IPN.

From the standpoint of the phase state, three cases of the formation of IPN are possible. The first arises when one network is formed much faster than the other, i.e. it is formed virtually in the liquid phase comprising the components of the second network, which results in a microphase structure with a fairly high degree of segregation. The second case occurs when the formation reactions of both networks are rapid and there is insufficient time for the occurrence of the MPS, whereupon the structure of the system characteristic of the single-phase state is frozen. The third, commonest case obtains when the rates of formation of both networks are comparable. The MPS begins in the course of the reaction and its continuation is inhibited as the network structure is produced. Among the three versions specified above, the formation kinetics as well as the relation with the microphase separation in the IPN have been studied in greatest detail for the third, commonest case, leaving the first two cases without due attention. All this demonstrates how far we are from a true understanding of the mechanism of the formation of IPN.

References

1. S C Kim, D Klempner, K C Frisch, et al. *Macromolecules,* 1976, **9** 258
2. P G Klein, J R Ebdon, D J Hourston *Polymer,* 1988, **29**(6) 1079
3. H Djomo, A Morin, M Damyanidu, G C Meyer *Polymer,* 1983, **24**(1) 65
4. Bi Xiping, Li Binyao, Zhang Donghua *Chin. J. Appl. Chem.,* 1988, **5**(5) 53
5. Bi Xiping, Li Binyao, Zhang Donghua *Chin. J. Appl. Chem.,* 1988, **5**(6) 39
6. R P Burford, R P Chaplin, Y W May *Rubber Con'88, Int. Rubber Conf.,* Chatswood, Sydney, 1988, p. 1
7. K B Visscher, J Manners, H R Allcock *Polym. Mater. Sci. Eng.,* 1991, **65** 3
8. P Knaub, Y Camberlin, J F Cerard *Polymer,* 1988, **29**(8) 1365
9. J Hermant, M Damyanidu, G C Meyer *Polymer,* 1983, **24**(11) 1419
10. M C O Chang, D A Thomas, L H Sperling *J. Polym. Sci.,* 1988, **B26**(8) 1627
11. J R Ebdon, D J Hourston, P G Klein *Polymer,* 1986, **27**(11) 1807
12. E F Cassidy, H X Xiao, K C Frisch, H L Frisch, *J. Polym. Sci., Polym. Chem. Ed.,* 1984, **22** 1851
13. G M Jordhamo, I A Manson, L H Sperling *Polym. Eng. Sci.,* 1986, **26**(8) 517
14. A M Fernandez, G D Wignall, L H Sperling *Multicomponent Polymer Materials,* ACS Adv. Chem., 1986, Vol. 211, p. 153
15. Yu S Lipatov *Advances in Interpenetrating Polymer Networks* [Edited by K Frisch and D Klempner (Basel)], Technomic Rubb. Co., Lancaster, 1990, Vol. 1, p. 262
16. Y S Lipatov *Rev. Macromol. Chem. Phys.,* 1990, **C30**(2) 209
17. G P Gladyshev, V A Popov *Radikal'naya Polimerizatsiya pri Glubokikh Stepenyakh Prevrashcheniya* (Radical Polymerisation at High Degrees of Conversion), Nauka, Moscow, 1974, 242 pp
18. G C Meyer *Macromol. Chem. Rapid Commun.,* 1983, **4** 221

19. D Jehl, J M Widmaier, G C Meyer *Eur. Polym. J.*, 1983, **19**(7) 597
20. H Djomo, J M Windmaier, G C Meyer *Polymer*, 1983, **24**(11) 1415
21. I Hermant, G C Meyer *Eur. Polym. J.*, 1984, **20**(1) 85
22. V Nevisas, J M Widmaier, G C Meyer *J. Appl. Polym. Sci.*, 1988, **36**(6) 1467
23. S R Jin, G C Meyer *Polymer*, 1986, **27**(4) 592
24. S R Jin, J M Windmaier, G C Meyer *Polymer Commun.*, 1988, **29**(2) 26
25. S N Derrough, C Rouf, J M Widmaier, G C Meyer *Polym. Mater. Sci. Eng.*, 1991, **65**(1)
26. T J Hsu, L J Lee *J. Appl. Polym. Sci.*, 1988, **36**(5) 1157
27. L J Lee *Polym. Eng. Sci.*, 1981, **21** 483
28. Yu S Lipatov, O P Grigor'eva *Dokl. Akad. Nauk Ukr. SSR*, 1983, Part B, (11) 43
29. Yu S Lipatov, V V Shilov, O P Grigor'eva, et al. *Dokl. Akad. Nauk Ukr. SSR*, 1983, Part B, (6) 35
30. Yu S Lipatov, V F Rosovitskii, T T Alekseeva, N V Babkina *Vysokomol. Soedin., Ser. A*, 1989, **31**(3) 1493
31. Y S Lipatov *J. Polymer Materals*, 1987, **4**(3) 173
32. L M Sergeeva, G M Semenovich, L V Karabanova, et al. *Dokl. Akad. Nauk SSSR*, 1986, **288**(5) 1134
33. Y S Yang, L J Lee *Macromolecules*, 1987, **20** 1490
34. Y C Chou, L J Lee *Polym. Mater. Sci. Eng.*, 1991, **65** 57
35. G M Semenovich, Yu S Lipatov, S I Skiba, et al. *Dokl. Akad. Nauk SSSR*, 1988, **301**(2) 384
36. S C Xue, Z-P Zhang, S-K Ving *Polymer*, 1989, **30**(7) 1269
37. Yu S Lipatov, T T Alekseeva, V F Rosovitskii *Dokl. Akad. Nauk SSSR*, 1989, **307**(4) 883
38. H E Stagg *Analyst*, 1946, **71**(849) 557
39. Yu S Lipatov, T T Alekseeva, V V Shilov *Polym. Networks Blends*, 1991, **1**(3) 129
40. Yu S Lipatov, V V Shilov, Yu P Gomza, N G Kruglyak *Rentgenograficheskie Metody Izucheniya Polimerov* (X-Ray Diffraction Methods for the Study of Polymers), Naukova Dumka, Kiev, 1982, 296 pp
41. C N R Rao, K J Rao *J. Phase Transitions in Soids*, McGraw-Hill, Great Britain, 1978, 330 pp
42. X He, J M Widmaier, G C Meyer *Polym. Mater. Sci. Eng.*, 1991, **65** 44
43. Yu S Lipatov, T T Alekseeva *Polym. Commun.*, 1991, **32**(8) 254
44. K Binder, H L Frisch *J. Chem. Phys.*, 1984, **81** 2126
45. Yu S Lipatov *Pure Appl. Chem.*, 1985, **57**(11) 1691
46. Yu S Lipatov *Dokl. Akad. Nauk SSSR*, 1987, **296**(3) 646

Received 4th March 1992

Translated from *Uspekhi Khimii* **61** 2215–2246 (1992) U.D.C. 547.241

Aliphatic organophosphorus nitro-compounds

G M Baranov, V V Perekalin
Gertsen Russian State Pedagogic Institute, St. Petersburg

ABSTRACT. The review presents data on the methods of synthesis and properties of aliphatic organophosphorus α-, β-, γ-, and δ-nitro-compounds. They are arranged in conformity with the structural types of the compounds, since there are no general methods of synthesis characteristic simultaneously of all the groups of organophosphorus nitro-compounds.

The bibliography includes 109 references.

Contents

I. Introduction 1220
II. Organophosphorus α-nitro-compounds 1220
III. Organophosphorus β-nitro-compounds 1224
IV. Organophosphorus γ-nitro-compounds 1231
V. Organophosphorus δ-nitro-compounds 1233
VI. Conclusion 1234

I. Introduction

The interest in the study of aliphatic organophosphorus nitro-compounds is due primarily to the wide variety of their reactions involving the electron-accepting groups (the nitro-group and the phosphoryl group) linked to alkyl and alkenyl residues, which is the reason for the great importance of such compounds in synthetic and theoretical organic chemistry.

The synthesis of aminoalkylphosphonic acids with functional group substituents via the nitro-derivatives opens the way to certain compounds which are otherwise difficult to obtain. Thus organophosphorus nitro-compounds can become important intermediates in the synthesis of pharmaceuticals, fungicides, herbicides, antibiotics, glutamate-ergic neuron blocking agents, etc.

In discussing the data, the aim was to trace (in so far as this was permitted by the published results) the dependence of the mode of the reactions on their experimental conditions and on the structure of the reactants, to demonstrate the relation between the physicochemical properties and structure of organophosphorus nitro-compounds, and also to describe their possible subsequent reactions.

Certain reactions, discovered as a result of the search for ways of synthesising organophosphorus nitro-compounds, are of fundamental importance in organic synthesis.

II. Organophosphorus α-nitro-compounds

1. Methods of synthesis of organophosphorus α-nitro-compounds

The use of the most reactive trivalent phosphorus compounds for the synthesis of organophosphorus nitro-derivatives was hindered by the occurrence of numerous oxidation-reduction processes involving phosphorus(III).[1-3]

The first representative of organophosphorus α-nitro-compounds was obtained by nitrating with ethyl nitrate potassium benzyldiphenylphosphine oxide metallated with the aid of potassium t-butoxide:[4]

$$Ph_2P-CH_2PH \xrightarrow[2)\ EtONO_2,\ 0\ ^\circ C]{1)\ t\text{-}BuOK} Ph_2P-CHPh(O)(NO_2).$$

Nitration of alkylphosphonates with alkyl nitrates in the lithium isopropylamide–tetrahydrofuran (THF) system leads to cleavage products (nitroalkanes and trialkyl phosphates) together with nitrophosphonates:[5]

$$(R^1O)_2P(O)-CH_2R \xrightarrow{(iso\text{-}Pr)_2NLi-THF-n\text{-}PrONO_2} (R^1O)_2P(O)-CHR(NO_2) + RCH_2NO_2 + n\text{-}PrOP(O)(OR^1)_2;$$

R = Bu, C_5H_{11}.

The attempt to suppress the cleavage of the initial ester by using bulky substituents at the phosphorus atom (for example, isopropoxy-groups) failed and the yield of the nitroalkylphosphonates is also low in this case.

The interaction of phosphorylated aldehydes and ketones with acetyl nitrate in acetic anhydride at 30–35 °C also leads to nitromethylphosphonates.[6,7] It has been suggested[8] that the reaction proceeds via an enol formation stage in accordance with the mechanism

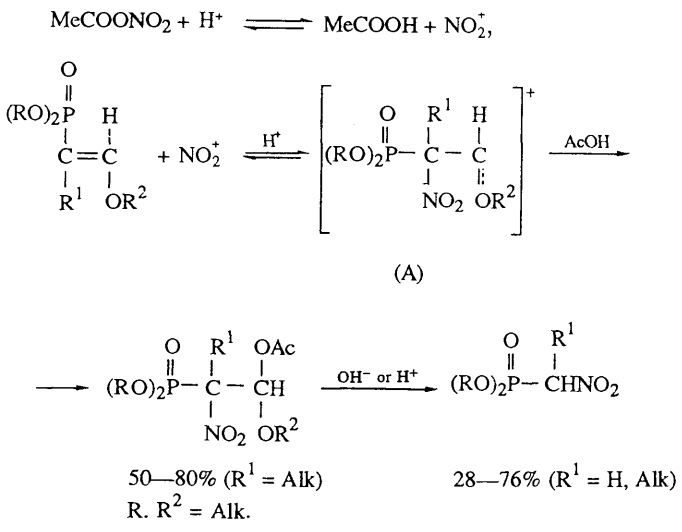
$$(RO)_2P(O)CH_2C(O)R^1 \rightleftharpoons (RO)_2P(O)CH=C(OH)R^1 \xrightarrow{AcONO_2} \left[(RO)_2P(O)CH(NO_2)C(OAc)(OH)R^1\right] \xrightarrow{HX} (RO)_2P(O)CH_2NO_2;$$

R = Alk; R^1 = H, Me; X = OH^-, AcO^-.

The introduction of electronegative substituents into the methylene group in β-ketophosphonates prevents this reaction. Thus diethyl

1-chloro-2-oxoalkylphosphonate does not react with acetyl nitrate at 33–35 °C, while at a higher temperature it decomposes under the reaction conditions.

A more convenient method of synthesis of 1-nitroalkylphosphonates involves the interaction of 2-alkoxyvinylphosphonate with acetyl nitrate. The final products can be readily separated from the initial reactants by converting them into the aci-form with subsequent acidification.[6,9] The reaction is catalysed by sulphuric acid (apparently as a consequence of the enhancement of the electrophilicity of the reagent $MeCOONO_2.H^+$).[7] The addition of acetyl nitrate is not stereospecific—diastereoisomers are formed in proportions of 45:55. The reaction apparently proceeds via a stage involving the addition of the nitronium cation to the vinylphosphonate with subsequent nucleophilic attack on the relatively stable planar carbonium ion (A) by acetic acid or the acetate ion, the attack being directed with equal probability "from the front and from the rear".

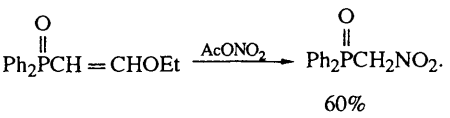


50—80% (R^1 = Alk) 28—76% (R^1 = H, Alk)
R. R^2 = Alk.

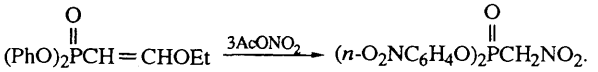
In the presence of an alkyl group in the α-position relative to the phosphonate group, the adduct is stable and on treatment with bases (sodium alkoxide, alcoholic alkali) or hydrochloric acid gives rise to 1-nitroalkylphosphonate.[10]

The stability of the adducts formed by the addition of acetyl nitrate to 2-alkoxy-1-alkylvinylphosphonates can be accounted for by the presence of the alkyl group, which causes steric hindrance to the conjugation between the C–C bond and the π-system of the nitro-group. The stability of the carbonium ion (A) is also affected by the 2-alkoxy-group, which hinders the nucleophilic attack: in its absence (diethyl 1-ethyl-2-oxoethylphosphonate), the ion (A) is cleaved in the instant of reaction. Thus slight changes in the structure of phosphonates affect the course of the reaction with acetyl nitrate and the structure of the products. For example, nitration products cannot be obtained from diethyl 2-ethoxy-2-methylvinylphosphonate.

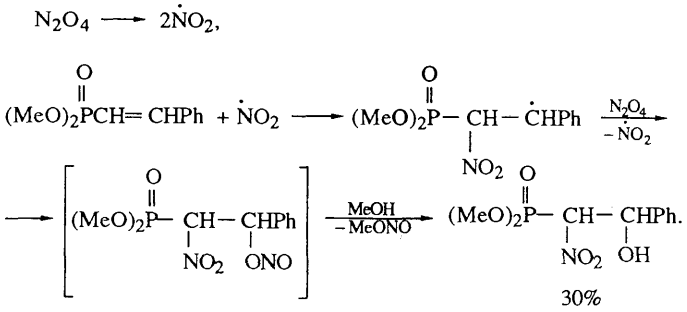
Nitration with acetyl nitrate of the corresponding 2-alkoxyalkenylphosphinates and 2-alkoxyalkenylphosphine oxides also leads to nitromethylphosphinates and nitromethylphosphine oxides.[11] The authors explain a certian passivity of phosphine oxides in the reaction by the competing protonation of the phosphoryl group, and not acetyl nitrate, by sulphuric acid, which lowers the activity of the catalyst. Only nitromethyldiphenylphosphine oxide, in which the phosphoryl group is less basic, is obtained in a high yield.



In the case of diphenyl esters of 2-ethoxyvinylphosphonic acid, acetyl nitrate nitrates simultaneously both the double bond and the benzene ring:[11]

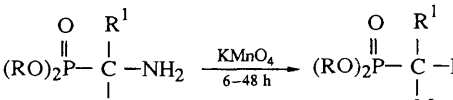


Nitration of 2-phenylvinylphosphonate with dinitrogen tetroxide leads to an organophosphorus α-nitroalcohol.[12] The reaction is accompanied by the cleavage of the C–P and C–C bonds, which was confirmed by the isolation of 2-nitrostyrene and 2-nitrophenol from the reaction mixture.



According to IR spectroscopic data, organophosphorus α-nitroalcohols form intermolecular hydrogen bonds in the crystal [ν(OH) = 3280 cm^{-1}], which are readily ruptured on dissolution with formation of free molecules [ν(OH) = 3590 cm^{-1}]. The chemical shift of the hydroxyl proton (δ_{OH} = 2.93 p.p.m.) in the ^1H NMR spectra also corresponds to the virtually free state of the OH group.

1-Aminoalkylphosphoantes substituted in the 1-position are oxidised by potassium permanganate or hydrogen peroxide to the corresponding α-nitroalkyl phosphonates:[6,13]



30—53%

1-Nitroalkylphosphonates have also been obtained by oxidising with *m*-chloroperbenzoic acid 1-*N*-hydroxyiminoalkylphosphonates synthesised beforehand from 1-oxoalkylphosphonates, which were

obtained in their turn by the reaction of acyl chlorides with triisopropyl phosphite.[14]

$$(\text{iso-PrO})_3\text{P} \xrightarrow{\text{RCOCl}} (\text{iso-PrO})_2\text{P}(\text{O})\text{C}(\text{O})\text{R} \xrightarrow[\text{2) m-ClC}_6\text{H}_4\text{COOOH/CH}_2\text{Cl}_2]{\text{1) NH}_2\text{OH·HCl/C}_5\text{H}_5\text{N}} (\text{iso-PrO})_2\text{P}(\text{O})\text{CH}(\text{NO}_2)\text{R};$$

50–65%

R = Me, Et, $PhCH_2$.

Only one instance of the synthesis of an organophosphorus(III) α-nitro-compound from the sodium salt of 1-nitropropane and diethyl phosphorochloridite has been described in the literature.[1]

$$(\text{CH}_3\text{CH}_2\text{CH}{=}\text{NO}_2)^-\text{Na}^+ + (\text{EtO})\text{P}{-}\text{Cl} \rightarrow (\text{EtO})_2\text{P}{-}\text{CH}(\text{NO}_2)\text{CH}_2\text{CH}_3.$$

13%

The phosphorylation with dialkyl phosphorochloridate of the dilithium salts of nitroalkanes obtained by the reaction of lithium diisopropylamide (LDA) with nitroalkanes at –78 °C takes place more sucessfully.[15] In order to diminish the occurrence of the Neff side reaction, the reaction product is protonated with glacial acetic acid to give a nitroalkylphosphonate.

$$\text{RCH}_2\text{NO}_2 \xrightarrow[\text{2) (EtO)}_2\text{POCl/THF}]{\text{1) 2LDA/THF, –78 °C}} \left[(\text{EtO})_2\text{P}(\text{O})\text{CR}(\text{NO}_2)\right] \xrightarrow[\text{THF, –78 °C}]{\text{AcOH}} (\text{EtO})_2\text{P}(\text{O})\text{CHR}(\text{NO}_2);$$

47–75%

R = Me. Et.

The dialkylphosphite anion phosphorylates 2-chloro- or 2-(toluene-*p*-sulphonyl)-2-nitropropane in a free-radical $S_{RN}1$ reaction via the radical-ion of dialkyl phosphite with formation of α-nitroalkyl phosphonates.[16]

$$\text{O}_2\text{NCR}_2\text{X} + (\text{R}^1\text{O})_2\text{PO}^-\text{K}^+ \xrightarrow[45–25\ ^\circ\text{C}]{\text{THF}} (\text{R}^1\text{O})_2\text{P}(\text{O})\text{CR}_2\text{NO}_2;$$

X = Cl. *p*-$MeC_6H_4SO_2$; R = Me. $(CH_2)_4$; R^1 = Me. Et.

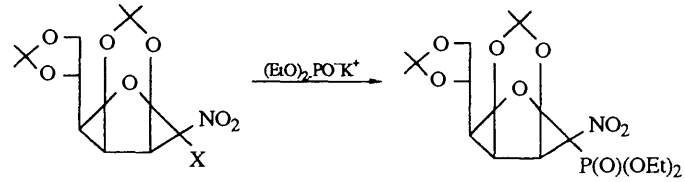
The reaction of 2,2-dinitropropane and 2-(toluene-*p*-sulphonyl)-2-nitropropane with the dialkyl phosphorothioite anion in dimethyl sulphoxide under irradiation takes place similarly.[17]

$$\text{Me}_2\text{C}(\text{X})\text{NO}_2 + (\text{RO})_2\text{PS}^-\text{K}^+ \xrightarrow[h\nu,\ 3.5\ \text{h}]{\text{M}_2\text{SO}} (\text{RO})_2\text{P}(\text{S})\text{CMe}_2\text{NO}_2 + \text{X}^-$$

30%

R = Me, X = NO_2; R = Et, X = *p*-$MeC_6H_4SO_2$.

The methods of synthesis of α-nitroalkylphosphonates have been used in carbohydrate chemistry to obtain phosphorus-containing derivatives.[18] Thus (1-*C*-nitroglycosyl)phosphonate was obtained from X-nitromannofuranose and potassium diethyl phosphite.



21—67%

X = Cl, *p*-$MeC_6H_4SO_2$.

The structure of organophosphorus α-nitro-compounds has been investigated by IR and NMR spectroscopy, which made it possible to discover the specific mutual influence of the nitro- and phosphoryl groups.

The ^{31}P chemical shift for α-nitroalkyl phosphonates (δ_P = 11–12 p.p.m.) is significantly lower than for other (β, γ, δ)-nitroalkylphosphonates. This can be explained by the strongly electron-accepting influence of the nitro-group.[12]

The characteristic absorption bands in the IR spectra of α-nitroalkyl phosphonates[5,6] at 1550–1560 [$\nu_{asym}(NO_2)$] and 1330–1360 [$\nu_{sym}(NO_2)$], 1260–1270 (P=O), 1120 and 1165 (POC), and 710 cm^{-1} (P–C bond) hardly differ from those for nitroalkanes and alkylphosphonates.

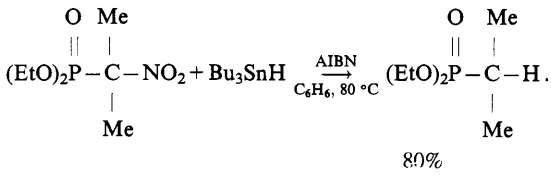
2. The chemical properties of organophosphorus α-nitro-compounds

The chemical properties of organophosphorus α-nitro-compounds are determined by their functional groups — the nitro-group and the phosphonate group. It is therefore useful to examine initially the chemical reactions associated with the nitro-group and then with the phosphonate group and finally other reactions specific to organophosphorus α-nitro-compounds.

Organophosphorus dialkyl nitro-compounds can be titrated potentiometrically in an aqueous medium with alkalis as weak monobasic acids.[6,7] Their ability to form sodium salts permits their purification via nitronic acids.[7,15]

The high CH acidity of organophosphorus α-nitroalkyl compounds is the cause of their reduced capacity for nucleophilic reactions. Thus they add with difficulty to derivatives of acrylic acid (the Michael reaction) and do not react with benzophenone.[19]

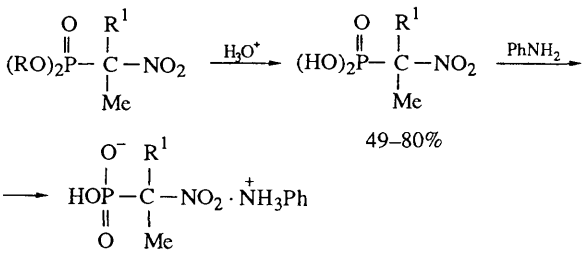
The nitro-group in tertiary organophosphorus α-nitro-compounds is readily substituted by hydrogen when the nitro-compound is treated with tributyltin hydride in the presence of azobisisobutyronitrile (AIBN).[20]



The interaction of diethyl (2,3 : 5,6-di-*O*-isopropylidene-1-nitro-α-D-mannofuranosyl)phosphonate with tributyltin hydride in the presence of AIBN leads to (2,3 : 5,6-di-*O*-isopropylidene-β-D-mannofuranosyl)phosphonate in 78% yield.[18]

Organophosphorus α-nitro-compounds are readily reduced catalytically in the presence of Raney nickel[4] and also with tin and hydrochloric acid[17] to the corresponding amino-derivatives.

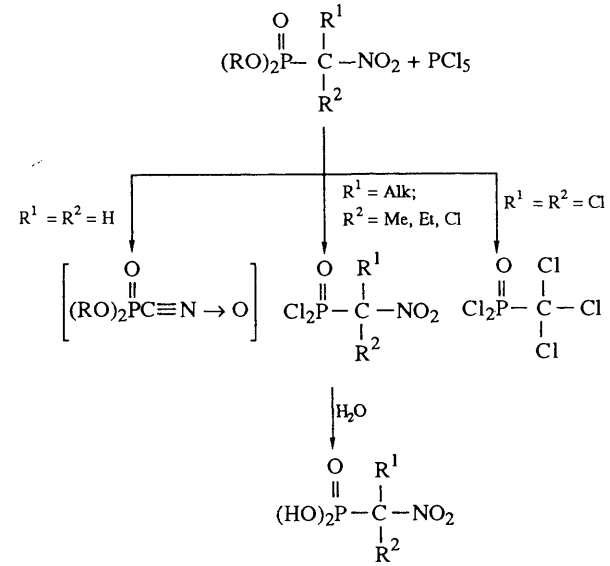
Acid hydrolysis of α-nitroalkylphosphonates not containing hydrogen atoms at the carbon atom linked to the nitro-group leads to high yields of the corresponding organophosphorus α-nitroacids, which were isolated in the form of monoanilinium salts.[6,13]



R, R^1 = Me, Et.

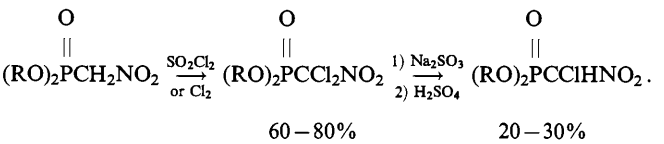
Hydrolysis of α-nitroalkylphosphonates containing hydrogen atoms at the α-carbon atom leads to their decomposition with formation of hydroxylamine hydrochloride (75%) and phosphoric acid.[7]

α-Nitroalkylphosphonates unsubstituted at the α-carbon atom, for example, diethyl nitromethylphosphonate, react with phosphorus pentachloride to form phosphonocyanidate *N*-oxide or its decomposition products, while the substituted derivative afford high yields of the hydrochlorides, which are then hydrolysed to the corresponding acids.[6,13] α-Nitroalkylphosphonates monochloro-substituted in the α-position,[21] for example, dimethyl 1-chloro-1-nitropropylphosphonate, react with phosphorus pentachloride to form the dichloride of 1-chloro-1-nitro-propylphosphonic acid in 72.5% yield. Its hydrolysis leads to the corresponding acid, which was isolated as the anilinium salt (64.8%). The interaction of dichloro-substituted diethyl nitromethylphosphonate with phosphorus pentachloride leads to the substitution not only of the alkoxy-group but also of the nitro-group by a chlorine atom, which results in the formation of the dichloride of trichloromethylphosphonic acid in 80% yield.



α-Nitroalkylphosphonates are readily brominated via the lithium salt to give the corresponding bromonitroalkylphosphonates.[5]

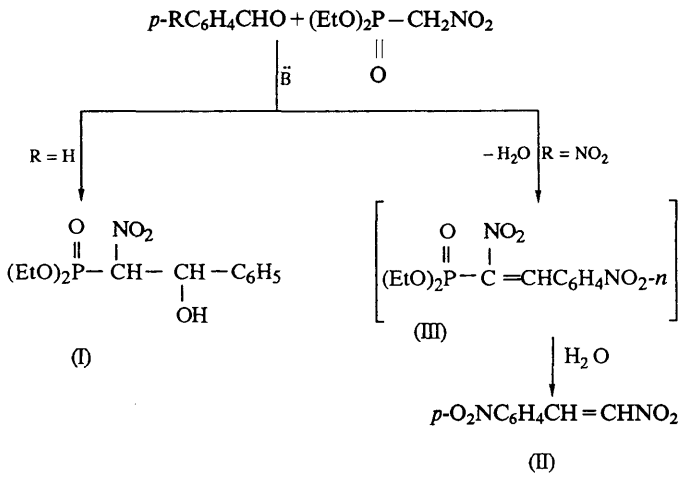
On treatment with sulphuryl chloride or chloride, the mobile hydrogen atoms in the methylene or methylidyne groups in α-nitroalkylphosphonates are substituted by a chlorine atom, which results in the formation of dichloronitroalkylphosphonates. These are readily converted into monochloro-derivatives on treatment with sodium sulphite.[21]



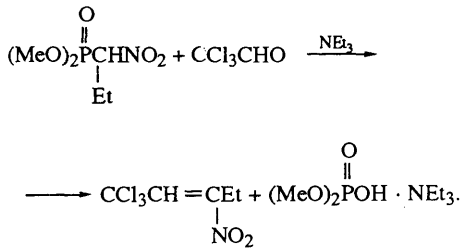
Chloronitromethylphosphonates behave in aqueous alcoholic solutions as weak monobasic acids. The IR spectra of these compounds are characterised by the presence of absorption bands at 1575 and 1350 cm^{-1} (NO_2), 1280 cm^{-1} (P=O), and 710 cm^{-1} (Cl). With increase in the number of chlorine atoms at the α-carbon atom, there is some increase in $\Delta\nu = \nu_{asym} - \nu_{sym}$ for the nitro-group: the corresponding frequencies ν_{asym} and ν_{sym} are 1560 and 1375 cm^{-1} for $(EtO)_2P(O)CH_2NO_2$, 1575 and 1350 cm^{-1} for $(EtO)_2P(O)CHClNO_2$, and 1600 and 1335 cm^{-1} for $(EtO)_2P(O)CCl_2NO_2$.

Diethyl nitromethylphosphonate reacts with benzaldehyde in the presence of piperidine to form diethyl 2-hydroxy-1-nitro-2-phenylethyl phosphonate (I) in 67% yield.[22] However, the reaction with *p*-nitrobenzaldehyde under the same or even milder conditions afforded 1-(*p*-nitrophenyl)-2-nitroethene (II) (80%). This course of the reaction is due to the presence of the electron-accepting nitro-group in the aromatic ring, which promotes the formation of the

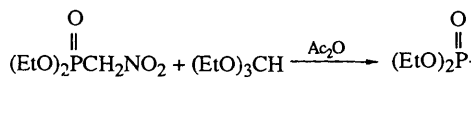
alkene (III), the latter being subsequently dephosphorylated to the more stable nitroalkene (II).



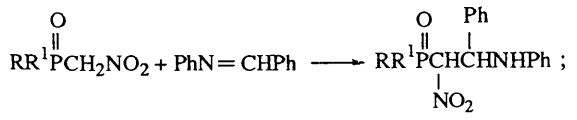
Similar elimination of the phosphonate group with formation of 1,1,1-trichloro-3-nitropent-2-ene is observed in the reaction of the highly electrophilic chloral with dimethyl 1-nitropropylphosphonate in the presence of triethylamine.[19]



Condensation of diethyl nitromethylphosphonate with triethyl orthoformate in acetic anhydride leads to diethyl 2-ethoxy-1-nitrovinylphosphonate in the form of a mixture of the (*E*)- and (*Z*)-isomers.[19]

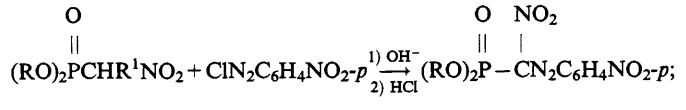


Organophosphorus α-nitro-compounds interact with benzylideneaniline in the absence of a catalyst.[19]



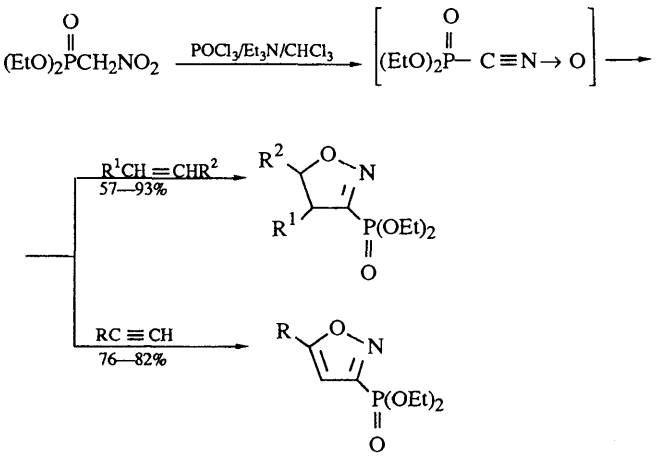
R, R^1 = OMe, OEt, Et, Ph.

α-Nitroalkylphosphonates enter into the azo-coupling reaction in an alkaline medium with *p*-nitrobenzenediazonium chloride.[19]



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

On treatment with phosphoryl chloride in the presence of triethylamine, diethyl nitromethylphosphonate gives rise to a phosphorocyanidate *N*-oxide which at the instant of formation adds via the 1,3-dipolar cycloaddition mechanism to alkenes and alkynes with formation of the corresponding 3-diethoxyphosphoryl-4,5-dihydroizoxazoles and 3-diethoxyphosphorylisoxazoles.[23]

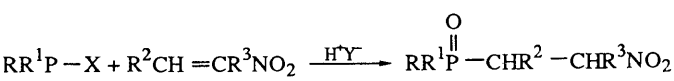


III. Organophosphorus β-nitro-compounds

1. Methods of synthesis of organophosphorus β-nitro-compounds

The study of the reactions of the full phosphites with nitroalkenes by a set of physicochemical methods demonstrated that the process proceeds via several competing pathways with formation of phosphoranes, alkenylphosphonates, β-nitroalkylphosphonates, oximes, nitriles, etc.[24]

The reactions of the full phosphites with nitroalkenes in proton-donating solvents lead mainly to organophosphorus β-nitro-compounds.[24–26]



R, R^1 = AlkO. PhO. Alk. Ph; R^2 = H. Alk. Ph;

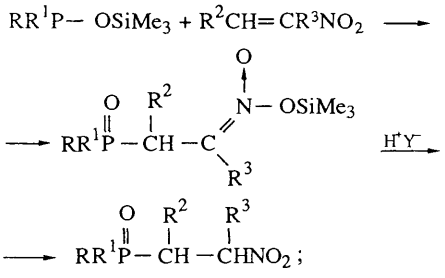
R^3 = H. Br. Et; X = AlkO; Y^- = OH^-. AcO^-.

The target products contain admixtures of α,β-unsaturated compounds. In order to reduce their content, appropriate protonating compounds and mixtures are selected: methanol,[27–29] phenol,[30] t-butyl alcohol–benzene,[31,32] water,[33,34] water–dioxane,[25,35,36] water–tetrahydrofuran,[37,38] water–dimethoxyethane,[39] acetic acid,[25] and *N*,*N*-diethylaniline hydrochloride in acetonitrile.[40]

The formation of the 1-nitroprop-1-ene radical-anion in the reaction of methyl diphenylphosphonite [methyl phenyl phenylphosphonite?] with 1-nitropropene was detected by the EPR method.[41,42] This reaction proved to be a convenient model for the determination of the thermodynamic parameters of the $P^{III} \leftrightarrows P^{V}$ equilibrium.[43]

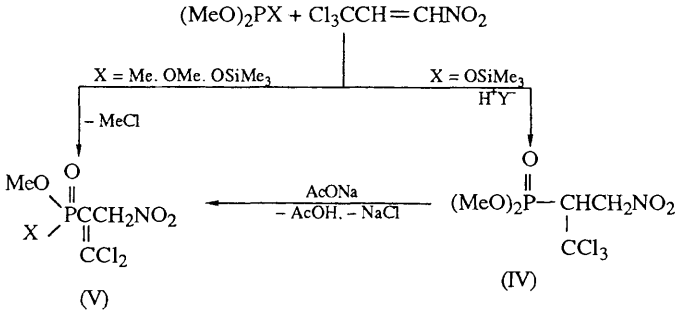
The reaction of silicon-containing derivatives of phosphorus(III) acids with nitroalkenes proved to be a more convenient method of synthesis of organophosphorus β-nitro-compounds. The first stage of this reaction involves the formation of the trimethylsilyl

esters of phosphorylated nitronic acids, which are then readily decomposed by water[34,44,45] and other proton-donating reagents (water-tetrahydrofuran,[37,38] dilute hydrochloric acid[46]).



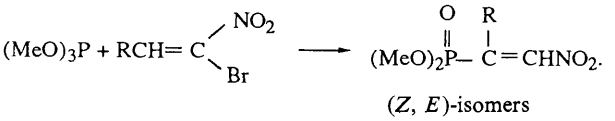
R = Alk. Ar. AlkO; R^1 = Alk; R^2 = Alk. CCl_3; R^3 = H. Br.

The reaction of the full esters of phosphorus(III) acids with 3,3,3-trichloro-1-nitroprop-1-ene proceeds under mild conditions.[47,48]



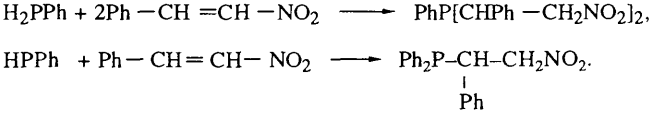
When the product of the interaction of dimethyl trimethylsilyl phosphite with 3,3,3-trichloro-1-nitroprop-1-ene[48] is treated with proton-donating reagents (water, methanol, acetic acid, and hydrogen chloride), dimethyl 2,2-dichloro-1-nitromethylvinylphosphonate (V) is formed together with dimethyl 1-trichloromethyl-2-nitroethylphosphonate (IV). This shows that the presence of the strongly electron-accepting trichloromethyl group at the α-carbon atom of the organophosphorus compound increases significantly the mobility of the α-CH proton, which is able to compete even with the trimethylsilyl group in terms of its capacity for migration. In aprotic solvents, 2,2-dichloro-1-nitromethylvinylphosphoryl derivatives (V) are formed exclusively. Since the chloride anion behaves more readily as a leaving group than the nitrite anion, in this case 1-trichloromethylvinylphosphoryl compounds are not formed. The nitro-derivative (IV) is readily dihydrochlorinated with sodium acetate in ether, affording the product (V).

(*Z*) 1-Bromo-1-nitroalk-1-enes[36,49,50] react with trialkyl phosphite to form nitroalkenylphosphonates. Thus the reaction of trialkyl phosphite with (*Z*)-1-bromo-1-nitro-3-methylbut-1-ene results in the formation of a mixture of the (*Z*)- and (*E*)-isomers of 2-nitroalkenylphosphonates and other compounds.

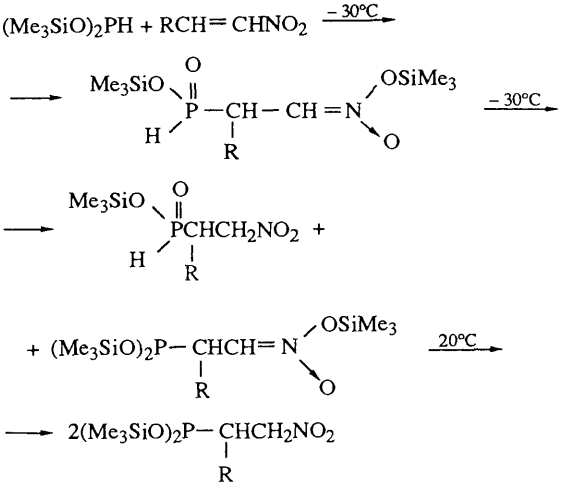


(*Z*, *E*)-isomers

One of the most thoroughly investigated methods of synthesis of organophosphorus β-nitro-compounds involves the nucleophilic addition of hydrophosphoryl compounds to conjugated nitroalkenes. Thus the interaction of phenylphosphine and diphenylphosphine with nitrostyrene leads to the formation of the corresponding di- and mono-adducts.[51]

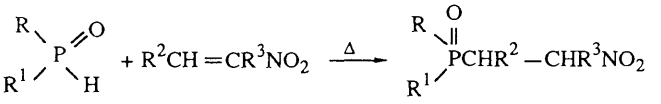


The interaction of bis(trimethylsilyl) hypophosphite with 1-nitroprop-1-ene and nitrostyrene is a multistep process. When the reaction is carried out at temperatures in the range −30 − 35 °C, trimethylsilyl 2-aci-nitroalkylphosphonites are formed. The latter are converted at room temperature into bis(trimethylsilyl) phosphonites.[52]



R = Me. Ph.

Dialkylphosphinties,[53,54] alkyl alkylphosphonates,[54] dimethyl phosphite,[54–56] and diethyl phosphite[57] add to conjugated nitroalkenes after prolonged heating at 100 °C in the absence of catalysts to form organophosphorus β-nitro-compounds.



19—96%

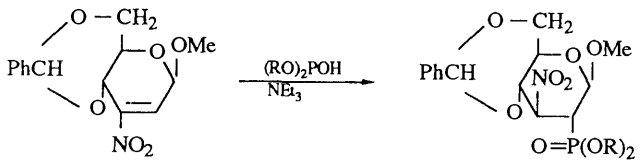
R, R^1 = Ph, $PhCH_2$, C_6H_{13}, OMe; R^2 = Me, Ph, Pr, Et, iso-Pr;

R^3 = H, Me, COOEt.

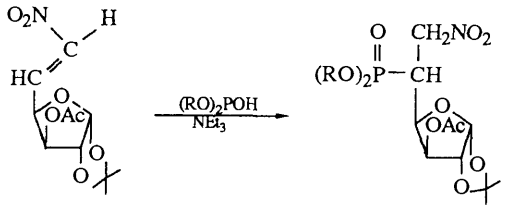
An attempt was first made to carry out this reaction in the presence of basic catalysts, but the competing polymerisation reaction of the nitroalkene reduced the yield of the organophosphorus β-nitro-compound or altogether prevented its formation.[58] The polymerisation of nitroalkenes was partly suppressed by using an excess of dialkyl phosphite and a polymerisation inhibitor.[59]

The addition of dialkyl phosphites to unsaturated nitrosugars is one of the ways of modifying the latter.[60] Phosphonites and phosphines have also been used to modify sugars.[61] Thus the addition of methyl ethylphosphonite to 3-*O*-acetyl-5,6-dideoxy-1,2-isopropylidene-6-*C*-nitro-α-D-xylohex-5-enofuranose takes place on heating at 70 − 80 °C for 7 − 10 h, the yield of the adduct being

90%. When phenylphosphine is used, monoadducts (63%) and diadducts (34%) are formed.[61]

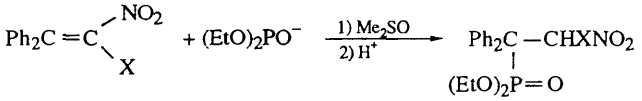


R = Me (69%); Et (3.4%)



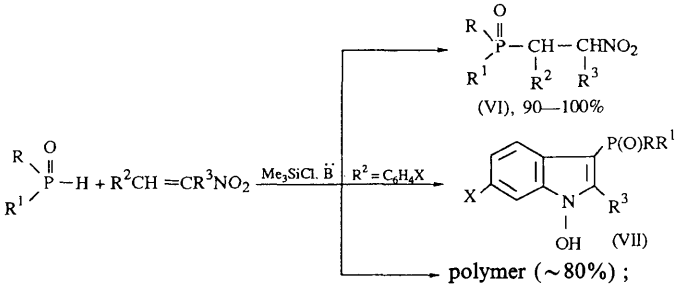
R = Me (43%); Et (3.4%)

The interaction of 1,1-dinitro-2,2-diphenylethene[62] and its derivatives[63] with one equivalent of diethyl phosphite in dimethyl sulphoxide leads to the corresponding adducts on acidification.



X = H, PhS, t-BuS, NO_2.

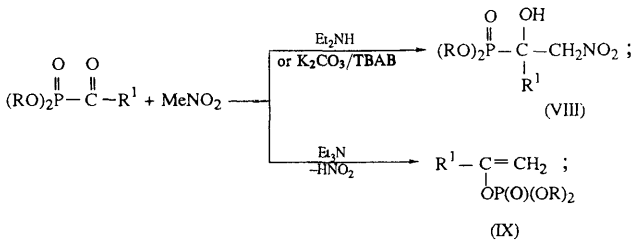
Reactions of partly esterified phosphites with nitroalkenes in the presence of trimethylsilyl chloride and a base, which proceed via a stage involving the formation of dialkyl trimethylsilyl phosphite, lead to organophosphorus β-nitro-compounds in almost quantitative yields.[64] It was later shown that, depending on the nature of the nitroalkene, the reactant ratio, and the reaction conditions, organophosphorus nitro-compounds (VI), *N*-hydroxyindoles (VII), and polymers are formed.[65,66]



R, R^1 = Alk, Ph, AlkO; R^2 = H, Alk, Ph, *p*-HOC_6H_4; R^3 = H, Me.

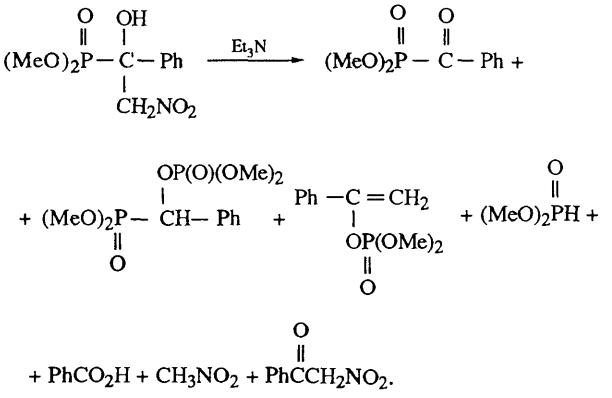
Thus polar solvents promote the formation of the organophosphorus compounds (VI). In terms of their effect on the formation of compounds (VI), the solvents can be arranged in the following sequence : DMF > Me_2CO > MeCN > CH_2Cl_2 > THF > Et_2O > C_6H_6.[65] When aromatic nitroalkenes with electron-donating substituents in the benzene ring, weakly polar solvents, and highly basic acid-binding reagent are used, the reaction proceeds mainly via the pathway leading to the formation of the indole derivative (VII). (The structure of *N*-hydroxyindoles was established by NMR spectroscopy and X-ray diffraction[65]). The formation of the polymeric adduct is promoted by inorganic bases.

The interaction of organophosphorus α-carbonyl compounds with nitroalkanes to form the corresponding organophosphorus β-nitro-compounds (VIII) takes place successfully in the presence of diethylamine and Triton B (OH)[67–69] and also under the conditions of phase transfer catalysis in the K_2CO_3–tetrabutylammonium bromide (TBAB) system.[70] When triethylamine is used, the enol phosphate (IX)—the product of the phosphonate–phosphate rearrangement of compound (VIII)—is formed preferentially.



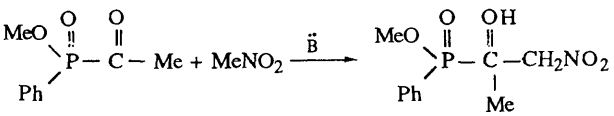
R = Me, Et, iso-Pr; R^1 = Me, Et, Pr, *m*-MeC_6H_4, *o*-MeC_6H_4, *p*-MeC_6H_4, *p*-FC_6H_4, *m*-FC_6H_4, *o*-FC_6H_4, *o*-ClC_6H_4, *p*-ClC_6H_4, $PhCH_2$, $PhCH_2CH_2$, *p*-$FC_6H_4CH_2$, C_6H_{11}.

Apart from the enol phosphate (IX), other products were also identified in the reaction mixture when the reaction was carried out in the presence of triethylamine, which indicates the reversibility of the reaction and the capacity for the cleavage of the C–C and C–P bonds in the initial compound (VIII).[70]

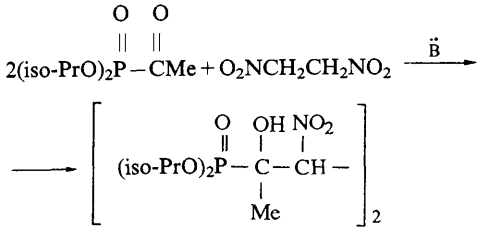


Thermographic studies showed that, in the absence of catalysts, the phosphonate–phosphate rearrangement does not occur, compound (VIII) being decomposed with rupture of the C–P bond and subsequent oxidation.[71]

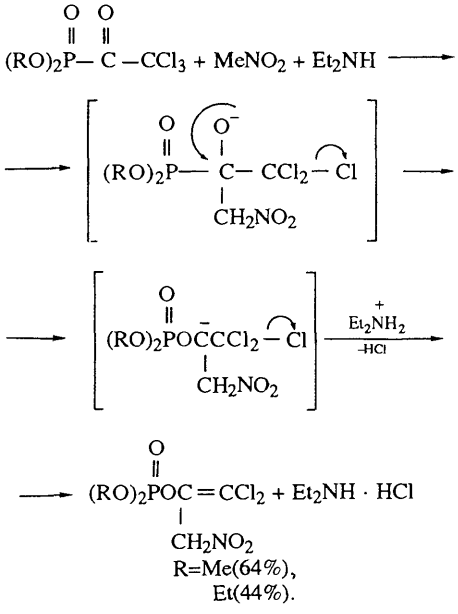
Apart from the α-carbonyl derivatives of phosphonates, acylphosphinates also react with nitroalkanes. Thus the reaction of nitromethane with methyl acetyl(phenyl)phosphinate affords methyl 2-hydroxy-1-nitropropyl(phenyl)phosphinate.[72]



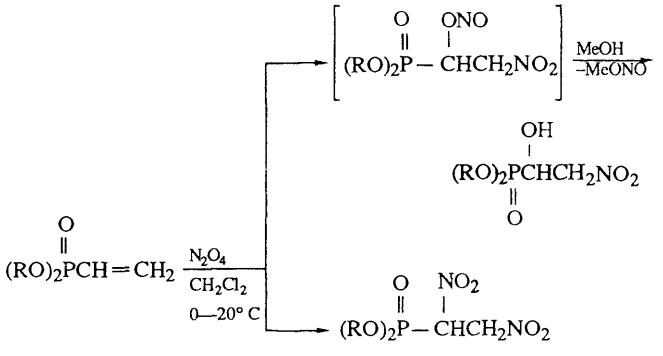
The vicinal dinitroethane reacts with diisopropyl acetylphosphonate in any molar proportions to form only the diadduct.[73]



The reaction of trichloroacetylphosphonate with nitromethane[74] affords the products of the phosphonate–phosphate rearrangement — dialkyl 2,2-dichloro-1-nitromethylvinyl phosphates.



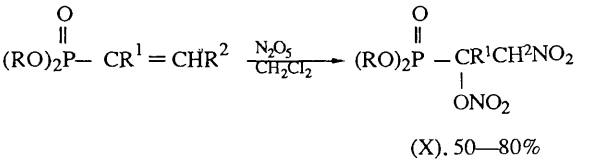
Nitration of unsubstituted vinylphosphonates with dinitrogen tetroxide leads predominantly to dialkyl 1-hydroxy-2-nitroethylphosphonates and dialkyl 1,2-dinitroethylphosphonates in a very low yield.[75,76]



R = Me, Et, iso-Pr, CH_2CH_2Cl.

Alkyl-substituted vinyl phosphonates could not be nitrated.

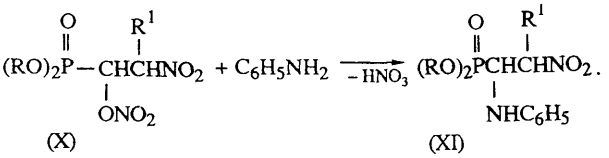
Dinitrogen pentoxide interacts with vinylphosphonates to form the relatively unstable dialkyl 2-nitro-1-nitroxyalkylphosphonates (X).[77] Certain alkyl-substituted vinylphosphonates also enter into this reaction.



(X). 50—80%

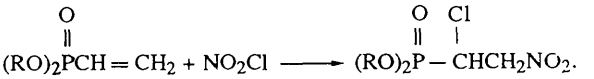
R = Me, Et, iso-Pr, CH_2CH_2Cl' R^1 = H, Me; R^2 = H, Ph.

In the nitration of dimethyl-2-phenylvinylphosphonate with dinitrogen pentoxide, the nitro-group adds to the β-position (δ_P = 21 p.p.m.) , in contrast to its nitration with dinitrogen tetroxide.[77] Compounds (X) react with aniline to form the stable crystalline products (XI):[77]



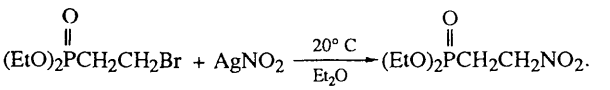
The reaction apparently proceeds via the intermediate formation of nitroalkenes.

The reaction of nitrosyl chloride with dialkyl vinylphosphonate results in the formation of 1-chloro-2-nitroalkylphosphonates.[78]



It is noteworthy that the interaction of nitrosyl chloride with the dichlorides of α-chloro-β-ethoxy- and β-chloro-β-ethoxy-vinylphosphonates and their full esters takes place in a complex manner and does not lead to organophosphorus nitro-compounds.[79]

2-Nitroethylphosphonates are also obtained by Kornblum's method from 2-bromoethylphosphonate and silver nitrite.[80]



2. The structure of organophosphorus β-nitro-compounds

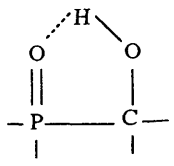
The structure of organophosphorus β-nitro-compounds has been investigated by IR and NMR spectroscopy and by X-ray diffraction.

The ^{31}P chemical shift for β-nitroalkylphosphonates (δ_P = 17–22 p.p.m.) is greater than for α-nitroalkylphosphonates (δ_P = 11–12 p.p.m.), which indicates a decrease in the influence of the nitro-group on the magnetic characteristics of the phosphorus atom.

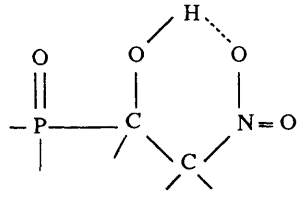
The absorption bands of the nitro- and phosphoryl groups in the IR spectra of organophosphorus β-nitro-compounds do not differ from the analogous bands in the spectra of organophosphorus and nitro-compounds.

The stereochemistry of α-aryl-β-nitroalkylphosphinates has been studied in greater detail.[66] The compounds were separated by recrystallisation into two pairs of diastereoisomers and the structure of each pair was determined by X-ray diffraction.

The structure of the organophosphorus β-nitroalcohols was also of theoretical interest. On the basis of their geometrical structure, one may postulate the formation of two types of hydrogen bonds: via the phosphoryl oxygen with closure of a five-membered ring [structure (A)] and via the oxygen of the nitro-group with closure of a six-membered ring [structure (B)].

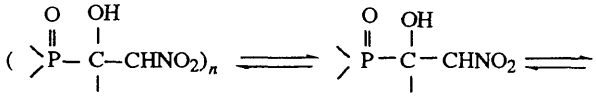


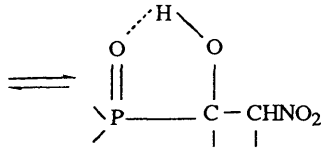
(A)



(B)

It has been shown by IR spectroscopy[81] that in the solid state β-nitro-alcohols form intermolecular hydrogen bonds [ν(OH) = 3220–3280 cm^{-1}] between the OH and P=O groups, whereas in solution an equilibrium is established between the free [ν(OH) = 3550 cm^{-1}] and associated molecules of the phosphonates.





In inert solvents, organophosphorus nitroalcohols form an intramolecular hydrogen bond via the oxygen of the phosphoryl group [structure (A)] with a very low interaction energy in the five-membered phosphorus-containing ring.

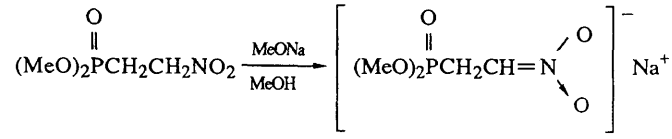
A hindered *gauche*-conformation with a transoid orientation of the phosphoryl and nitro-groups has been established for tertiary organophosphorus nitroalcohols by NMR. It is stable in the temperature range from −40 °C to 100 °C in various solvents.[12]

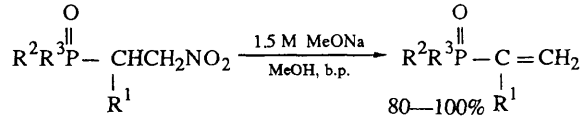
3. Chemical properties of organophosphorus β-nitro-compounds

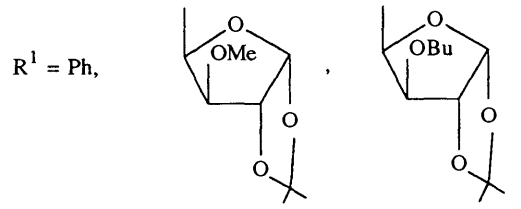
It is natural to expect that chemical reactions involving the nitro-, phosphoryl, and other functional groups as well as isomerisation processes and reactions involving cleavage at the C–P bond are characteristic of organophosphorus β-nitro-compounds.

(a) Reactions with participation of the nitro-group

2-Nitroethylphosphonates are converted into sodium nitronates in the reaction with sodium methoxide in methanol at room temperature,[31] whilst on boiling they afford the corresponding vinylphosphonates, vinylphosphinates, and vinylphosphine oxides.[82]



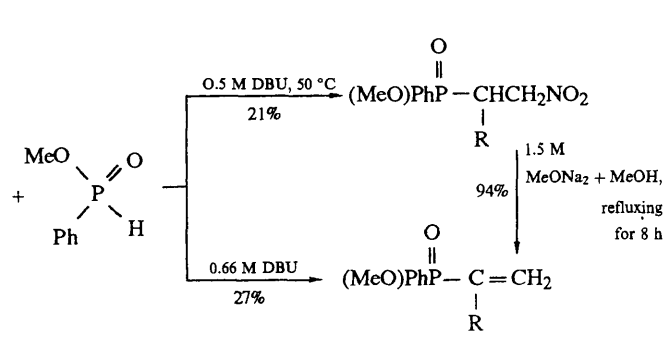


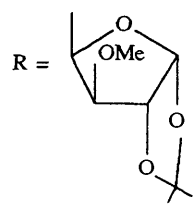


R^2, R^3 = OMe. Ph.

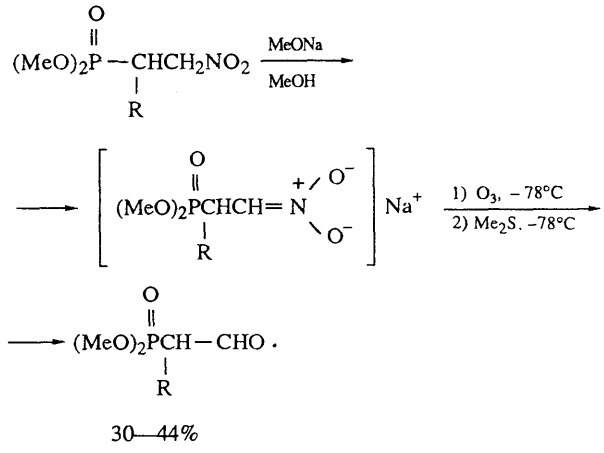
Proton exchange in the sodium methoxide–methanol system has been observed by the ^1H NMR method. It was demonstrated unambiguously that only the hydrogen atom at the β-carbon atom is acidic, whereas this was not observed for the hydrogen atoms at the α-carbon atom.[31]

Nitrovinyl-containing sugars have been converted into vinyl-substituted phosphorus-containing sugar derivatives either by the addition of the hydrophosphoryl compound in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) followed by denitration with sodium methoxide or by heating the initial reactants at 60 °C in the presence of DBU.[82]



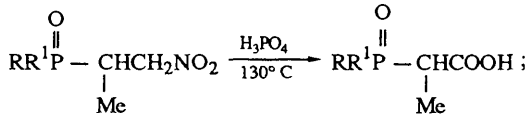


Treatment of sodium nitronate with ozone at −78 °C leads to the corresponding aldehyde:[55,56]



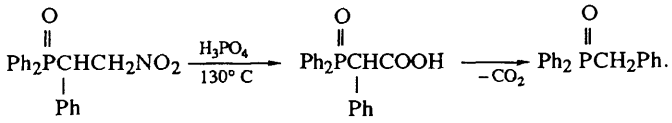
30—44%

When 2-nitroalkylphosphine oxides are heated to 130 °C with 85% orthophosphoric acid, the nitro-group is readily converted into a carboxy-group.[53]

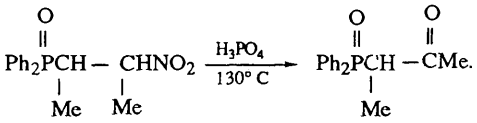


R, R^1 = Ph, $PhCH_2$, C_6H_{13}.

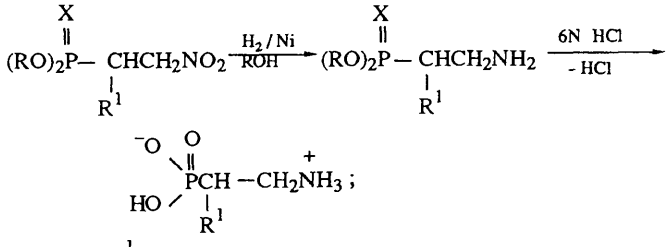
In the presence of a phenyl substituent at the α-carbon atom, the carboxy-group formed on treatment with orthophosphate decarboxylates under the reaction conditions. Thus benzylidiphenylphosphine oxide is formed from β-nitro-α-phenylethyl(diphenyl)phosphine oxide.[53]



The nitro-group in β-alkyl-substituted 2-nitroalkylphosphine oxides is converted into a keto-group under analogous conditions.[53]

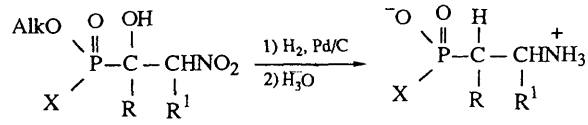


Organophosphorus β-nitro-compounds are reduced with hydrogen in the presence of the Raney nickel catalyst.[59,83,84] Subsequent acid hydrolysis of the 2-amino-derivatives leads to the corresponding aminoacids.



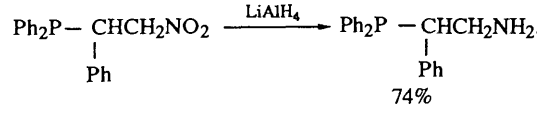
R = Alk; R^1 = Alk, Ph; X = O, S.

The reduction of 1-hydroxy-2-nitroalkylphosphonates with hydrogen in the presence of Raney nickel is accompanied by their partial decomposition at the C—P and C—C bonds.[72,85] Hydrogenation on palladium catalysts[72,86] or on Raney nickel in the presence of acetic acid[87] is more suitable. The reduction products are either isolated as picrates or are converted by acidic hydrolysis into the corresponding acids.[72,86–88]

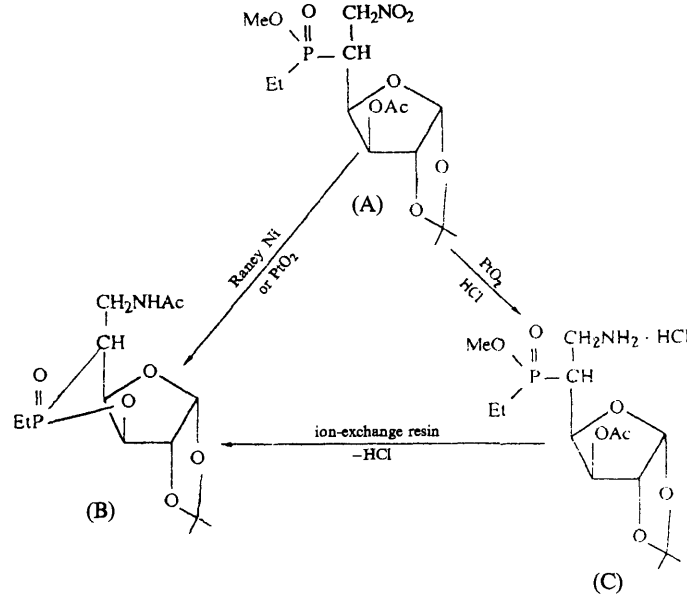


R, R^1 = Alk, Ph; X = OAlk, OH, Ph.

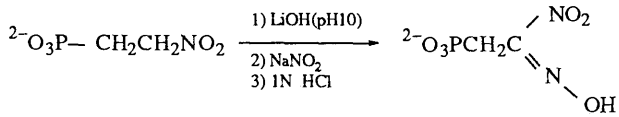
Lithium tetrahydroaluminate reduces 2-nitro-1-phenylethyl(diphenyl)phosphine to the corresponding amine.[51]



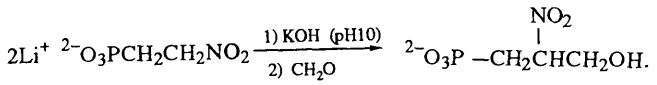
However, in the reduction of nitrosugars—for example, 3-*O*-acetyl-5,6-dideoxy-5-*C*-[ethyl(methoxy)phosphinyl]-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-glucofuranose (A)—with lithium tetrahydroaluminate or with sodium dihydrobis(2-methoxyethoxy)aluminate (SDMA), the sugar derivatives are decomposed. The reduction of compound (A) with hydrogen in the presence of Raney nickel affords a 69% yield of crystalline 6-acetamido-5-(3-*O*-cyclophosphinato)-5,6-dideoxy-1,2-*O*-isopropylidene-α-*D*-glucofuranose (B). In order to rule out cyclisation and the transfer of the acetyl group, compound (A) is reduced in the presence of hydrochloric acid in methanol using platinum oxide as the catalyst. The latter reaction leads to the formation of the unstable hydrochloride of 3-*O*-acetyl-6-amino-5,6-dideoxy-5-*C*-[ethyl(methoxy)phosphinyl]-1,2-*O*-isopropylidene-α-D-glucofuranose (C) in 80% yield. When compound (C) is treated with an ion-exchange resin in methanol, it is converted into compound (B).[61]



2-Phosphonoethylnitronic acid can be obtained by Mayer's method—by treating 2-nitroethylphosphonic acid with sodium nitrite at pH 10 (lithium hydroxide) on ice with subsequent slow acidification with 1 M solution of hydrochloric acid.[80]

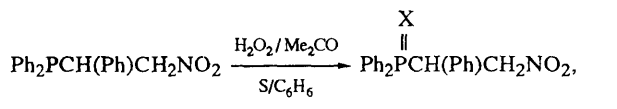


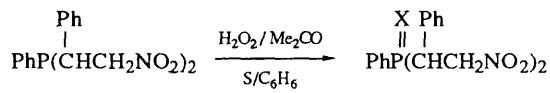
The lithium salt of 2-nitroethylphosphonic acid combines with two equivalents of formaldehyde at pH 10, affording 3-hydroxy-2-nitropropylphosphonic acid.[80]



(b) Reactions of the phosphorus-containing group

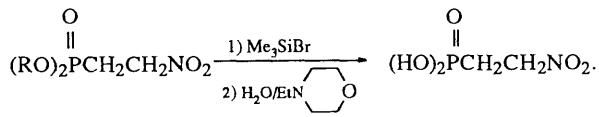
β-Nitro-derivatives of trivalent phosphorus are readily oxidised by a solution of hydrogen peroxide in acetone to *P*-oxides or are converted into *P*-sulphides on treatment with sulphur in benzene.[51]





X = O, S.

Dialkyl 2-nitroalkylphosphonate can be converted into the free acid by treatment with bromotrimethylsilane and subsequent hydrolysis of the resulting bis(trimethylsilyl) 2-nitroethylphosphonate with 0.5 M solution of *N*-ethylmorpholine.[80]



After the neutralisation of the reaction mixture with 1 M HCl solution, 85% of the nitro-groups remain unhydrolysed.

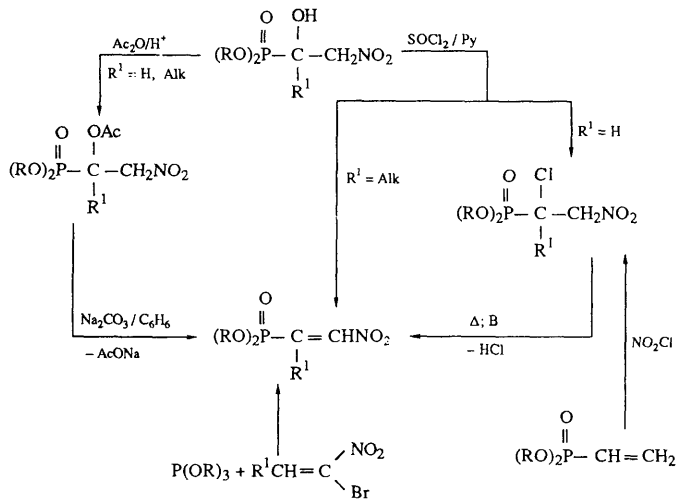
(c) Other reactions

The synthesis and properties of 2-nitrovinylphosphonates. The first representatives of 2-nitrovinylphosphonates were synthesised by deacetylating the acetyl derivatives of organophosphorus nitroalcohols[68] and by dehydrohalogenating 1-chloro-2-nitroalkylphosphonates.[78] Several representatives of 1-alkyl-substituted nitrovinylphosphonates have been obtained by the reaction of trialkyl phosphites with conjugated *gem*-bromonitroalkenes.[36,50]

The present authors investigated in detail the possibilities of the synthesis of 2-nitroalkenylphosphonates from organophosphorus nitroalcohols and nitronitrates.[89]

Direct dehydration of β-nitroalcohols with diphosphorus pentoxide or phthalic anhydride proved to be impossible owing to the low strength of the C–P bond. The acetyl derivatives of β-nitroalcohols are therefore formed initially, their deacetylation occurring readily in inert solvents in the presence of sodium carbonate.[68]

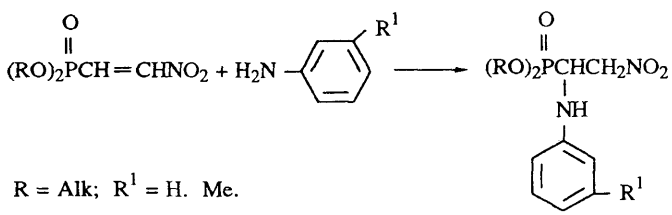
Thionyl chloride reacts with tertiary organophosphorus nitroalcohols in the presence of pyridine, affording satisfactory yields of nitrovinylphosphonates, while its reaction with secondary organophosphorus nitroalchols gives rise to 1-chloro-2-nitroalkylphosphonates which are isolated by column chromatography. On the other hand, chloronitroalkylphosphonates split off hydrogen chloride during distillation and on treatment with organic bases, forming the corresponding nitrovinylphosphonates in a low yield.[89]



It has been shown by ^{1}H and ^{31}P NMR spectroscopy that 2-nitrovinylphosphonates give rise predominatly to the (*E*)-isomers.

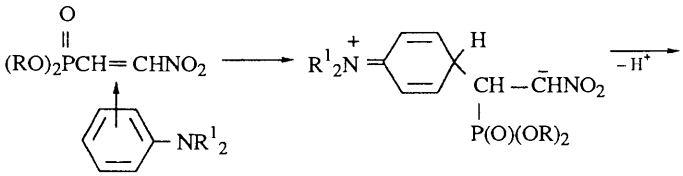
Nucleophilic reactions of 2-nitrovinylphosphonates. Condensation of 2-nitrovinylphosphonates with many nucleophiles and their involvement in the diene synthesis[90] have expanded their synthetic possibilities.

Aromatic amines (aniline, *m*-toluidine) readily add to 2-nitrovinylphosphonate in acetic acid, affording the corresponding products in satisfactory yields.[90]

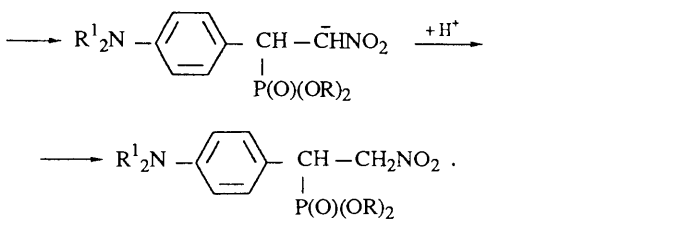


R = Alk; R^1 = H, Me.

It has been observed that 2-nitrovinylphosphonates are arylated by *N,N*-dialkylanilines.[90]

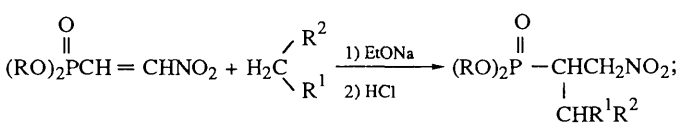


π-complex σ-complex



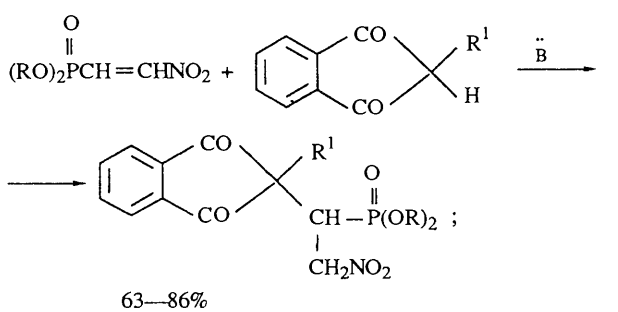
The reaction apparently proceeds via stages involving the formation of π- and σ-complexes.

The general mechanism of the addition of aliphatic CH acids to nitrovinylphosphonates can be represented as follows:[90,91]



R = Alk; R^1. R^2 = H. COOAlk. CN. NO_2. C(O)Me.

The conditions for the addition of β-diketones to 2-nitrovinylphosphonates depend on the structure of the β-diketones.

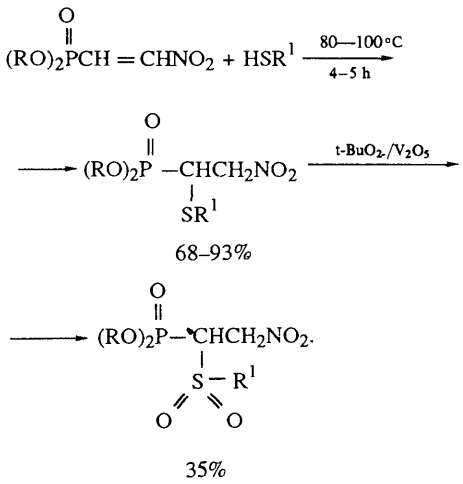


63—86%

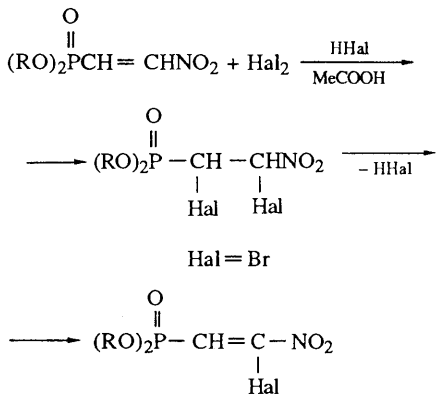
R = Alk; R^1 = H, Ph, *p*-$MeOC_6H_4$, MeCO.

It has been established[90,92] that β-diketones which do not enolise in their usual state (indan-1,3-dione, 2-phenylindan-1,3-dione, 2-anisylindan-1,3-dione, and 2-acetylindan-1,3-dione) react with 2-nitrovinylphosphonate in aprotic solvents (benzene) in the presence of triethylamine, i.e. under conditions suppressing enolisation according to Mayer's inverse rule,[93] whereas enolisable β-diketones (dimedone, barbituric acid) react in the presence of sodium ethoxide in ethanol, i.e. under conditions promoting enolisation in conformity with Mayer's inverse rule.

Alkanethiols interact with organophosphorus nitroalkenes on heating in a sealed tube.[90,94] The reaction apparently proceeds via a radical mechanism. The organophosphorus nitrosulphides formed as a result are oxidised to the corresponding sulphones by t-butyl peroxide in the presence of divanadium pentoxide.



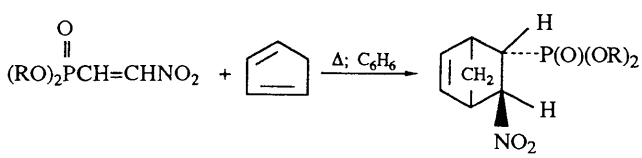
The increased nucleophilicity of the double bond in 2-nitrovinylphosphonates permits their halogenation only under the conditions of nucleophilic addition, namely in acetic acid in the presence of a hydrogen halide as the catalyst.[90]



Hal = Cl. Br.

In the bromination of an organophosphorus nitroalkene, it is possible to obtain in the first stage an adduct, which after isolation and during storage is gradually converted into a bromonitroalkenylphosphonate. However, on chlorination of the nitroalkene, the intermediate could not be isolated.

The reaction with cyclopentadiene takes place stereospecifically for 2-nitrovinylphosphonate with retention of the(*E*)-configuration.[91]



IV. Organophosphorus γ-nitro-compounds

Organophosphorus γ-nitro-compounds are interesting as precursors of phosphonic analogues of γ-aminobutyric acid, which exhibit a broad spectrum of biological activity.[95]

1. Synthesis of organophosphorus γ-nitro-compounds

The addition of nitryl chloride to diethyl allenylphosphonate and subsequent dehydrochlorination of the adduct with triethylamine lead to nitroallenylphosphonate.[78]

$$(EtO)_2P(O)CH_2CH{=}CH_2 + NO_2Cl \longrightarrow (EtO)_2P(O)CH_2CHClCH_2NO_2 \xrightarrow{Et_3N} (EtO)_2P(O)CH_2CH{=}CHNO_2$$

53.8%

Nitromethane adds to vinylphosphonates under the conditions of the Michael reaction with formation of mono-, di-, and tri-adducts. The monoadduct was obtained by the reaction of nitromethane with diethylvinylphosphonate.[96,97] However, di-(2-chloroethyl) vinylphosphonate reacts with nitromethane to form predominantly di- and tri-adducts, which were isolated by column chromatography.[90]

$$(RO)_2P(O)-CH{=}CH_2 + MeNO_2 \xrightarrow{\ddot{B}} \left[(RO)_2P(O)CH_2CH_2\right]_n CH_{(3-n)}NO_2$$

R = Et. n = 1 (37%); R = CH_2CH_2Cl. n = 2 (70%); n = 3 (9%).

Diethyl 1-cyanovinylphosphonate also combines actively with nitroalkanes under the conditions of the Michael reaction.[98]

$$(EtO)_2P(O)-C(CN){=}CH_2 + RR^1CHNO_2 \longrightarrow (EtO)_2P(O)-CH(CN)-CR^1(NO_2)-R;$$

R, R^1 = H, Me.

Trinitromethane reacts with diethyl vinylphosphonate in ether without a catalyst at room temperature.[99]

$$(EtO)_2P(O)-CH{=}CH_2 + HC(NO_2)_3 \longrightarrow (EtO)_2P(O)CH_2CH_2C(NO_2)_3.$$

Nitroacetic ester reacts with vinyl phosphonates under the conditions of the Michael reaction, affording either mono- and di-adducts or dihydroisoxazole depending on the nature of the aklkoxy-substituents at the phosphoryl and carbonyl groups.[90]

$$(RO)_2P(O)CH{=}CH_2 + CH_2(NO_2)COOR^1 \xrightarrow{\ddot{B},\ -H_2O} [(RO)_2P(O)CH_2CH_2]_n CH_{(2-n)}(NO_2)COOR^1;$$

$$(RO)_2P(O)-CH(CH_2)-C(=N)-COOR^1;$$

n = 1. 2;

R = R^1 = Et.

Triethyl phosphonacetate adds to 1-nitroalkenes in the presence of bases to form organophosphorus γ-nitro-compounds.[58,59]

$$(EtO)_2P(O)CH_2COOEt + RCH{=}CHNO_2 \xrightarrow{\ddot{B}} (EtO)_2P(O)CH(R)-CHCH_2NO_2-COOEt;$$

R = Me, iso-Pr.

The interaction of triethyl phosphonacetate with *p*-di(β-nitrovinyl)-benzene leads to a crystalline diadduct.[100]

$$O_2NCH{=}CHC_6H_4CH{=}CHNO_2 + (EtO)_2P(O)CH_2COOEt \xrightarrow{\ddot{B}}$$

$$\longrightarrow O_2NCH_2-CH(EtOOC-CH(P(O)(OEt)_2))-C_6H_4-CH(CH-COOEt)-CH_2NO_2$$

As a weak CH acid, dimethyl methylphosphonate reacts with nitroalkenes only in the presence of a superbase—lithium diisopropylamide.[101]

$$(MeO)_2P(O)-Me \xrightarrow[2)\ ClC_6H_4-CH{=}CHNO_2]{1)\ LDA/THF/\ -78\ ^\circ C} (MeO)_2P(O)CH_2CH(C_6H_4Cl)CH_2NO_2$$

71%

Methoxycarbonylmethylenetriphenylphosphorane (a CH acid) reacts with conjugated nitroalkenes at 90 °C to form ylides—methoxycarbonylalkylidenetriphenylphosphoranes.[102,103]

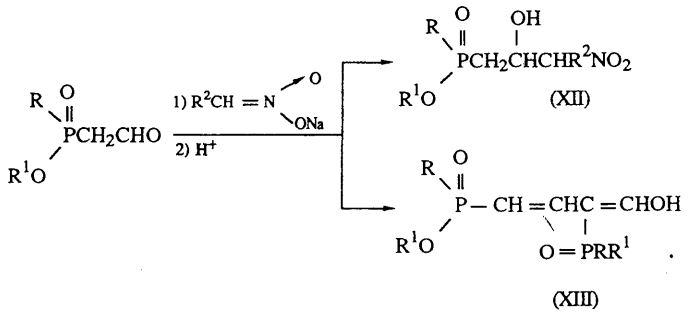
$$Ph_3P{=}CHCO_2Me + R(H)C{=}C(NO_2)R^1 \longrightarrow$$

$$\longrightarrow Ph_3P{=}C(CO_2Me)-CH(R)-CH(R^1)NO_2 \underset{Na_2CO_3}{\overset{Br_2}{\rightleftharpoons}}$$

$$\rightleftharpoons Ph_3P^+-C(Br^-)(Br)-CH_2-CH(NO_2)-CH_3(CO_2Me).$$

The preferential formation of ylides rather than a phosphonium salt in this reaction has been demonstrated by bromination.

Organophosphorus β-aldehydes react with nitroalkanes in the presence of bases to form β-hydroxy-γ-nitro-derivatives (XII), which were isolated by molecular distillation.[104] The reaction is accompanied by aldol self-condensation to compound (XIII).



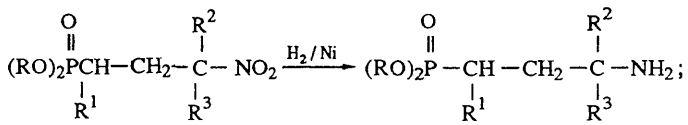
(XIII)

Organophosphorus γ-nitroalcohols (XII) form associated species characterised in the IR spectra by an OH absorption band in the range 3229–3267 cm^{-1}. On dilution with non-polar solvents and also on raising the temperature, the associated species decompose into monomers with intramolecular OH...O=P [ν(OH) = 3320–3400 cm^{-1}] and OH...O_2N [ν(OH) = 3488–3550 cm^{-1}] hydrogen bonds.

2. Chemical reactions of organophosphorus γ-nitro-compounds

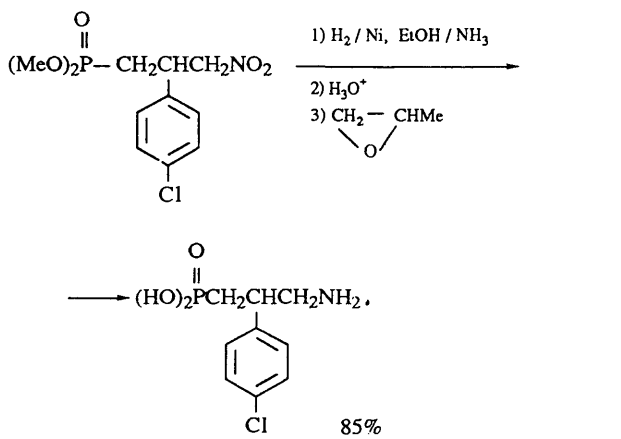
The chemical reactions of organophosphorus γ-nitro-compounds are predominantly reduction reactions.

Amino-derivatives are obtained by hydrogenating nitro-compounds in the presence of Raney nickel. In most cases they were isolated as the picrates.[83]



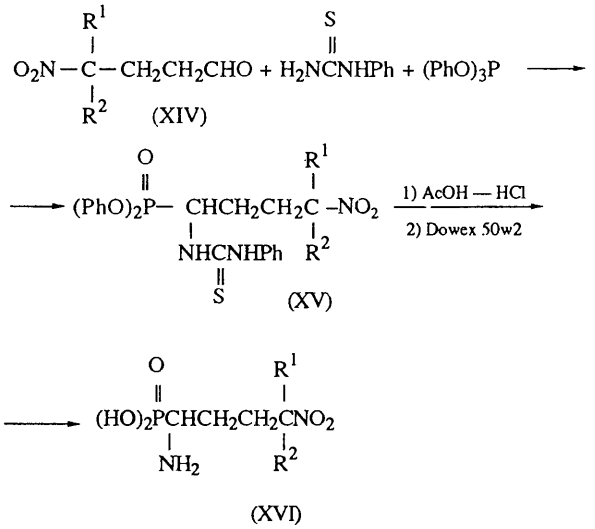
R = Et; R^1 = H, CN; R^2 = H, Me; R^3 = H, Me.

3-Aminopropylphosphonic acid was synthesised by condensing nitromethane with diethyl vinylphosphonate and subsequent reduction and hydrolysis.[97] (±)-3Amino-2-(4-chlorophenyl)propylphosphonic acid (phaclofen)—an antagonist of γ-aminobutyricacid (GABA)—is obtained similarly from the adduct resulting from the addition of dimethylmethylphosphonate to β-nitrostyrene.[101]



V. Organophosphorus δ-nitro-compounds

The condensation of nitroaldehydes (XIV) with triphenyl phosphite and phenylthiourea followed by decomposition of complexes (XV) by acid hydrolysis leads to α-amino-δ-nitroalkylphosphonic acids (XVI).[105]

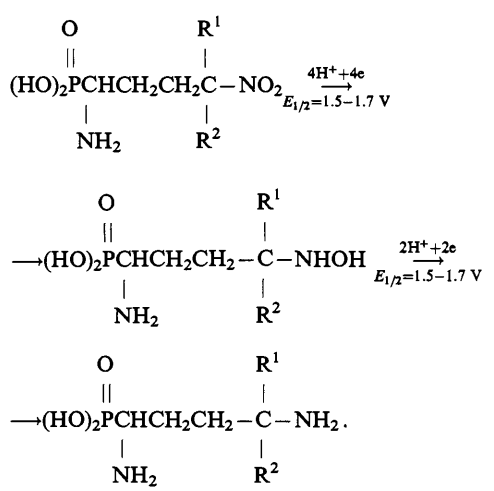


(XVI)

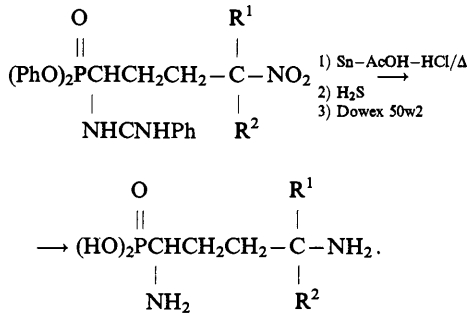
Compound	R^1	R^2	Yield of (XV), %	Yield of (XVI), %
a	H	H	72	10
b	Me	H	75	10
c	Me	Me	70	60

The acid hydrolysis of the nitro-compound (XVc), which contains no hydrogen atoms in the *gem*-positions relative to the nitro-group, takes place more successfully (60%). The hydrolysis of other nitro-derivatives is apparently accompanied by the Nef reaction.

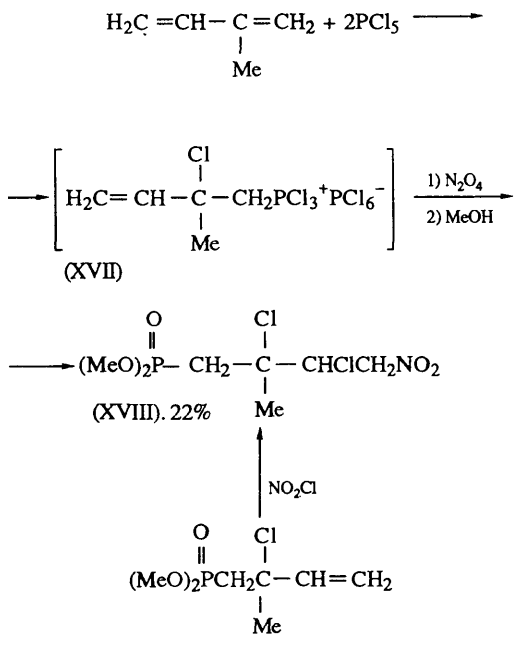
Compound (XVI) is reduced electrochemically initially to α-amino-δ-hydroxyamino-derivatives and then to α, δ-diaminoalkylphosphonic acids.[105]



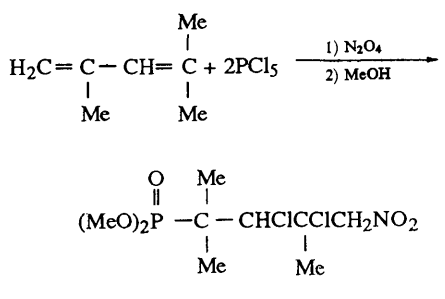
The reduction of diphenyl phosphonates (XV) with tin in the presence of acetic and hydrochloric acids affords in one stage α, δ-diaminoalkylphosphonic acids.[105]



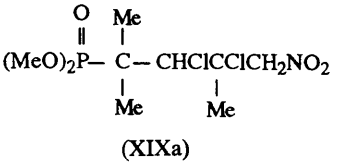
The decomposition with dinitrogen tetroxide of the complex between phosphorus pentachloride and isoprene (XVII) at 0 °C in an inert solvent with subsequent esterification is completed by the synthesis of dimethyl 2,3-dichloro-2-methyl-4-nitrobutylphosphonate (XVIII).[106–108] The structure of the product (XVIII) was confirmed by unambiguous synthesis.



The complex of 2,4-dimethylpenta-1,3-diene and phosphorus pentachloride reacts with dinitrogen tetroxide under analogous conditions to form dimethyl 3,4-dichloro-2,4-dimethyl-5-nitropentylphosphonate (XIXa).[107]

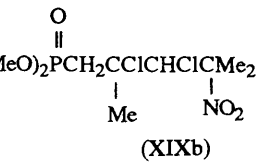


The δ_P = 16 p.p.m. signal in the ^{31}P NMR spectrum of the product (XIXa) confirms the postulated structure. On the other hand, nitrochlorination with nitryl chloride of the ester obtained form 2,4-dimethylpenta-1,3-diene and PCl_5 affords a mixture of the isomers (XIXa) and (XIXb) according to ^{31}P NMR data.



(XIXa)

δp = 16 p.p.m.

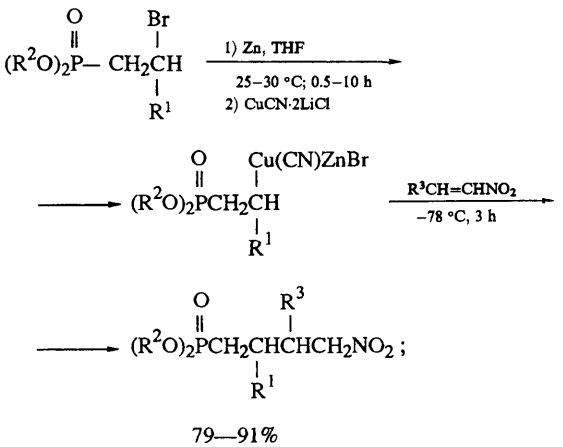


(XIXb)

δp = 26 p.p.m.

The formation of one isomer in the first case can be explained by the greater stability of compound (XIXa), containing a tertiary phosphonate group, in the stage involving the decomposition of the complex with dinitrogen tetroxide.

Certain zinc- and copper-containing β-metal-substituted alkylphosphonates also give rise to organophosphorus δ-nitro-compounds on reaction with nitroalkenes.[109]



79—91%

R^2 = H, Me, Et, Pr; R^1 = Me, Et; R^3 = Pr, Ph.

VI. Conclusion

Analysis of data on aliphatic organophosphorus nitro-compounds shows that the relative positions of the phosphoryl and nitro-groups influence significantly the choice of reactions for the synthesis of such compounds and also determine their chemical properties. Thus organophosphorus α-nitro-compounds are obtained by nitrating the corresponding alkoxyvinylphosphonates with acetyl nitrate, while organophosphorus β-nitro-compounds are obtained by nitrating vinylphosphonates with dinitrogen tetroxide or pentoxide.

It has been established that trivalent phosphorus (P^{III}) compounds can scarcely be used for the synthesis of organophosphorus α-nitro-compounds, whereas the reactions of dialkyl and trialkyl phosphites with conjugated nitroalkenes have been used successfully to synthesise organophosphorus β-nitro-compounds. Reactions involving addition to 2-nitrovinylphosphonates are of special interest for the synthesis of various organophosphorus β-nitro-compounds containing functional-group substituents. The high electrophilicity of 2-nitrovinylphosphonates is manifested by their ability to alkylate *N,N*-dialkylanilines in the *para*-position in the aromatic ring.

Organophosphorus γ-nitro-compounds are obtained as a rule by the nucleophilic addition of nitroalkanes to vinylphosphonate or of phosphorus-containing CH acids to nitroalkenes. Only specific reactions are used for the synthesis of organophosphorus δ-nitro-compounds, for example, the reaction of nitroaldehydes with triphenyl phosphite and phenylthiourea.

Among all types of organophosphorus nitro-compounds, only α,α-disubstituted α-nitroalkylphosphonates readily withstand acid hydrolysis and conversion into acid chloride on treatment with phosphorus pentachloride. The capacity of aliphatic organophosphorus nitro-compounds for reduction opens a new way to the synthesis of aminoalkylphosphonic acids with functional-group substituents which are difficult to obtain otherwise but are of interest as biologically active compounds.

References

1. T Mukaiyama, H Nambu *J. Org. Chem.*, 1962, **27** 2201
2. A E Arbuzov, B A Arbuzov, B N Lugovkin *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1947, (5) 535
3. F Allen *J. Am. Chem. Soc.*, 1957, **79** 3071
4. L Horner, H Hoffman, H Ertell, et al. *Tetrahedron Lett.*, 1961, (1) 9
5. H Feuer, W D Van Buren, J B Grutzner *J. Org. Chem.*, 1978, **43** 4676
6. K A Petrov, V A Chauzov, N N Bogdanov, et al. *Zh. Obshch. Khim.*, 1974, **44** 1649
7. K A Petrov, V A Chauzov, N N Bogdanov, et al. *Zh. Obshch. Khim.*, 1986, **46** 1242
8. A A Neimysheva, S S Muratov, E V Smirnov, et al. *Zh. Obshch. Khim.*, 1976, **46** 940
9. M V Vasil'eva, G M Baranov, V V Perekalin *Metody Sinteza, Stroenie i Khimicheskie Prevrashcheniya Nitrosoedinenii: Sbornik Trudov* (Collection. Methods of Synthesis, Structure, and Chemical Reactions of Nitro-compounds), Izd. LGPI, Leningrad, 1980, p. 20
10. K A Petrov, V A Chauzov, N N Bogdanov *Zh. Obshch. Khim.*, 1976, **46** 1250
11. K A Petrov, V A Chauzov, N N Bogdanov *Zh. Obshch. Khim.*, 1976, **46** 1495
12. G A Berkova, G M Baranov, L A Zhidkova, et al. *Zh. Obshch. Khim.*, 1981, **51** 757
13. K A Petrov, V A Chauzov, I V Pastukhova, et al. *Zh. Obshch. Khim.*, 1976, **46** 1246
14. J Zon *Synthesis*, 1984, (8) 661
15. Ali A Kandil, T M Porter, K N Slessor *Synthesis*, 1987, (4) 411
16. G A Russell, J Hershberger *J. Chem. Soc., Chem. Commun.*, 1980, (5) 216
17. G A Russell, Fr Ros, J Hershberger, et al. *J. Org. Chem.*, 1982, **47** 1480
18. R Meuwly, A Vasella *Helv. Chim. Acta*, 1985, **68**(4) 997
19. K A Petrov, V A Chauzov, N N Bogdanov, et al. *Zh. Obshch. Khim.*, 1979, **49** 90
20. N Ono, H Miake, A Kamimura, et al. *Tetrahedron*, 1985, 41(19) 4013
21. K A Petrov, V A Chauzov, N N Bogdanov *Zh. Obshch. Khim.*, 1976, **46** 1499
22. M V Vasil'eva, G M Baranov, V V Perekalin *Zh. Obshch. Khim.*, 1979, **49** 1904
23. R Zhang, J Chen *Synthesis*, 1990, (9) 817
24. R D Gareev, A N Pudovik *Zh. Obshch. Khim.*, 1986, **56** 241
25. E E Vorisova, R D Gareev, G A Guseva, et al. *Dokl. Akad. Nauk SSSR*, 1976, **226** 1330
26. USSR P. 504 782; *Byull. Izobret.*, 1976, (8)
27. R D Gareev, G M Loginova, A G Abul'khanov, et al. *Zh. Obshch. Khim.*, 1976, **46** 2385
28. R G Gareev, A N Pudovik *Zh. Obshch. Khim.*, 1977, **47** 220
29. R G Gareev, A N Pudovik *Zh. Obshch. Khim.*, 1977, **47** 222
30. R D Gareev, A G Abul'khanov, A N Pudovik *Zh. Obshch. Khim.*, 1978, **48** 276
31. D Ranganathan, C B Rao, S Ranganathan *J. Chem. Soc., Chem. Commun.*, 1979, (21) 975
32. P Brushan, D Ranganathan, S Ranganathan, et al. *J. Org. Chem.*, 1980, **45** 1185
33. R D Gareev, G M Loginova, E E Borisova, et al. *Zh. Obshch. Khim.*, 1981, **51** 2626
34. R D Gareev, G M Loginova, A N Pudovik *Zh. Obshch. Khim.*, 1976, **46** 1906
35. R D Gareev, I M Shermergorn, A N Pudovik *Zh. Obshch. Khim.*, 1981, **51** 2135
36. R D Gareev, G M Loginova, I N Zykov, et al. *Zh. Obshch. Khim.*, 1979, **49** 25
37. R D Gareev, G M Loginova, Yu Yu Samitov, et al. *Zh. Obshch. Khim.*, 1977, **47** 2663
38. R D Gareev, G M Loginova, E E Borisova, et al. *Zh. Obshch. Khim.*, 1977, **47** 2676
39. W E Kruger, M B McLean, A Rizwaniuk, et al. *J. Org. Chem.*, 1978, **43** 2877
40. H Teichmann, W Thierfelder, A Weigt *J. Prakt. Chem.*, 1977, **319** 207
41. R D Gareev, A V Il'yasov, Ya A Levin, et al. *Zh. Obshch. Khim.*, 1982, **52** 1278
42. R D Gareev, V I Savin, A V Il'yasov, et al. *Zh. Obshch. Khim.*, 1981, **51** 2137
43. R D Gareev, A N Pudovik, I M Shermergorn *Zh. Obshch. Khim.*, 1983, **53** 38
44. R D Gareev, G M Loginova, A N Pudovik *Zh. Obshch. Khim.*, 1978, **48** 1688
45. R D Gareev, G M Loginova, A N Pudovik *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1978, (6) 1398
46. R D Gareev, E E Borisova, I M Shermergon *Zh. Obshch. Khim.*, 1975, **45** 944
47. E A Borisova, R D Gareev, I M Shermergon *Zh. Obshch. Khim.*, 1977, **47** 2622
48. E A Borisova, R D Gareev, I M Shermergon *Zh. Obshch. Khim.*, 1980, **50** 2215
49. R D Gareev, G M Loginova, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, (2) 462
50. USSR P. 654 619; *Byull. Izobret.*, 1979, (12)
51. K Issleib, P V Malotki *J. Prakt. Chem.*, 1973, **315** 463
52. R D Gareev, R Yu Nazmutdinov, R N Burangulova, et al. *Zh. Obshch. Khim.*, 1990, **60** 226
53. K A Petrov, V A Chauzov, S V Agafonov, et al. *Zh. Obshch. Khim.*, 1983, **53** 56
54. M Yamashita, M Yamanda, M Suqiura, et al. *Nippon Kagaku Kaishi*, 1987, (7) 1207
55. M Yamashita, M Nomoto, H Imoto *Synthesis*, 1987, (8) 716
56. M Yamashita, M Suqiura, T Oshikawa, et al. *Synthesis*, 1987, (1) 62
57. C Shin, J Jonezawa, K Katayama *Bull. Chem. Soc. Jpn.*, 1973, **46** 1727

58. A N Pudovik, S N Sitdikova *Dokl. Akad. Nauk SSSR*, 1959, **125** 826
59. M V Lazareva, T A Mastryukova, V V Perekalin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, (5) 1164
60. H Paulsen, W Greve *Chem. Ber.*, 1973, **106**(7) 2114
61. H Takayanagi, K Seo, M Yamashita, et al. *Carbohydr. Res.*, 1978, **63**(1) 105
62. G A Russell, D Dedolph *J. Org. Chem.*, 1985, **50** 3878
63. G A Russell, Ching-Fa Yao, H I Tashtoush, et al. *J. Org. Chem.*, 1991, **56** 663
64. USSR P. 1 293 187; *Byull. Izobret.*, 1987, (8)
65. Li Yu-Gui, Wang Guo-Hong, Zhang Din-Kun *Science in China (Ser. B)*, 1989, **32**(5) 522
66. Y Li, Y Liu, F Miao, et al. *Phosphorus, Sulfur, Silicon Relat. Elem.*, 1990, **47**(1–2) 229
67. USSR P. 186 462; *Byull. Izobret.*, 1966, (19)
68. T A Mastryukova, G M Baranov, V V Perekalin, et al. *Dokl. Akad. Nauk SSSR*, 1986, **171**(6) 1341
69. A V Serdyukova, G M Baranov, V V Perekalin *Zh. Obshch. Khim.*, 1974, **44** 1243
70. V Yuan, G Wang, S Cui, et al. *Proceedings of Sino-Soviet Bilateral Symposium on Organophosphorus Chemistry. October 29–31, 1990.* Shanghai, China, C-9, p. 144
71. G M Baranov, L A Zhidkova *Khimiya i Promenenie Elementoorganicheskikh Soedinenii: NMezhvuzovskii Sbornik Trudov* (The Chemistry and Applications of Organoelement Compounds: Intercollegiate Collection of Reports), Leningrad, 1990, p. 74
72. A V Serdyukova, G M Baranov, V V Perekalin *Zh. Obshch. Khim.*, 1978, **48** 522
73. G M Baranov, V V Perekalin, L V Zhuchkova, et al. *Khimiya i Primenenie Fosfororganicheskikh Soedinenii* (The Chemistry and Applications of Organophosphorus Compounds), Naukova Dumka, Kiev, 1981, p. 308
74. T A Mastryukova, G M Baranov, V V Perekalin, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, (2) 2842
75. USSR P. 435 246; *Byull. Izobret.*, 1974, (25)
76. L A Zhidkova, G M Baranov, T A Mastryukova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, (12) 2787
77. L A Zhidkova, M G Ivanova, G M Baranov, et al. *Zh. Obshch. Khim.*, 1978, **48** 1290
78. S Z Ivin, V N Promonenkov *Khimiya Organicheskikh Soedinenii Fosfora* (The Chemistry of Organic Compounds of Phosphorus), Nauka, Leningrad, 1967, p. 142
79. V M Ismailov, A N Guliev *II Respublikanskaya Nauchnaya Konferentsiya Aspirantov Vuzov Azerbaidzhana: Tezisy Dokladov* (The IInd All-Republic Scientific Conference of Postgraduates at the Higher Educational Establishments of Azerbaijan: Abstracts of Reports), 1979, p. 112
80. V E Anderson, P M Weiss, W W Cleland *Biochemistry*, 1984, **23**(12) 2779
81. E I Matrosov, G M Baranov, V V Perekalin, et al. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1971, (11) 2572
82. M Yamashita, Yo Tamada, A Iida, et al. *Synthesis*, 1990, 420
83. G M Baranov, V V Perekalin, M V Ponomarenko, et al. *Khimiya i Primenenie Fosfororganicheskikh Soedinenii: Sbornik Trudov IV Konferentsii FOS* (The Chemistry and Applications of Organophosphorus Compounds: Collected Reports from the IVth Conference on Organophosphorus Compounds), Nauka, Moscow, 1972, p. 228
84. M V Lazareva, V V Perekalin, T A Mastryukova *Izv. Akad. Nauk SSSr, Ser. Khim.*, 1973, (6) 1382
85. G M Baranov, T A Mastryukova, V V Perekalin, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, (1) 179
86. G Richtarski, M Soroka, P Mastalerz, et al. *Rocz. Chem.*, 1975, **49**(12) 2001
87. C Yuan, G Wang, S Chen *Phsosphorus, Sulfur, Silicon Relat. Elem.*, 1991, **63**(1–2) 111
88. L V Zhuchkova, G M Baranov *Issledovanie Komponentov Rastitel'nogo, Zhivotnogo i Mineral'nogo Syr'ya Dal'nego Vostoka* (The Components of the Plant, Animal, and Mineral Raw Materials of the Far East), Izd. Khabarovsk. Gos. Ped. Inst., Khabarovsk, 1984, p. 50
89. G M Baranov, V V Perekalin *Zh. Obshch. Khim.*, 1987, **57** 793
90. G M Baranov, V V Perekalin, L I Deiko, et al. *Khimiya i Primenenie Fosfororganicheskikh Soedinenii: Trudy VIII Konferentsii* (The Chemistry and Applications of Organophosphorus Compounds: Proceedings of the VIIIth Conference), Nauka, Moscow, 1987, p. 235
91. T K Kostina, G M Baranov, V V Perekalin *Zh. Obshch. Khim.*, 1981, **51** 712
92. V K Kostina, G M Baranov, V V Perekalin *Sintez i Issledovanie Nitrosoedinenii i Aminokislot: Mezhvuzovskii Sbornik Nauchnykh Trudov* (The Synthesis and Study of Nitro-compounds and Aminoacids: Intercollegiate Collection of Scientific Reports), Izd. LGPI, Leningrad, 1983, p. 5
93. O Neilands *Tsiklicheskie β-Diketony* (Cyclic β-Diketones) (Edited by G Vanags), Izd. Akad. Nauk Latv. SSR, Riga, 1961, p. 41
94. G M Baranov, T K Kostina *Sintez i Issledovanie Nitrosoedinenii i Aminokislot: Mezhvuzovskii Sbornik Nauchnyk Trudov* (The Synthesis and Study of Nitro-compounds and Aminoacids: Intercollegiate Collection of Scientific Reports), Izd. LGPI, Leningrad, 1986, p. 39
95. E De-Tinguy-Moreaud, B Bioulac, E Neuzil *Biochem. Soc. Trans.*, 1981, (3) 246
96. US P. 2 535 175; *Chem. Abs.*, 1951, **45** 3408h
97. T A Mastryukova, M V Lazareva, V V Perekalin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, 1353
98. M V Lazareva *The Synthesis and Investigation of Certain 2-Aminoalkylphosphonic Acids*, Candidate's Thesis in Chemical Sciences, Leningrad State Pedagogic Institute, Leningrad, 1972, 120 pp
99. US P 3 021 353; *Chem. Abs.*, 1962, **57** 3484d
100. A N Pudovik, F N Sitdykova *Zh. Obshch. Khim.*, 1964, **34** 1682
101. R G Hall *Synthesis*, 1989, (6) 442
102. J Asunskis, H Schechter *J. Org. Chem.*, 1968, **33** 1164
103. D T Cannor, M Strandtmann *J. Org. Chem.*, 1973, **38** 1047
104. A I Razumov, B G Liorber, Z N Khammatova, et al. *Zh. Obshch. Khim.*, 1977, **47** 567
105. Z H Kudzir, M Tasz, R Skowronski *XI International Conference on Phosphorus Chemistry, Tallin. July 3–7, 1989;* Abstr. Post., Tallin, 1989, Vol. 2, p. 4/15
106. L D Zhuchkova, G M Baranov *Fiziko-khimicheskie Biokhimicheskie Issledovaniya Priorodnykh i Sinteticheskikh Soedinenii* (Physicochemical and Biochemical Studies on Natural and Synthetic Compounds), Izd. Khabarovsk. Gos. Ped. Inst., Khabarovsk, 1980, p. 8

107. L D Zhuchkova, G M Baranov, V V Perekalin *XXVIII Gertsenovskie Chteniya* (The XXVIIIth Gertsen Lectures), Izd. LGPI, Leningrad, 1976, p. 129
108. G M Baranov, V V Perekalin, L D Zhuchkova, et al. *Khimiya i Prakticheskoe Primenie Kremnii- i Fosfororganicheskikh Soedinenii: Mezhvuzovskii Sbornik Nauchnykh Trudov* (The Chemistry and Practical Applications of Organosilicon and Organophosphorus Compounds: Intercollegiate Collection of Scientific Reports), Izd. LTI, Leningrad, 1977, p. 23
109. C Retherford, T S Chou, R M Schelku, et al. *Tetrahedron Lett.*, 1990, **31**(13) 1833

Received 29th June 1992